"Biofly" brick-engineering reuse of fly ash and sewage sludge

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“BIOFLY” BRICK-ENGINEERING REUSE OF FLY ASH AND SEWAGE SLUDGE

Volume I

A thesis submitted in fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY from

THE UNIVERSITY OF WOLLONGONG

by

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1996
This thesis is submitted to The University of Wollongong, and has not been submitted for a higher degree to any other University or Institution.

Fady G. Sidrak

June, 1996
"Then the Lord God took some soil from the ground and formed a man out of it, he breathed life-giving breath into his nostrils and the man began to live."

Genesis 2:7
To Mary

whose support and patience made it possible
ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisor, Associate Professor M. Sivakumar for his advice, assistance and encouragement throughout this project.

Thanks are also due to Associate Professor R. N. Chowdhury, who co-supervised me during early years of the thesis, for his support and advice.

I also wish to acknowledge the persons and companies who have financially supported and made the production of this work possible, particularly Pacific Power of New South Wales, Sydney Water Board and Boral Limited.

I also wishes to express sincere appreciation to Prof. A. Samarin, Consultant, Boral Research for his assistance, Mr. John Bacchus and Mr. Ian Finney of the Water Board, Mr. John Schlafring and Mr. Peter Wood of Pacific Power for their input and contribution.

Special thanks are also due to Technical Staff Ms. J. George, Mr. N. Gal, Mr. C. Allport, Mr. J. Britton, Mr. K. Cunningham, Mr. A. Depers and Mr. G. Hamilton who in one way or another contributed.

Thanks are also due to Technical Staff Mrs. J. Eshman, Mr. R. Eshman, Mr. L. Reilly, Lab Manager Microwave Applications Research Centre for their contribution.

Special thanks are also due to Technical Staff Mr. J. Banks and Mr. J. Phillips from Advanced Technologies Division of Pacific Power for their contribution.

Finally I would like to thank my wife and my children for tolerating my part-time membership in the family over the past few years.

"Yet when I surveyed all that my hands had done and what I had toiled to achieve, everything was meaningless, a chasing after the wind; nothing was gained under the sun."

Ecclesiastes 2:11
ABSTRACT

Waste disposal has become one of the major problems of the industrialised world. With increasing world population the amount of solid waste generated has increased dramatically. Sewage sludge and fly ash, are two waste products which are produced in large quantities and pose several environmental hazards. With better wastewater treatment processes, the quantity of sewage sludge generated worldwide has risen significantly. In Sydney area alone, 125 dry tonnes of sewage sludge is produced daily, and safe and reliable disposal method need to be found. Fly ash is a waste product generated from coal fired power plants and most of these waste are stockpiled in storage areas. An estimated 6 million tonnes of fly ash is produced in NSW in one year. In an effort to introduce a satisfactory means of disposal, these two wastes were combined to produce a structural material called “Biofly brick”. It is an innovative approach to convert largely unacceptable wastes to a beneficial and useful material. This thesis contains two volumes. Volume I describes the detailed work undertaken for the Biofly brick process. Volume II gives the summary of all test results.

A comprehensive investigation into the production of full size Biofly bricks in a pilot plant scale has been undertaken. Biofly bricks were made from various proportions of fly ash, four types of sewage sludge and clay/shale mixture. The structural and environmental suitability of the Biofly brick was evaluated.

Full size Biofly and 100% clay bricks were manufactured at the University of Wollongong, Civil Engineering laboratories, and 2200 bricks were made. These Biofly and clay bricks have been tested for various engineering and environmental properties. The results indicate that the average compressive strength ranged between 21.4 to 49.7 MPa for Biofly brick and 39.1 MPa for ordinary clay brick, average transverse strength ranged between 4.5 to 10.5 MPa for Biofly brick and 4.2 MPa for conventional clay brick, absorptivity averaged between 0.83 to 1.09 for Biofly brick and 0.97 for clay brick, characteristic expansion ranged between 0.15 to 1.86 mm/m for Biofly brick and 1.70 mm/m for ordinary clay brick, and initial rate of absorption ranged between 0.17 to 1.52 kg/m²/min for Biofly brick and 0.50 kg/m²/min for conventional clay brick. Test results for efflorescence, examination for pitting due to lime particles and resistance to salt attack are also reported. Other properties, such as linear shrinkage was 8.7% for Biofly brick and 13.9%
for clay brick, bulk density ranged between 1520 to 1750 kg/m$^3$ for Biofly brick and 2170 kg/m$^3$ for ordinary clay brick, and weight loss was 28.5% for Biofly brick and 20% for clay brick. Assessment of these structural properties were evaluated according to the Australian standard 1226 which indicates that the Biofly bricks exhibit superior structural properties in comparison to the ordinary clay brick. This is primarily attributed to the combination of fly ash and sewage sludge used as replacement materials.

A comprehensive leachate study was undertaken for three different size fractions on all the bricks made. All leachate samples were analysed for trace metals: copper, iron, manganese, nickel, lead, zinc, cadmium, chromium and aluminium, utilising atomic absorption spectrophotometry. The concentration of heavy metals from the Biofly brick leachate was similar or lower than that of the conventional clay brick except in the case of cadmium and iron, but it is well within the standard limits proposed by Victoria EPA and US CFR. It was expected that the concentration of metals in the leachate should be increased with the increased exposed surface area of the smaller particles. However, this was not the case, and the metals remained "locked up" even in the small particles. This may be due to the greater ion exchange capacity of the smaller particles which prevents significant leaching of the metals.

The gas consumption and gas emission study indicated that the Biofly brick process uses less energy and emits smaller amount of air pollutants compared to a standard clay making process. The Biofly process has the potential to control the emission of air pollutants during the firing of bricks. Heavy metals, fluoride, chloride and acid gases emissions, generally associated with the conventional clay brick manufacturing process, are also reduced during the Biofly brick process. The concentration of metals emission from Biofly brick were found to be lesser than that of the conventional clay bricks and lower than the standard limits proposed by Victoria EPA. The contained metals were believed to be physico-chemically locked inside the vitrified brick, possibly due to a silicate-based entrapment mechanism.

The large scale laboratory experimental results indicated that, Biofly bricks have been successfully made using fly ash, sewage sludge and clay/shale. The characteristics of the full
Biofly bricks have been found to depend on the sludge type and waste mix however by suitably selecting the sludge type and mix composition, the Biofly bricks can be produced 20 - 25% lighter, 10 - 30% stronger and with significant energy savings of up to 44% in comparison to conventional clay bricks. The Biofly brick also was fired in approximately less than one half of the time required for firing clay brick and hence the kiln throughput will be increased by almost 100%.
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Waste disposal has become one of the major problems of the industrialised world. With increasing world population the amount of solid waste generated has increased dramatically. Sewage sludge (also referred as Biosolids) and fly ash, are two waste products which are produced in large quantities and pose several environmental hazards. With more and more wastewater treatment processes, the quantity of sewage sludge generated worldwide has risen significantly. In Sydney metropolitan area alone, 125 dry tonnes of sewage sludge is produced daily, and safe and reliable disposal method need to be found. Coal fired power plants generated fly ash and most of these waste are stockpiled in storage areas. An estimated 6 million tonnes of fly ash is produced in NSW in one year. The following sections outlines the generation and disposal problems associated with these two waste products.

1.1.1. Municipal sludge

All conventional wastewater treatment processes produce large quantities of waste material in the form of a dilute solids mixture known as sludge. The composition and solids content of these sludges are a function of the raw wastewater flow and the treatment processes that generate from the sludge.

The characteristics of sludges are as varied as the wastes from which they originate. Although some generalisation can be made about sludge from municipal and/or industrial waste treatment processes, none clearly describes all sludges.

Sludge or Biosolids can be qualitatively defined as a muddy or slurry mass produced as a precipitated or settled solid matter from water or wastewater treatment processes. More precisely, sludge is composed of flocculent, and hydrophilic solids and tends to be voluminous in nature. The hydrophilic solids bind water and contribute to the volume of waste material. The term Biosolids instead of sludge is becoming increasingly accepted in
Australian water authorities in recent years. However in this project sludge will be used for continuity of terminology between Stage I and Stage II.

Most sludges are typically semi-liquid in form, with a general solids content ranging between 1 to 3 percent prior to dewatering. This low concentration of sludge accounts for the voluminous nature of this material. Dewatering is a physical operation that can reduce the volume of sludge and improve its inherent characteristics. Dewatering is accomplished by either mechanical and/or thermal processes. Depending on the type of dewatering procedure employed, and the type of sludge to be dewatered, final solids concentrations ranging from 10 to 35 percent are generally produced. After dewatering most of the sludge is in an acceptable state for most forms of ultimate disposal.

Disinfection is required for some sludges to decrease the number of viable pathogenic organisms contained within the sludge. Many types of sludges require disinfection depending upon the origin of the wastes. The disinfection operation is performed either before dewatering or is incorporated into the dewatering operation. Disinfection prior to dewatering is accomplished by exposure of the waste stream to chlorine, ozone or ultra-violet light. When disinfection is incorporated into the dewatering operation, lime is used as a coagulant. Lime elevates the pH of the sludge, thereby inhibiting the growth of pathogens.

Many methods exist for the disposal of sludges. The basic problem arises in where to dispose of the final product. There are only three areas in which the final product may be placed, on the land, in the ocean, and in the air.

Land disposal incorporates systems in which the sludge, or residuals thereof, and ash from incineration of sludge, are either applied to the soils for agricultural purposes or stockpiled. Sludge can be beneficially used as a fertiliser and soil conditioner for farming and other purpose. In Sydney, over 60% of solid material discharged into sewerage system is now being captured at sewage treatment plants. This amounts to over 177,000 tonnes per annum of processed sludge products being generated by Sydney Water, 70% of which is now being used beneficially in agriculture, forestry, land rehabilitation and composting projects.

Ocean disposal of sludge is carried out by either of two methods. The first method employs a pipeline or outfall which extends offshore to the discharge site. Sludge is then
released on the ocean floor where subsequent degradation may occur depending upon existing conditions, such as dilution, sufficient viable microorganism or nutrients. Offshore ocean dumping may also be accomplished by towing a scow to a predetermined site and releasing its contents from the surface. Both methods can lead to undesirable contamination of specific coastal areas, resulting in loss of recreational areas, aquatic life and a possibility that toxic materials might enter the aquatic food chain. Spoils from certain ocean dumping operations have also been known to wash ashore on many beachfront areas, causing localised clean-up problems.

Incineration of sludge considerably reduces the volume of sludge to be disposed on land or dumped into the ocean, but the volatilised portion is released into the atmosphere. Proper scrubbing of the flue gases can effectively remove most hazardous materials and fine dust particles, but again a residue is produced which must be dealt with by one of the aforementioned alternatives.

Although these processes effectively prepare the waste for an environmentally safe disposal, the full resource potential of the sludge is not utilised. Constructive management or "reuse" might therefore pose a desirable goal rather than sludge disposal. Proper return of sludge into a productive cycle can permit the beneficial use of constituents and avoid the ultimate disposal problems. Biologically treated organic sludges can be beneficially applied to soils. Sludge is applied in dried, dewatered and liquid forms and serves to improve the physical characteristics and nutrient level of the soil.

Many industries have been reclaiming and marketing sludge, instead of considering it a waste product. Sludge can be combined with oil and the residual water will be removed through evaporation. Solids then will be separated from the oil for use as an animal feed supplement and the excess grease will be marketed. Lime has also been reclaimed from water softening sludge by recalcination and from precipitates produced by chemical waste treatment for phosphate removal. Similarly, alum can be recovered from sludges produced by clarification of water. Countless other examples of recovery and reclamation can be found in practice. These processes deal mainly with environmentally safe sludges or sludges in which the hazardous components can be economically separated. There exists still another group of sludges that contain hazardous and toxic materials which cannot be economically reused and requires some form of ultimate disposal.
Solidification is one technique for the ultimate disposal of hazardous wastes. Many of the approaches used in the solidifying or stabilisation of hazardous wastes originated in the area of radioactive waste management. Initially, the major goal in radioactive waste stabilisation was the production of a solid material that could safely be transported in compliance with transportation regulations. Additional research in developing solid materials that are suitable for long term containment of radioactive wastes has produced many feasible systems. Solidification requirements in the radioactive waste management area were satisfied by using systems with cement mixtures, bituminous materials, urea-formaldehyde resins or glass.

Many of the techniques employed for management of radioactive waste may be applied after modification to industrial sludges. Industrial waste solidification differs from radioactive waste containment in that industrial processes produce copious amounts of waste with a relatively low toxicity. Therefore, the extensive containment procedures employed in the management of radioactive waste would not be necessary for industrial waste containment.

Many of the most dangerous industrial waste products are organic chemicals which can be oxidised by incineration. For this reason, most solidification techniques have been developed primarily for the containment of inorganic wastes which cannot be readily destroyed by oxidation. These inorganic wastes often have high concentrations of toxic metals, such as, cadmium, chromium, mercury and lead. Although these heavy metals are usually present in sludges as insoluble hydroxides, carbonates or sulphides, changes in pH or oxidising conditions can solubilize these toxic metals and release them into the surrounding environment.

Although many solidification processes exist, only a few can constructively manage the waste material. Most operations simply immobilise the waste to provide for an environmentally safe waste material, but do not provide for ultimate disposal. These techniques still require landfilling and ocean disposal.

1.1.2. Fly ash

Fly ash from coal-burning power plants has been a major solid disposal problem for years. With the energy crisis and a shift from oil and gas back to coal, figures indicate that the annual production in NSW would be about 6 million tons. Data show that only about
10% of fly ash produced was utilised. Some of these uses are as a construction fill material, as an additive in cement and asphalt, as a soil nutrient, and as an aid in treating polluted waters and reclaiming surface mine spoil. However, the greatest part of the fly ash produced must be disposed of either by trucking to a dumping ground or by sluicing to an ash pond. Mass movements occur from fly ash disposal tips and these incidents have drawn the attention of environmental and geotechnical engineers to resolve the problems of mass scale dumping of waste from power plants. The main problems related to fly ash disposal are summarised below.

Discharge of fly ash into inland rivers and lakes directly affects the ecology of the region and causes pollution of potential drinking water sources. This problem can also be alarming in situations where coastal power plants discharge waste ash to the ocean for convenience.

Disposal of untreated dry fly ash to open land areas can be catastrophic in two ways. Firstly, as this fine dust can be easily transported by wind, human settlements even a considerable distance away can be affected by inhalation. Secondly, the eventual deposition of fly ash on surrounding ground can cause a gradual change in soil properties affecting vegetation and future agriculture.

The failure of large fly ash dumps after heavy rainfall can have permanent devastating effects on the environment. These may lead to catastrophic "mudflows".

In view of the disposal problems associated with fly ash and wastewater sludge and the trends toward greater quantities of these wastes becoming available in the near future, the investigation of other disposal alternatives appears warranted. This report describes one such investigation. Since fly ash and wastewater sludge have some mutually complementary characteristics, it was proposed that these two waste products could be beneficially combined with clay/shale to create a material which would be suitable for structural brick making. Potential advantages of this technique include:

- the reuse and utilisation of two waste products
- environmentally safe waste disposal
- waste products become assets instead of liabilities
- light weight brick production
- significant energy savings during brick making
• Strength similar to clay brick.

1.2. Development stages

Stage I (1989-1990)

The project commenced in 1989 primarily to look at the suitability of using two waste products namely fly ash and sewage sludge with a view to solidify and make full size bricks. These bricks are were called “Biofly” bricks.

What has been achieved?

Small scale trials were conducted at The University of Wollongong and Boral laboratories in Sydney for the following:

• Determination of appropriate source and properties of the three materials namely fly ash, sewage sludge and clay/shale.
• Optimum moisture content and workability of mixture
• Investigation into the types of extrusions, pressed versus pug mill and their suitability for Biofly brick
• Laboratory mixing and extrusion of 75 mm x 10 mm cylindrical samples with various percentage combinations of fly ash, sewage sludge and clay/shale.
• Drying and firing of the above samples in electric muffle furnace. Problems associated with pyrolysis, such as tar, oil and odour problems were solved.
• The occupational and health issues were identified and solutions suggested.
• The environmental issues associated with high temperature firing such as heavy metals and gas emissions were analysed for the small laboratory samples.
• The structural and other aesthetic properties necessary for marketing the bricks as well as satisfying Australian Standard were studied for the laboratory samples.
• Investigation of energy savings during the firing process and the establishment of a firing curve.
• Determination of optimum mixture based on the overall properties of burnt brick samples.
Conclusions

It has been proven from this work that fly ash, sewage sludge and clay/shale can be appropriately combined on a laboratory scale to make the so called "Biofly" brick.

- The results of chemical analysis of fly ash and clay/shale are similar.
- The extrusion process is more suitable for making Biofly brick than pressed brick operations.
- The small laboratory cylindrical sample was 20% lighter in weight when compared with ordinary clay/shale brick.
- The structural strength of various mixtures up to about 20% sludge content are always above the strength of normal clay/shale bricks.
- The importance of using gas kilns instead of an electric muffle furnace was demonstrated based on odour and other concerns.
- It has been shown that up to 50% energy savings can be achieved by the Biofly brick production process.

The limited data on gas emissions showed that the heavy metals as well as other gases emitted during the firing process are not excessive. However there are no established emission standards for this type of work and the quality of the emissions also depend on the source of sewage sludge. More work needs to be done in this area.

A number of problems were encountered due to lack of equipment and working in various locations. It is recommended that this study should be completed at one location. A comprehensive report has been produced based on small sample laboratory trials.

Stage II (1991-1995)

Preliminary testing indicated that further research needed to be conducted. Two broad objectives were established for this investigation:

- To determine whether the resulting materials would be physically suitable for use as building brick.
- To determine the extent of adverse environmental effects, especially leaching/gas emission of potentially harmful trace elements.
1.3. Aims and objectives

More specifically the main aim of this thesis is to conduct systematic research into the production of full size Biofly brick in the laboratory. The following aims and objectives are identified:

• Design and build an apparatus to manufacture full size Biofly bricks in the laboratory using gas kiln.

• Investigate the viability and use of raw sewage sludge in “as is” condition rather than in dry condition.

• Conduct and determine the broad consequences associated with mixing fly ash and clay/shale with different types of municipal sewage sludge.

• Determine the mixing proportions for the actual size Biofly bricks and recommend the optimum mix proportion.

• Extrude actual size Biofly brick on a continual basis to simulate the conditions in the brick factory using a large extruder.

• Develop drying time, and firing curve for the Biofly brick process.

• Review and recommend occupational and health guidelines and precautions that should be taken by all associated with the Biofly brick making process.

• Determine engineering and other aesthetic properties of the Biofly bricks in accordance with Australian Standards.

• Conduct comprehensive gas emission studies throughout the firing process of the Biofly brick to determine the concentration and nature of the metals emitted from the Biofly process.

• Determine energy savings during firing and suggest an appropriate firing curve for the Biofly brick process.
• Conduct leachability tests with different particle sizes to understand the mechanisms of leachate production from the Biofly brick and compare results with the Standard.

1.4. Scope

In Chapter 1, a brief review of the disposal processes associated with fly ash and sludge waste products has been presented, and the aims and objectives of the research has been clearly identified.

A comprehensive literature review was conducted to study the state of the art knowledge and this has been reported in Chapter 2. The Biofly brick process being a new process and the three materials, clay/shale, sewage sludge and fly ash being combined for the first time worldwide. Various other mixing processes involving sewage sludge and clay/shale, fly ash and clay/shale were studied individually for making bricks in other countries. A general concept of the structural potential of these materials can be obtained from this overview.

The conventional clay brick making processes and the various stages of the Biofly brick making process are described in Chapter 3. The equipment used for making the actual size pilot scale brick samples, the mixer, the extruder and the kiln used for firing the bricks and the firing process are discussed.

In Chapter 4, theoretical considerations of firing process through high-temperature reactions in disilicate minerals and reaction in typical clay bodies using DTA and TGA techniques are discussed. X-ray diffraction and optical microscopic techniques have been used to further investigate the difference in mineralogy and microscopic properties between Biofly brick and conventional clay brick.

In Chapter 5, the equipment procedures and methods used for sampling and analysis of the Biofly bricks are described. The reagent preparation methods are also discussed for gas analysis and leachability tests.

In Chapter 6, the results of the analysis of the structural and other aesthetic properties are discussed and compared with Australian Standards.
In Chapter 7, development of the firing curve through the preliminary trials of the Biofly bricks and clay/shale bricks are provided. The colour development and cooling stresses encountered in the bricks are discussed.

In Chapter 8, an overview of the leachability from processes using waste products has been described. The results of the leachate for different particle sizes are discussed and the ability of the Biofly brick to solidify the heavy metals are noted. Since appropriate Australian Standards are not available, the comparison of leachate concentration was carried out using the Standards of the US. CFR and Vic. EPA.

In Chapter 9, special occupational and health precautions associated with Biofly brick making have been identified from this pilot study. It is envisaged that basic sanitary and health precautions need to be observed by all workers in accordance with clearly established precautions.

In Chapter 10, an overview of the emission of pollutants from processes using the same two waste products has been presented. The results of air pollution and gas analysis are provided at different stages of firing of the Biofly bricks. Possible reasons for the trace emissions and containment of the different pollutants during all stages of firing are described. The results are compared with the available emission standards. Investigation of energy consumption and savings during the firing process as well as emission of trace metals are discussed.

The conclusions of the study are presented in Chapter 11. The recommendations for further research to be carried out are also provided in this Chapter.

Figure 1.1 shows the flowchart of this thesis.
Chapter 1: Introduction

Figure 1.1 Flowchart of this thesis

GENESIS 11:1-4

2.1. Introduction

Man has improved upon many different aspects of the brickmaking process since its inception. Evolution from a simple hand formed moulding process to a highly complex automated manufacturing system has been made possible through many innovative advances in the brickmaking machinery. Attempts to improve the clay’s physical properties and characteristics have also proved beneficial.

Material additions have been known since man has laid out his first brick to dry in the sun. These bricks or adobe were commonly made with clay and straw. The straw was used as a binding agent to improve the durability and strength of the brick. Many other materials have been added since straw, in an attempt to either improve the clay’s physical properties or processing characteristics.

These additions can be naturally occurring such as oil bearing clays or manmade. Generally, materials added to the clay alter the intrinsic properties such as: reduce shrinkage, reduce plasticity and reduce energy requirements during the manufacturing process.

Non-plastic materials such as grog, sand or shale have been used to reduce the shrinkage that occurs during the drying and firing processes. Grog was an admixture used in the nineteenth century, made by grinding broken bricks into a fine sand-like powder.
Addition of carbonaceous materials to the clay will reduce the energy required to burn the brick. Dependent on the size of the carbonaceous particle an increase in porosity of the brick can also be expected. Some carbonaceous materials which have been added to clay include: breeze, coal dust, oil and sawdust. Breeze was used predominantly in London, England in the mid-nineteenth century as a means to reduce shrinkage, increase porosity and to reduce the amount of fuel required to burn the brick.

Coal dust was primarily used in the same manner as breeze except that coal dust is completely combustible, unlike the breeze which is only partially combustible. Coal was also much more readily available than breeze, along with greater control over the particle size distribution.

Oil, which is the finest carbonaceous material introduced into the brickmaking process, was used to reduce the quantity of fuel required to burn the brick, while not appreciably increasing the porosity. The oil also enhances the extrusion characteristics of the clay. Oil can be naturally occurring in many clays, such as Oxford clays, or can be added into the clay as an admixture.

The use of coal dust and oil has been sharply curtailed due to the prohibitive cost of this non-renewable energy source. Sawdust is added to the clay to increase the porosity of the brick which allows for faster water absorption and helps to prevent freezing of the mortar.

2.2. Bricks made with fly ash

2.2.1. Bricks made with dry and wet fly ash, U.K.

2.2.1.1. Introduction

There is nothing new in adding coal ashes to clay in brickmaking. Lloyd (1928) makes it clear that this practice goes back at least to the eighteenth century in South East, England, and it still continues. Research work on the subject of making bricks with fly ash started at the U.K. Building Research Station in 1952 in a small way. It was soon realised that it was technically possible to make fired bricks from fly ash with quite small admixtures of a plastic clay to increase green strength.
2.2.1.2. Composition of fly ash

Table 2.1 shows the comparison of mineral composition of a typical fly ash and clay. It seems that the composition of fly ash is fairly close to those of fired brick clays by Butterworth (1954). The average percentage of silica, alumina and iron oxide in both fly ash and clay are nearly the same, and therefore it seems logical to expect that the fly ash and clay can be combined to make brick.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fly ash % Maximum</th>
<th>Fly ash % Minimum</th>
<th>Fly ash % Average</th>
<th>Clay %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.1</td>
<td>40.6</td>
<td>45.6</td>
<td>43</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>30.4</td>
<td>22.7</td>
<td>26.7</td>
<td>35</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>22.4</td>
<td>10.8</td>
<td>14.2</td>
<td>12</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.3</td>
<td>0.6</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>7.8</td>
<td>2.1</td>
<td>5.5</td>
<td>26</td>
</tr>
<tr>
<td>MgO</td>
<td>3.9</td>
<td>1.0</td>
<td>2.3</td>
<td>13</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.1</td>
<td>0.5</td>
<td>1.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Cl</td>
<td>0.11</td>
<td>0.02</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>(Na,K)₂O</td>
<td>0.19</td>
<td>-</td>
<td>0.06</td>
<td>8</td>
</tr>
</tbody>
</table>

Physically, fly ash consists mainly of minute spheres of fused ash, most of them solid, though a few are hollow, with the carbon present as coke both as separate particles and as a discontinuous coating on the surface of the grains of ash. The fine nature of the fly ash can work as a filler material to make a good brick.

2.2.1.3. Fly ash bricks with a clay bond

Scope of pilot-scale Laboratory experiments

Almost 40 years ago, extensive tests were made in the U.K. by Butterworth (1954) on two particular mixtures of fly ash and clay. These two case studies covered a wide range of experimental conditions. In one study ash was available in the dry state and the problems of dry mixing it with ground clay were examined. In the other study, ash was available only as a slurry and problems of dealing with an ash of high water content was examined. Some hundreds of bricks were made successfully from each combination of materials, generally in the proportion of 85:15 (fly ash/clay) by volume or 80:20 by weight. No observations were made during the drying and firing of the bricks, but the bricks were fired in the laboratory at different temperatures to study structural properties.
Chapter 2: Literature review

Manufacture based on dry fly ash

Several attempts were made to produce semi-dry-pressed bricks from a mixture of fly ash with ground clay. Whilst some bricks of tolerable appearance were produced, their quality as shown by exposure test was so poor that it is unnecessary to discuss them further.

It was found by Butterworth (1954) that the dry ash mixed with dry powdered clay, if wetted down immediately before extrusion, had remarkable working properties. It tended to stiffen up after extrusion, so that the green bricks were resistant to damage in handling, and were very easy to dry, with a linear drying shrinkage of only about 2%. It was possible to put freshly-made bricks into an oven at 70°C and dry them in about 6 hours, a treatment which few ordinary clay bricks would stand. It is probable that the early stiffening, and the insensitivity to drastic conditions of drying, was due to the early removal of some of the mixing water by absorption on the large surface area of glassy particles in the fly ash, and by combination with the small amount of anhydrous calcium sulphate which it contained. At least, it was found that the same advantages were not possessed by the same mixture of fly ash and clay if it were kept wet overnight before extrusion. The bricks made from the mixture so treated were much more sensitive to drying conditions.

Manufacture based on wet fly ash

These experiments were made at the Power Station where the ash were discharged wet to a lagoon, and could not be extracted readily from the system in the dry state. The preparation of a mixture of fly ash and clay suitable for brickmaking was more troublesome and likely to involve higher costs for plant than at a power station where dry ash was available.

The basic difficulty with fly ash from a lagoon is the high water content. It remains high even when the fly ash has been allowed to settle in a tank and as much water as possible has drained away. Under such conditions, a water content of at least 55%, calculated on the wet weight, is likely. Further reduction in the water content is essential, and vacuum filtration is capable of bringing the water content down to about 40% fairly rapidly. If the bond clay was then introduced as a dry powder, the result would be a
mixture which might be suitable for machine moulding, though it would probably not be stiff enough for the wirecut process unless more water was removed.

2.2.1.4. Firing of fly ash bricks

Some attention must be paid to the carbon content (4-8%) of any fly ash that might be used for a brick containing 70% or 80% fly ash. This is a problem which is already familiar to makers of colliery shale common bricks, since many colliery shales contain more coal than is really required to fire the bricks, with the result that the air supply to the kiln has to be restricted to prevent overfiring. As a result, the bricks tend to have black cores owing to insufficient oxidation. The same situation could arise with fly ash bricks if an ash of high carbon content of 8% were used, and this would make it impossible to produce good quality facing bricks.

However in Great Britain at modern base-load power stations it is perfectly possible for the carbon content to remain below 4% by weight for long periods, and this should not pose any problem.

2.2.1.5. Properties considered

When the original exploratory work on fly ash bricks was done (Watts, 1954; Butterworth, 1954), the conventional tests for water absorption and compressive strength were used as a rough method of assessment, in spite of their known short-comings. Soluble salts analysis were made on a number of samples, because soluble salts are frequently a problem with the clay of that formation, but not on all samples. These analyses were considered separately from the physical properties. In addition, bricks from the various test batches were exposed to the weather under severe conditions, and useful information was subsequently accrued from these exposure tests.

The form of exposure test generally used in the U.K. was the "tray" test, in which representative specimens, usually two, were placed, on edge, in metal trays 76 mm deep and left out-of-doors. During the winter the trays normally contained water, so that the bricks were saturated when frozen. In addition, similar specimens were exposed on a level concrete slab outside the trays. The tray test is very severe and bricks decay at roughly one-third the time needed for similar effects to occur in the brick-on-edge coping of a parapet. Exposure outside the trays is not quite so severe as inside. The condition of the
bricks in exposure tests is shown in Tables 2.2 and 2.3 as good (G) meaning no significant decay in 7 years, moderate (M) meaning decay to a depth not exceeding about 6.3 mm or bad (B) means more extensive decay, according to their condition after 7 years' exposure.

In addition, a few brick piers were built. These were built and capped in such a way that rainwater drained from the capping into the middle of the pier which was filled with sand. The conditions were therefore those of severe exposure, comparable with, say an earth-retaining wall.

**Moderate addition of fly ash**

Reasonable comparisons are available for the effect of addition of fly ash on the properties of two types of clay, each represented by two examples. The types are:

1. Coal Measure shales (Carboniferous)
2. Keuper Marl (Triassic)

The results in Table 2.2. show that the effect of fly ash on the properties of the bricks varies from clay to clay. The porosity and strength are hardly affected at all within the limits of variation to be expected in the field tests of ± 5%, however, the durability of the bricks in severe exposure is not affected adversely, indeed it seems to be marginally better. The number of bricks used in the exposure test is rather small, usually two, so that it is difficult to be sure of small differences in performance. The temperature of the laboratory firing was adjusted to the needs of the fly ash mixture and was about 50°C higher than the temperature used in the kiln for firing the clay without fly ash. Normally, the semi-dry brick (fly ash brick) needs a higher firing temperature than a plastic made brick (clay brick) to mature it. It is concluded that moderate addition fly ash bricks have properties very similar to those of clay bricks.

**High proportion of fly ash**

Information about the properties of bricks made mainly from fly ash with Carboniferous clay bond rests chiefly on the results of pilot-scale tests in which the bricks were fired under laboratory control, although one or two trials with a high proportion of fly ash have been made under work conditions. It is incorrect here to compare properties of the bond clay without fly ash, since the clays selected for this purpose are not
necessarily suitable for brickmaking on their own, and no bricks were made from the clays alone. Representative test results on two samples are given in Table 2.3.

**Table 2.2. Effect of moderate proportions of fly ash on the properties of bricks**

<table>
<thead>
<tr>
<th>Clay bricks 1030 °C</th>
<th>Bricks containing fly ash 1080 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Condition after 7 years</td>
</tr>
<tr>
<td>Water absn, % by wt.</td>
<td>Compr. strength</td>
</tr>
<tr>
<td>22.7</td>
<td>24.9 MPa</td>
</tr>
<tr>
<td>21.5</td>
<td>27.9 MPa</td>
</tr>
<tr>
<td>18.3</td>
<td>21.6 MPa</td>
</tr>
<tr>
<td>12.2</td>
<td>31.3 MPa</td>
</tr>
<tr>
<td>20.8</td>
<td>32.4 MPa</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

G: Good (no significant decay) C: Carboniferous
M: Moderate (decay not exceeding 6.3 mm) T: Triassic
B: Bad (extensive decay) FA: Fly Ash

It is shown that these bricks of high ash content have properties very similar to those of many other facing and common bricks in general use, though their water absorption amounts are generally very high. Whilst an engineer accustomed to the dense bricks from the Coal Measures shale might tend to regard these high water absorption figures as unacceptable, Table 2.3 contains evidence that this perception is not justified. The excellent durability in the very severe conditions of the tray exposure test of nearly all the specimens tested would compare favourably with any random selection of ordinary clay bricks. It is not easy to find a satisfactory reason why these fly ash bricks are as good as they are.

A possible explanation may be found in their generally uniform pore size indicated by Butterworth (1954) since for theory, for which there is good support, frost action takes place in a structure in which ice lenses in coarse pores can be fed by water in adjacent very fine pores. It should not be overlooked that the high porosity of these bricks of high fly ash content will have a very favourable effect upon their thermal insulation properties.
Chapter 2: Literature review

Table 2.3. Properties of bricks with a high proportion of fly ash

<table>
<thead>
<tr>
<th>FA/clay % by volume</th>
<th>Method of making</th>
<th>Firing Temperature</th>
<th>Water absorption % by weight</th>
<th>Compressive strength MPa</th>
<th>Condition after 7 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>95/5</td>
<td>HM</td>
<td>lab., 1070</td>
<td>35.5</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>95/5</td>
<td>HM</td>
<td>lab., 1080</td>
<td>48.4</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>95/5</td>
<td>HM</td>
<td>lab., 1080</td>
<td>46.9</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>95/5</td>
<td>HM</td>
<td>lab., 1080</td>
<td>47.3</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>95/5</td>
<td>HM</td>
<td>lab., 1080</td>
<td>46.6</td>
<td>-</td>
<td>G</td>
</tr>
<tr>
<td>90/10</td>
<td>HM</td>
<td>lab., 1070</td>
<td>31.6</td>
<td>15.0</td>
<td>G,M</td>
</tr>
<tr>
<td>85/15</td>
<td>M</td>
<td>works, 1030</td>
<td>29.2</td>
<td>17.1</td>
<td>G,G</td>
</tr>
<tr>
<td>85/15</td>
<td>M</td>
<td>lab., 1080</td>
<td>25.5</td>
<td>25.5</td>
<td>G,G</td>
</tr>
<tr>
<td>85/15</td>
<td>HM</td>
<td>lab., 1080</td>
<td>26.8</td>
<td>23.1</td>
<td>G,G</td>
</tr>
<tr>
<td>85/15</td>
<td>HM</td>
<td>lab., 1070</td>
<td>30.2</td>
<td>18.2</td>
<td>G,G</td>
</tr>
<tr>
<td>85/15</td>
<td>WC</td>
<td>lab., 1080</td>
<td>22.1</td>
<td>21.1</td>
<td>M,M</td>
</tr>
<tr>
<td>85/15</td>
<td>SD</td>
<td>lab., 1000</td>
<td>29.0</td>
<td>10.5</td>
<td>B,B</td>
</tr>
<tr>
<td>85/15</td>
<td>HM</td>
<td>lab., 1080</td>
<td>32.7</td>
<td>15.1</td>
<td>G,M</td>
</tr>
<tr>
<td>85/15</td>
<td>WC</td>
<td>lab., 1080</td>
<td>30.7</td>
<td>22.5</td>
<td>M,M,M</td>
</tr>
<tr>
<td>75/25</td>
<td>WC</td>
<td>Works, 1030</td>
<td>15.0</td>
<td>39.0</td>
<td>G</td>
</tr>
<tr>
<td>75/25</td>
<td>M</td>
<td>Works, 1030</td>
<td>31.6</td>
<td>19.4</td>
<td>G,M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method of making</th>
<th>Condition after 7 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>HM</td>
<td>G</td>
</tr>
<tr>
<td>M</td>
<td>Moderate</td>
</tr>
<tr>
<td>WC</td>
<td>G</td>
</tr>
<tr>
<td>SD</td>
<td>G,M</td>
</tr>
<tr>
<td>FA</td>
<td>Fly Ash</td>
</tr>
</tbody>
</table>

The possibility of excessive amounts of soluble salts being found in clay/fly ash mixtures was studied. Sample bricks made from fly ash and clay (95:5) by volume taken from different depths in a number of different boreholes, were fired to 960°C, 1020°C and 1080°C. All batches tested showed a very similar composition, as indicated in Table 2.4.

Table 2.4. Soluble salts analysis of fly ash/clay bricks (95:5)

<table>
<thead>
<tr>
<th>Mineral %</th>
<th>960°C</th>
<th>1020°C</th>
<th>1080°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total soluble salts</td>
<td>2.58</td>
<td>2.31</td>
<td>0.99</td>
</tr>
<tr>
<td>Silicate (SiO3)</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulphate (SO4)</td>
<td>1.50</td>
<td>1.42</td>
<td>0.65</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>0.71</td>
<td>0.59</td>
<td>0.28</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>0.03</td>
<td>&lt;0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Chapter 2: Literature review

The soluble salts consisted mainly of calcium sulphate, and the amount was well within the limits found with other bricks in common use. Soluble salts content of bricks of high proportion fly ash provide no grounds for alarm.

2.2.2. Brick making using different types of fly ash, U.S.A.

The fly ash bricks used in these tests were produced by Slonaker (1978) at a pilot plant operated by the Coal Research Bureau, West Virginia University, under a contract to the Energy Research and Development Administration, Fossil Energy, Morgantown, USA.

A typical fly ash brick composition consists of 75 percent fly ash, 22 percent bottom slag, and 3 percent sodium silicate by weight. The ingredients are mixed at an overall 7% moisture content. The bricks are formed by pressing and are fired in a shuttle kiln. All bricks are tested in accordance with the American Society for Testing and Materials (ASTM C62) designations for grade severe weathering brick.

Four types of fly ash were tested: lignite, Northern West Virginia, Southern West Virginia, and Western Kentucky.

2.2.2.1. Bricks made with lignite fly ash

The chemical analysis of the lignite fly ash is shown in Table 2.5. It should be noted from Table 2.5 that both calcium and magnesium oxides have higher values in the lignite fly ash than is normally found in a bituminous fly ash. However, this will increase the strength of the fly ash bricks.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.40</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.73</td>
</tr>
<tr>
<td>CaO</td>
<td>31.10</td>
</tr>
<tr>
<td>MgO</td>
<td>9.02</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Table 2.5. Composition of lignite fly ash
Chapter 2: Literature review

The sodium silicate added to the fly ash brick to act as a binder in the unfired state. It is significant to note that with the addition of sodium silicate, it was possible to press brick which had satisfactory unfired compressive strength for particular type of fly ash.

The lignite fly ash batch containing 3 percent grade 47 sodium silicate stuck severely to the mixer. It is thought that the sticking was caused by a reaction between the alkaline sodium silicate and the calcium and magnesium salts in the lignite fly ash. Such a reaction would cause thickening of the batch and a tendency of the sodium silicate to build up on the metal surfaces of the mixer rather than disperse properly over the grain surfaces of the fly ash during mixing.

A similar lignite fly ash batch in which the sodium silicate was left out did not stick to the mixer. It is significant to note that with this particular lignite fly ash, it was possible to press brick which had satisfactory unfired compressive strength without the addition of sodium silicate. The sodium silicate in the fly ash brick acts as a binder in the unfired state. It is the most costly item in the fly ash brick process and its elimination for this particular lignite fly ash would result in considerable cost savings.

An exothermic reaction was observed after water had been added to this fly ash and the mix had been completed. This indicates that there is free or unreacted calcium oxide and/or magnesium oxide in the fly ash.

Slonaker (1978) reported when fired at 1214°C, neither of the aforementioned batches met A.S.T.M. designations for a grade as severe weathering brick. When these bricks were fired at 1236 °C, they produced a brick, meeting A.S.T.M. designations. Additional bricks were fired at 1258 °C at which temperature they suddenly vitrified and completely melted. The bricks produced with the lignite fly ash have an extremely narrow firing range which requires that firing conditions be carefully controlled. The possible reason that fly ash is a pre-fired raw material is because it has undergone considerable heat work in the electric utility boiler, so little additional heat work is required to form the ceramic bonds.

It has been shown in Table 2.6a that the most satisfactory lignite fly ash brick can be produced using 75% lignite fly ash and 25% bottom slag at a 7% moisture level by dry press method and firing the brick at 1236 °C.
Table 2.6. (a) Typical composition and properties of lignite fly ash brick having 40 percent core area

<table>
<thead>
<tr>
<th>Properties</th>
<th>Lignite Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash %</td>
<td>75</td>
</tr>
<tr>
<td>Bottom slag-20 mesh %</td>
<td>25</td>
</tr>
<tr>
<td>Water content %</td>
<td>7</td>
</tr>
<tr>
<td>Final firing temp., °C</td>
<td></td>
</tr>
<tr>
<td>% Abs, 24 hr soak</td>
<td>1197</td>
</tr>
<tr>
<td>% Abs, 5 hr boil</td>
<td>21.69</td>
</tr>
<tr>
<td>Saturation coefficient</td>
<td>26.49</td>
</tr>
<tr>
<td>% Apparent porosity</td>
<td>0.82</td>
</tr>
<tr>
<td>Bulk density, kg/m³</td>
<td>44.66</td>
</tr>
<tr>
<td>% Shrinkage</td>
<td>2.9</td>
</tr>
<tr>
<td>Unfired compressive strength (MPa)</td>
<td></td>
</tr>
<tr>
<td>Fired compressive strength (MPa)</td>
<td></td>
</tr>
<tr>
<td>A.S.T.M. grade</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>SW</td>
</tr>
</tbody>
</table>

2.2.2.2. Bricks made with Northern West Virginia Fly ash

The initial attempt at pressing 40 percent core area fly ash brick from a Northern West Virginia fly ash was made using a mix which had been optimised during work with standard fly ash brick. This mix contained 2.9 percent grade 47 sodium silicate and 4.5 percent moisture. It was readily apparent that this mix did not possess adequate unfired strength to allow the brick to be removed by hand from the press.

The grade 47 sodium silicate was increased in 0.1 percent increments until it was shown from the unfired compressive strength that the brick had adequate unfired strength to be removed from the press. The minimum amount of sodium silicate was found to be 3 percent.

For each fly ash, there is an optimum percentage of moisture which results in maximum compaction during the pressing of the brick. For the Northern West Virginia fly ash, the optimum percentage of moisture was 7 percent.

The Northern West Virginia fly ash had 24.90 percent iron, and this quantity of iron caused the brick to have a very narrow firing range. If the firing temperature was slightly higher than normal, the brick would "overfire" as indicated by partial melting accompanied by excessive entrapped gas pockets.
It has been shown in Table 2.6b that the most satisfactory Northern West Virginia fly ash brick could be produced using 69.62% fly ash, 27.38% bottom slag, 3% grade 47 sodium silicate at 7% moisture level and firing the brick to 1236 °C.

**Table 2.6. (b) Typical composition and properties of Northern West Virginia fly ash brick having 40 percent core area**

<table>
<thead>
<tr>
<th>Properties</th>
<th>Northern West Virginia Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash %</td>
<td>69.62</td>
</tr>
<tr>
<td>Bottom slag-20 mesh %</td>
<td>27.38</td>
</tr>
<tr>
<td>Water content %</td>
<td>7</td>
</tr>
<tr>
<td>Silicate %</td>
<td>3</td>
</tr>
<tr>
<td>Silicate Grade</td>
<td>47</td>
</tr>
<tr>
<td>Final firing temp., °C</td>
<td>1164 1175 1197 1214 1236</td>
</tr>
<tr>
<td>% Abs, 24 hr soak</td>
<td>10.75 9.85 9.15 7.78 4.73</td>
</tr>
<tr>
<td>% Abs, 5 hr boil</td>
<td>14.56 13.72 12.86 11.44 8.37</td>
</tr>
<tr>
<td>Saturation coefficient</td>
<td>0.74 0.72 0.71 0.68 0.56</td>
</tr>
<tr>
<td>% Apparent porosity</td>
<td>26.70 25.57 24.31 22.10 17.06</td>
</tr>
<tr>
<td>Bulk density, kg/m²</td>
<td>7 7.2 7.3 7.4 7.8</td>
</tr>
<tr>
<td>% Shrinkage</td>
<td>4.2 4.6 4.8 5.7 5.5</td>
</tr>
<tr>
<td>Unfired compressive strength (MPa)</td>
<td>5.5</td>
</tr>
<tr>
<td>Fired compressive strength (MPa)</td>
<td>41.1 44.3 45.8 49.8 41.7</td>
</tr>
<tr>
<td>A.S.T.M. grade</td>
<td>MW</td>
</tr>
</tbody>
</table>

2.2.2.3. Bricks made with Southern West Virginia Fly ash

The fly ash brick produced from Southern West Virginia fly ash had excellent unfired compressive strength and could be moved from the press and stacked upon the kiln car without undue care to prevent breakage of the brick.

With this fly ash, the sodium silicate was reduced from 2.1 percent to 1.1 percent in 0.1 percent increments. As the sodium silicate content was decreased, the unfired compressive strength showed a decrease, however, all of the brick in this series could be moved from the press to the kiln car. Also, as the sodium silicate content was decreased, there was a very gradual increase in the water absorption and saturation of the brick. All the fired bricks met the A.S.T.M. standard for severe weathering grade. The data indicates that the major role of sodium silicate is as a strengthening agent in the unfired state and that sodium silicate has minor effects on the fired properties of the brick. Attempts were made to increase the fly ash content, however, a noticeable increase of drying cracks
occurred. The bottom slag provides a means for the release of moisture during drying and it must be maintained in the batch.

It has been shown in Table 2.6c that the most satisfactory Southern West Virginia fly ash brick can be produced using 76.66% fly ash, 21.24% bottom slag, 2.1% grade 47 sodium silicate at 6% moisture level and firing the brick to 1197 °C.

Table 2.6. (c) Typical composition and properties of Southern West Virginia fly ash brick having 40 percent core area

<table>
<thead>
<tr>
<th>Properties</th>
<th>Southern West Virginia Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash %</td>
<td>76.66</td>
</tr>
<tr>
<td>Bottom slag-20 mesh %</td>
<td>21.24</td>
</tr>
<tr>
<td>Water content %</td>
<td>6</td>
</tr>
<tr>
<td>Silicate %</td>
<td>2.1</td>
</tr>
<tr>
<td>Silicate Grade</td>
<td>47</td>
</tr>
<tr>
<td>Final firing temp., °C</td>
<td>1136 1142 1153 1164 1175 1197</td>
</tr>
<tr>
<td>% Abs, 24 hr soak</td>
<td>11.04 11.73 11.01 9.83 9.39 8.51</td>
</tr>
<tr>
<td>% Abs, 5 hr boil</td>
<td>14.42 15.12 14.40 13.17 12.83 11.93</td>
</tr>
<tr>
<td>Saturation coefficient</td>
<td>0.77 0.78 0.76 0.74 0.73 0.71</td>
</tr>
<tr>
<td>% Apparent porosity</td>
<td>25.71 26.68 25.73 23.91 23.46 22.10</td>
</tr>
<tr>
<td>Bulk density, kg/m^3</td>
<td>6.9 6.8 6.9 7.0 7.0 7.1</td>
</tr>
<tr>
<td>% Shrinkage</td>
<td>2.4 2.5 2.6 3.1 3.2 3.8</td>
</tr>
</tbody>
</table>

2.2.2.4. Bricks made with Western Kentucky Fly ash

The first brick made with Western Kentucky fly ash showed scumming. Scumming is the appearance of white, fluffy deposits on the surface of an unfired brick. The white, fluffy deposits are composed of water soluble salts which migrate with the water to the surface of a brick during the drying process. The effect of scumming upon a brick is to decrease the unfired compressive strength.

Extensive prior research by the Coal Research Bureau in the U.S. has shown that certain chemical additives will markedly reduce or eliminate scumming. For the Western Kentucky fly ash, it was found that 1.2 percent sodium hydroxide eliminated the scumming.
As far as the addition of sodium silicate was concerned, when the amount of sodium silicate was reduced to 2.7 percent or less, drying cracks occurred. It appears that 2.8 percent sodium silicate is the most favourable amount to use.

Any reduction in the moisture level in fly ash brick will result in a decrease in the migration of undesirable water soluble salts to the surface of the brick during the drying process. The moisture level was reduced from 10.0 percent to 5.0 percent in 1.0 percent increments. There was a rapid loss of unfired compressive strength, accompanied by cracking, as the moisture level was reduced below 10.0 percent. Therefore, a 10.0 percent moisture level appears to be the optimum level for this fly ash.

The feasibility of using more fly ash and less bottom slag was explored with this fly ash. As the percentage of fly ash was increased, there was a gradual deterioration in the physical properties of the brick, accompanied by an abrupt increase in drying cracks.

It has been shown in Table 2.6d that the most satisfactory Western Kentucky fly ash brick can be produced using 70.4% fly ash, 26.8% bottom slag, 2.8% grade 45 sodium silicate at 10.0% moisture level and firing the brick at 1164 °C. A 1.2% sodium hydroxide addition is used with this fly ash to eliminate scumming.

Table 2.6. (d) Typical composition and properties of Western Kentucky fly ash brick having 40 percent core area

<table>
<thead>
<tr>
<th>Properties</th>
<th>Western Kentucky Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash %</td>
<td>70.4</td>
</tr>
<tr>
<td>Bottom slag-20 mesh %</td>
<td>26.8</td>
</tr>
<tr>
<td>Water content %</td>
<td>10</td>
</tr>
<tr>
<td>Silicate %</td>
<td>2.8</td>
</tr>
<tr>
<td>Silicate Grade</td>
<td>45</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>1.2</td>
</tr>
<tr>
<td>Final firing temp., °C</td>
<td>1114</td>
</tr>
<tr>
<td>% Abs, 24 hr soak</td>
<td>10.98</td>
</tr>
<tr>
<td>% Abs, 5 hr boil</td>
<td>14.28</td>
</tr>
<tr>
<td>Saturation coefficient</td>
<td>0.77</td>
</tr>
<tr>
<td>% Apparent porosity</td>
<td>28.38</td>
</tr>
<tr>
<td>Bulk density, kg/m^3</td>
<td>7.6</td>
</tr>
<tr>
<td>% Shrinkage</td>
<td>2.9</td>
</tr>
<tr>
<td>Unfired compressive strength (MPa)</td>
<td>1.9</td>
</tr>
<tr>
<td>Fired compressive strength (MPa)</td>
<td>30.5</td>
</tr>
<tr>
<td>A.S.T.M. grade</td>
<td>SW</td>
</tr>
</tbody>
</table>

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Chapter 2: Literature review

The results of the physical testing of the brick are presented in Table 2.6a, b, c and d. The data indicates the ranges over which fly ash brick can be fired. The firing range is different for each fly ash. From the data it can be seen that the approximate firing temperatures necessary to produce a quality fly ash brick are as follows:

- Lignite fly ash: 1236 °C
- Northern West Virginia fly ash: 1236 °C
- Southern West Virginia fly ash: 1197 °C
- Western Kentucky fly ash: 1164 °C

Table 2.6a, b, c and d also indicates how fly ash brick are affected by different firing temperatures within their firing range. The water absorption of the Western Kentucky fly ash brick is relatively unchanged as the firing temperatures are decreased or increased. The Southern West Virginia fly ash brick and Northern West Virginia fly ash brick decrease in water absorption as the firing temperature is increased. The water absorption of the lignite fly ash brick decreases rapidly as the firing temperature is increased. The Western Kentucky fly ash brick can tolerate the most latitude in firing temperatures and the lignite fly ash brick can tolerate the least latitude in firing temperatures.

The saturation coefficient is the ratio of absorption by 24 hour soak to the absorption by 5 hour boil and is an indication of the ratio of easily filled to total fillable pore space. The data for the saturation coefficients are presented in Table 2.6a, b, c and d. The saturation coefficient of the majority of the fly ash brick tested is within the range of 0.70 to 0.78. Only the lignite and Northern West Virginia fly ash brick exhibit a noticeable change in saturation coefficient as the firing temperature is changed. In these instances the saturation coefficient decreases as the firing temperature is increased.

Table 2.6a, b, c and d indicates the data for the apparent porosity at varying firing temperatures. Although there are no direct ASTM limitations concerning porosity, a brick with low porosity is less likely to become permeated with water and possibly chip and spall if frozen while permeated. The apparent porosity of the majority of the fly ash brick tested is within the range of 20 percent to 30 percent. As indicated in Table 2.6a, b, c and d, the apparent porosity will be decreased by firing the fly ash brick to a higher temperature.
Bulk density and shrinkage are closely related, in as much as an increase in shrinkage of a fly ash brick causes an increase in bulk density. As can be noticed from Table 2.6a, b, c and d, an increase in firing temperatures causes an increase in bulk density and shrinkage. It is interesting to note that the Western Kentucky fly ash has one of the heaviest bulk densities and the least amount of shrinkage. This indicates that the Western Kentucky fly ash is compacted densely during the forming operation of the fly ash brick.

This study shows that there is a different firing range for each fly ash and each fly ash has an optimum firing temperature.

2.2.3. Utilisation of Sulcis Coal Ash in the Production of Masonry Bricks, Italy

Masonry bricks have been produced by Usai (1985) using Sulcis Coal ash and a slurry by-product of an Industry operating in Sardinia, Italy. The chemical compositions of these materials are shown on Table 2.7. Both materials were finely ground in a ball-mill, and a paste was prepared with the granulometric fraction passing through the sieve of 5.600 mesh.

Cylindrical samples of height 20 mm and diameter 40 mm, were extruded by means of a hydraulic press at 5 MPa of pressure. The samples were finally fired in an electric furnace at temperatures of 1000, 1100 and 1200 °C for a period of 10 hours. The samples were cooled to room temperature and taken out of the furnace at 20°C. The bricks had a dark grey colour.

Table 2.7. Chemical composition of raw materials for masonry brick

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Paste% (90% Sulcis coal ash, 10% Slurry by weight)</th>
<th>Sulcis coal ash % by weight</th>
<th>Slurry % by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>15.52</td>
<td>16.00</td>
<td>({Al_2O_3+Fe_2O_3}) 15.30</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>28.31</td>
<td>31.00</td>
<td>-</td>
</tr>
<tr>
<td>SiO₂</td>
<td>28.40</td>
<td>31.50</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.35</td>
<td>1.50</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>21.38</td>
<td>15.00</td>
<td>78.80</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>4.55</td>
<td>4.40</td>
<td>5.94</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>-</td>
<td>0.60</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.8. Characteristics of fired masonry brick samples

<table>
<thead>
<tr>
<th>Properties</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak firing temperature, °C</td>
<td>1000</td>
<td>1100</td>
<td>1200</td>
</tr>
<tr>
<td>Bulk density, kg/m³</td>
<td>1698</td>
<td>2050</td>
<td>1180</td>
</tr>
<tr>
<td>Porosity, m³/kg</td>
<td>0.000366</td>
<td>0.000098</td>
<td>0.000113</td>
</tr>
<tr>
<td>Compressive strength, MPa</td>
<td>0.380</td>
<td>7.318</td>
<td>2.658</td>
</tr>
<tr>
<td>Firing shrinkage %</td>
<td>2.5</td>
<td>2.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Non-reacted CaO kg/100 kg</td>
<td>1.01</td>
<td>1.01</td>
<td>0.60</td>
</tr>
<tr>
<td>(Mullite %)</td>
<td>13.00</td>
<td>45.00</td>
<td>47.00</td>
</tr>
</tbody>
</table>

Table 2.8. shows the characteristics of the fired coal ash-slurry brick. The amount of mullite present in the brick increases with the firing temperature, and this is the most important compound with regard to the mechanical characteristics of the bricks. The increase in peak firing temperature from 1000 to 1100 °C gives the product a very compact structure and a compressive strength of 7.32 MPa, greatly higher than the requirements of Italian Standards. The porosity, equally, decreases rapidly with the compaction due to the rise of temperature. An increase of porosity is produced at the peak firing at 1200 °C, probably because the temperature rise has caused holes and distortions in the structural lattice of the material, correspondingly this has decreased the compressive strength. This corresponds also to an irregular variation of the specific weights in connection with the porosity. This indicates that the best firing temperature for this type of paste is 1100°C.

2.2.4. Fly ash bricks with and without chemical accelerator, India

The manufacturing of these brick processes were developed in two national research laboratories, namely, Central Building Research Institute (CBRI) and Central Fuel Research Institute (CFRI) in India and reported by Ghosh (1992).

2.2.4.1. CBRI Process

Sintered method

The main raw materials used in this method are fly ash (60% maximum), clay (37% minimum) and sand (3% approximately). The manufacturing sequences are as follows:
- fly ash and clay are mixed with water to obtain a paste of mouldable consistency
- weathering of the mixture for 12 hours
- moulding of bricks from weathered mix
• natural drying of green bricks
• burning of the dried bricks at a temperature of 950-1000 °C for 4-5 hours
• natural cooling of bricks. Figure 2.1 shows the above mentioned process schematically.

Unsintered method

The main raw material used in this method is fly ash (60% maximum), sand (3% minimum) and clay (37% approximately). Green bricks are steam conditioned to produce the final product. The manufacturing steps are similar to CFRI process which is described below. Physical characteristics of the fly ash brick produced in the process is not available.

2.2.4.2. CFRI Process

Unsintered method with chemical accelerator

The main ingredients used in this process are 80-85% fly ash, 7-10% quick lime and 8-10% sand. In addition, a small quantity of a chemical accelerator is added in the mix. The manufacturing sequences are as follows:
• fly ash, lime, sand, accelerator and water are proportioned and mixed thoroughly in a mechanical mixer
• green bricks are formed by pressing the above mixture in moulds using a hydraulic press
• green bricks are stored under cover for natural curing
• green bricks are conditioned by low pressure steam in an Autoclave for a few hours
• natural cooling of bricks.

Figure 2.2 shows the CFRI process schematically.

Unsintered method without chemical accelerator

This process is essentially the same as that described above except that the chemical accelerator is not used and a high pressure steam (20 bar) is used in place of low pressure steam.

Figure 2.2. Fly ash brick manufacturing process developed by central fuel research institute (CFRI), India
2.2.4.3. Properties of fly ash brick

Physical characteristics of a typical fly ash brick produced in the CFRI process is presented in Table 2.9. below and compared with that of a typical burnt clay brick.

**Table 2.9. Properties of fly ash bricks using CFRI process**

<table>
<thead>
<tr>
<th>Description</th>
<th>CFRI Process</th>
<th>Burnt clay brick</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With</td>
<td>Without</td>
</tr>
<tr>
<td></td>
<td>Accelerator</td>
<td>Accelerator</td>
</tr>
<tr>
<td>Crushing Strength (MPa)</td>
<td>9.8-12.8</td>
<td>&gt;14.7</td>
</tr>
<tr>
<td>Water Absorption (%)</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Bulk Density (kg/m³)</td>
<td>1550</td>
<td>1400</td>
</tr>
</tbody>
</table>

It may be observed from Table 2.9 that fly ash bricks have superior physical characteristics over burnt clay bricks. Ghosh (1992) indicated that fly ash bricks also have better sulphate resisting properties and show better corrosion resistance than burnt clay bricks in a saline environment. The resulting property of fly ash bricks is also superior to burnt clay bricks. It has been reported that the colour of the brick was shining bluish grey and looked like decorative bricks.

2.3. Sewage sludge in bricks

2.3.1 Patents for use of sewage sludge in brick manufacture

2.3.1.1 Patent using sewage sludge as a supplement material in brick making

In 1889 Thomas Shaw of Manchester, England, patented the process of using sewage sludge as an organic supplement in brick manufacture. According to his invention he took the sludge and added an equal quantity of clay, and mixed well using a pug mill. The material was then semi-dried and afterwards forced into or through dies in the ordinary manner of making bricks. Which when subsequently dried and burnt in the usual manner were found to possess valuable qualities such as hardness, durability, and colour far superior to ordinary clay bricks. The bricks were suitable for building purposes.
2.3.1.2 Patent using sewage sludge and waste oil in brick making

Hans Lingl (1978) from Germany has patented a process of using sewage sludge and waste oil to make bricks. The process is described in Figure 2.3. This method also be used for industrial sludges, (eg. poisonous sludges) for making bricks or other ceramic articles. Sludge is mixed with clay to form a mixture of approximately 30 to 50% sludge by volume. The mixture may then be stored, and then extruded by conventional means. After extrusion and cutting or shaping, the articles are dried and fired in a kiln. Preferably, the exhaust gases from the dryer should be vented into the kiln as combustion gases, where odours or poisonous compounds of the exhaust air can be destroyed. Also, used or waste oil may be added during mixing to reduce odours and to supply extra heat during firing in the kiln.

Figure 2.3. Sewage sludge-oil brick making process

According to the invention insulating bricks were produced. Sewage sludge having an approximate moisture content of 20% was mixed with brick clay using a conventional clay preparation system, mixed in the ratio of 35:65 by volume. Residual oil comprising approximately 10% of the volume of the mix was also added during the mixing. The mixture so formed was then stored to be kneaded in a conventional silo for a period of approximately 24 hours, and then was extruded. The extrusion column was then cut into standard insulating brick sizes. The bricks were then advanced to a continuous dryer, and
the exhaust gases from the dryer were vented into the tunnel kiln, whereby all aromatic compounds in the exhaust air are destroyed. The maximum temperature within the kiln was 1000°C, with each brick being in the tunnel for approximately 45 hours. According to Lingl, the bricks produced were indistinguishable from similar bricks produced without the addition of sewage sludge, except that they had enhanced insulating properties.

It will be seen that a method has been disclosed for utilising sewage sludge as a resource. While the invention is conceived to be the most practical and preferred method, it is apparent that many modifications could be made within the scope of the invention.

2.3.2. Bricks manufactured using sewage sludge

2.3.2.1 Constructive sludge management “biobrick”

This work had been reported by Alleman and Berman (1984) in the United States of America. Alleman and Berman established bench scale methodologies to simulate a conventional full scale operation. Dried clay/shale materials were obtained from a regional brick manufacturing facility. A variety of sludges produced by four metropolitan Washington, D. C., wastewater treatment plants was employed, with sludge solids concentration typically ranging between 15% and 25%. Further details regarding the relative characteristics of these sludge materials are provided in Table 2.10.

<table>
<thead>
<tr>
<th>Number</th>
<th>Wastewater source</th>
<th>Chemicals applied</th>
<th>Final solids content %</th>
<th>Sludge treatment scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Domestic and industrial</td>
<td>Lime</td>
<td>15-20</td>
<td>Raw sludge, chemically conditioned, vacuum filtered</td>
</tr>
<tr>
<td>2</td>
<td>Domestic and industrial</td>
<td>FeCl₃</td>
<td>15-20</td>
<td>Anaerobic digestion, chemically conditioned, vacuum filtered</td>
</tr>
<tr>
<td>3</td>
<td>Domestic and industrial</td>
<td>Polymer</td>
<td>20-30</td>
<td>Anaerobic digestion, chemically conditioned, belt pressed</td>
</tr>
<tr>
<td>4</td>
<td>Domestic</td>
<td>Cl₂</td>
<td>50-95</td>
<td>Anaerobic digestion, super chlorination, air dried at sand beds</td>
</tr>
<tr>
<td>5</td>
<td>Domestic</td>
<td>Polymer</td>
<td>15-20</td>
<td>Dissolved air flotation, heat treated, chemically conditioned, centrifuged</td>
</tr>
<tr>
<td>6</td>
<td>Domestic</td>
<td>Polymer</td>
<td>25-30</td>
<td>Dissolved air flotation, chemically conditioned, centrifuged</td>
</tr>
</tbody>
</table>

Table 2.10. Sludge forms employed during bench scale brick production

Addition of specific sludges to the basic clay/shale ingredients was handled on a volumetric basis with maximum sludge input of 50%. The combined clay/shale/sludge
mixture was then uniformly blended in a commercial grade mixer. Maintenance of desired plasticity levels, qualitatively identified using a crude Atterburg type assay, occasionally necessitated water addition.

Brick extrusion was arranged by placing the wet clay/shale/sludge mixture into a specially fabricated hopper for hydraulic compression. An aluminium die attached to the outlet chute of the hopper provided the desired cross sectional configuration. Individual bricks were manually sliced from the extruded ribbon at appropriate specimen depths.

Still wet, freshly extruded bricks were initially air dried over a period of several days. The green bricks were further dried in the oven at 110°C for 36 hrs before firing. A standard electric kiln was used for this operation with temperatures automated stair stepped between 200°C and 1100°C during the designated firing 36-42 hr and cooling 8-10 hr periods. Figure 2.4 shows the process schematically. Consistently attractive results warranted further evaluation of the concept under full scale conditions.

The same brick manufacturer that donated the clay/shale ingredients was encouraged to test the sludge amended procedure on a limited full scale basis. Thirty tons of domestic grade sludge were utilised for the test. A front end loader initially measured and blended the raw ingredients in a covered storage yard. The mixture was then passed through a conventional series of grinders and sieves before reaching the pug mill for desired extrusion. Subsequent drying, firing, and cooling measures were all conducted according to the brick manufacturer's standard operating procedures. At the completion of this short term full scale study, over 50,000 sludge amended brick had been produced. Several brick variations were manufactured, including cored with holes specimens at volumetric sludge fractions of one sixth, one third, and one half. Solid body bricks at the one third sludge level were also produced. The aesthetic quality of these bricks was extremely good.
Structural test results on full-scale bricks/bench scale bricks proved to be even more encouraging. Representative results on compressive strength, freeze-thaw durability and water absorption are given in Table 2.11. The compressive strength figures were surprisingly higher than expected and considerably beyond the ASTM standard criteria. Water absorption values were similarly attractive. Although compressive strength is higher than ASTM standard, the addition of sludge to clay reduces the strength and increases the water absorption in general.

Table 2.11. Structural properties of biobrick

<table>
<thead>
<tr>
<th>Brick specimen</th>
<th>Aesthetic quality</th>
<th>Compressive strength MPa</th>
<th>Residual freeze/thaw strength MPa</th>
<th>24 hour cold water absorption %</th>
<th>5 hour hot water absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>% by volume</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 sludge</td>
<td>Excellent</td>
<td>45.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>30 sludge</td>
<td>Excellent</td>
<td>43.2</td>
<td>37.8</td>
<td>6.1</td>
<td>11.5</td>
</tr>
<tr>
<td>50 sludge</td>
<td>Excellent</td>
<td>44.0</td>
<td>36.6</td>
<td>6.5</td>
<td>9.3</td>
</tr>
<tr>
<td>Unamended/Regular full scale bricks</td>
<td>Excellent</td>
<td>60.5</td>
<td>39.6</td>
<td>5.1</td>
<td>5.1</td>
</tr>
<tr>
<td>15 -25 sludge bench scale bricks</td>
<td>Excellent</td>
<td>20.7</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>ASTM standard</td>
<td>SW</td>
<td>20.7</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
</tbody>
</table>

Further field work, have been conducted on biobrick process. Sludge was trucked from an on site sludge hopper, the residue was directly pumped to the pug mill/extruder to avoid moisture related problems in the preceding grinder and sieve systems. Sludge addition in this fashion replaced the water previously added at the pug mill to develop desired plasticity (8-10%) moisture content in the extruded mixture.

2.3.2.2 Bricks manufactured from dried sludge and sludge ash

Research studies have been carried out by Joo Hwa Tay (1987) in the School of Civil and Structural Engineering, Nanyang Technological Institute, to investigate the feasibility of using sludge as building and construction related materials. Dried sludge and sludge ash were used for this purpose.
Chapter 2: Literature review

Digested and dewatered sludge samples were collected from a sewage treatment works. Clay samples were collected from the brick yard. Sludge mixed with clay was ground and crushed into fine pieces by a crushing machine. Two types of brick samples were prepared for comparison. One sample was made from clay mixed with various percentages of dried sludge. For the other sample, the sludge was first fired in a furnace at above 600°C to remove the organic matter. The sludge ash collected after the burning process was then mixed with clay at various percentages to produce a second set of brick samples. The percentages of dried sludge used for the first sample were 10, 20, 30, and 40% by weight. The percentages of sludge ash used for the other sample were 10, 20, 30, 40, and 50%. A control sample with no sludge or sludge ash was prepared as a reference. Each mixture was fed into an extrusion machine, and brick samples with dimensions of 40 mm long, 20 mm wide and 10 mm thick were manufactured. The brick samples were then dried in an oven at 100°C for 24 hrs. The dried bricks were fired in a kiln at a temperature of more than 1000°C for about 24 hrs. Samples then were tested to determine their characteristics.

Physical and chemical properties of dried sludge, sludge ash and clay are presented in Tables 2.12 and 2.13.

<table>
<thead>
<tr>
<th>Table 2.12. Properties of dried sludge, sludge ash, and clay</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measurement</strong></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Dried sludge</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Sludge ash</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Clay</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

The specific gravity of dried sludge ranges from 1.64-1.72 with an average value of 1.69. However, the specific gravity of sludge ash is higher, with a range of 2.79-2.83 and an average value of 2.81. The specific gravities of the clay samples are quite different, ranging from 2.34-2.40 with an average of 2.38. The effect of using sludge will be to produce a brick with less weight. The water content of the sludge samples collected from the sewage treatment works show a range of 50-70% with an average of 60%. The moisture content of the clay samples is lower, with a range of 8.5-9.5% and an average
value of 9% at the time of collection. This type of sludge can produce brick without any additional water for desired plasticity. The values of moisture content depends on the weather conditions and the duration of sludge drying before collection. Loss on ignition ranges from 59.2-60.8% with an average of 60.0% and 13.0-13.3% with an average of 13.2% for the dried sludge and clay samples, respectively. During firing, the carbon content of the sludge will produce energy which decrease with the total energy consumption. The dried sludge has pH values ranging from 8.10-8.50 with an average of 8.30. The average pH value for sludge ash is 9.0 with a range of 8.97-9.03. However, the average pH value for clay samples is 4.40 with a range of 4.10-4.60.

Average values of various minerals in sludge ash and clay are reported in Table 2.13. Si + Fe + Al are the main components for brick making found to be about one quarter of the sludge component to the clay. However the sludge contains a reasonable amount of Ca producing higher strength.

Table 2.13. Chemical composition of sludge ash and clay (g/kg)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Sludge ash</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>102.8</td>
<td>468.0</td>
</tr>
<tr>
<td>Fe</td>
<td>80.6</td>
<td>89.2</td>
</tr>
<tr>
<td>Al</td>
<td>50.3</td>
<td>327.6</td>
</tr>
<tr>
<td>Ca</td>
<td>29.2</td>
<td>0.14</td>
</tr>
<tr>
<td>Zn</td>
<td>26.8</td>
<td>15.0</td>
</tr>
<tr>
<td>Mg</td>
<td>7.9</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>6.1</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Pb</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>1.1</td>
<td>-</td>
</tr>
</tbody>
</table>

Tables 2.14 and 2.15 show the various properties of the bricks manufactured from the mixtures of dried sludge and clay, and sludge ash and clay, respectively. The maximum percentage of dried sludge and sludge ash that could be mixed with clay for brick making were 40% and 50%, respectively. Beyond that, the bonding of the mixtures was poor and extrusion of the bricks results in dog earing of the product. The surface texture of the bricks was found to be uneven, especially for dried sludge bricks. The degree of surface roughness also increased with the amount of sludge in the brick. This is mainly due to the organic component being burnt off during the firing process. Loss on ignition of the brick samples before firing is 5.4% for 0% dried sludge and 22.3% for 40% dried sludge. For
the brick samples made with sludge ash, loss on ignition decreases from 5.4% for 0% sludge ash to 4.6% for 50% sludge ash. The loss on ignition for dried sludge bricks are mainly due to the organic matter of the clay being burnt off. This parameter affects the porosity and bulk density of the bricks.

The specific gravity of the brick samples decreases as the percentage of dried sludge in the bricks increases. However, the specific gravity of the brick samples increases slightly as the percentage of sludge ash in the bricks increases. The specific gravities of bricks are 2.38 for 0% sludge, 1.98 for 40% dried sludge, and 2.58 for 50% sludge ash. This is mainly related to the actual specific gravity of the raw materials. The shrinkage after drying at 100°C for 24 hrs is about 4% for both the clay brick samples and the brick samples with dried sludge and 3% for the sludge ash. During mixing of different types of brick, moisture content were the same, resulting to equal shrinkage.

Table 2.14. Properties of bricks using dried sludge (Tay, 1987)

<table>
<thead>
<tr>
<th>Dried sludge % by wt.</th>
<th>Specific gravity</th>
<th>Shrinkage %</th>
<th>Loss on ignition %</th>
<th>Compressive strength MPa</th>
<th>Water absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before firing</td>
<td>After firing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.38</td>
<td>4.0</td>
<td>9.91</td>
<td>5.4</td>
<td>87.2</td>
</tr>
<tr>
<td>10</td>
<td>2.32</td>
<td>4.2</td>
<td>10.15</td>
<td>10.7</td>
<td>59.9</td>
</tr>
<tr>
<td>20</td>
<td>2.24</td>
<td>3.7</td>
<td>10.84</td>
<td>14.3</td>
<td>45.9</td>
</tr>
<tr>
<td>30</td>
<td>2.17</td>
<td>4.2</td>
<td>12.26</td>
<td>19.7</td>
<td>39.5</td>
</tr>
<tr>
<td>40</td>
<td>1.98</td>
<td>4.0</td>
<td>12.87</td>
<td>22.3</td>
<td>37.9</td>
</tr>
<tr>
<td>ASTM standard</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tables 2.14 and 2.15 indicates that the percentage of water absorption of both bricks increases as the sludge percentage in the bricks increases. The water absorption for bricks is 0.3% for 0% sludge and increases with the use of dried sludge up to 3.63% for 40% dried sludge. The water absorption for brick samples made with sludge ash also increases but at a lower level of 1.70% for 50% sludge ash bricks. This indicates that bricks made with sludge ash are likely to have lower and better water absorption characteristics than bricks made with dried sludge.
Table 2.15. Properties of bricks using sludge ash (Tay, 1987)

<table>
<thead>
<tr>
<th>Sludge ash % by wt.</th>
<th>Specific gravity</th>
<th>Shrinkage %</th>
<th>Loss on ignition %</th>
<th>Compressive strength MPa</th>
<th>Water absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Before firing</td>
<td>After firing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.38</td>
<td>4.0</td>
<td>9.91</td>
<td>5.4</td>
<td>87.2</td>
</tr>
<tr>
<td>10</td>
<td>2.42</td>
<td>2.5</td>
<td>9.55</td>
<td>4.9</td>
<td>85.7</td>
</tr>
<tr>
<td>20</td>
<td>2.46</td>
<td>2.5</td>
<td>9.10</td>
<td>4.8</td>
<td>80.0</td>
</tr>
<tr>
<td>30</td>
<td>2.50</td>
<td>3.4</td>
<td>9.36</td>
<td>4.7</td>
<td>70.7</td>
</tr>
<tr>
<td>40</td>
<td>2.55</td>
<td>3.2</td>
<td>9.79</td>
<td>4.7</td>
<td>70.5</td>
</tr>
<tr>
<td>50</td>
<td>2.58</td>
<td>3.0</td>
<td>10.51</td>
<td>4.6</td>
<td>69.4</td>
</tr>
<tr>
<td>ASTM standard</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.7</td>
</tr>
</tbody>
</table>

As shown in Tables 2.14. and 2.15, the compressive strength of bricks made from the mixture of clay and dried sludge is 87.2 MPa for 0% dried sludge and decreases to 37.9 MPa for 40% dried sludge. For the bricks made with sludge ash, compressive strength decreases gradually to 69.4 MPa with 50% sludge ash. The compressive strength of brick samples with 10% dried sludge is about 30% lower than the strength of the control brick samples with 0% sludge. The compressive strength for brick samples with 10% sludge ash is similar to the control samples. The addition of dried sludge or sludge ash to clay decreases their compressive strength and increases water absorption. However this type of compressive strength for sludge ash brick is nearly double that of dried sludge brick and was expected as less organic material was available, 13% for sludge ash and 60% for dried sludge, respectively.

2.3.2.3 Use of sewage sludge with poor material clay brick

Roza Mesaros (1989) at the University of Novom Sadu, Faculty of Gradevinski, Subotica, Yugoslavia has conducted a study of making bricks using sewage sludge with poor material clay. A low clay minerals content containing large quantities of sand and lime was used to produce the bricks. The chemical composition of the clay is shown in Table 2.16. Table 2.17 provides the average values of the various sludge components.
Table 2.16. Percentage oxide composition of the brick making clays used

<table>
<thead>
<tr>
<th>L.O.I at 1000°C</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>17.47</td>
<td>49.94</td>
<td>7.93</td>
<td>3.36</td>
<td>0.76</td>
<td>13.28</td>
<td>4.91</td>
<td>1.11</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 2.17. Sludge components

<table>
<thead>
<tr>
<th>Component</th>
<th>Contents %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic material</td>
<td>31-61</td>
</tr>
<tr>
<td>Humus</td>
<td>22.47</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>0.230-0.728</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>2.16-6.00</td>
</tr>
<tr>
<td>Total P</td>
<td>2.37-4.95</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0244-0.0525</td>
</tr>
<tr>
<td>Cr</td>
<td>0.029-0.459</td>
</tr>
<tr>
<td>Zn</td>
<td>0.095-0.341</td>
</tr>
<tr>
<td>Insoluble materials</td>
<td>12-23</td>
</tr>
</tbody>
</table>

Laboratory determination of the technological characteristics:

A large number of test specimens were produced of the following types and composition.

1. Pure brick making clay
2. 80% brick making clay plus 20% sludge by volume
3. 60% brick making clay plus 40% sludge by volume

After homogenisation of the raw material, cylindrical test specimens of 120 mm length and 50 mm² cross-section were produced on a de-airing extruder. The results given in Table 2.18 were the mean value of measurements carried out on six test specimens.

The test specimens were first air dried and then finished in the dryer to give a constant mass. Firing was in a muffle kiln at temperatures of 950 and 1050°C. The holding time at maximum firing temperature was three hours. The specimens were then cooled in the closed kiln for a period of 16-18 hours. It was observed that during drying and firing longitudinal cracks occurred on the specimens containing 40% sludge, which indicated
that this was an excessive admixture of sludge. In the case of the test specimens with 20% sludge, the cracking was negligible.

Owing to the higher mixing water content in clay and sludge specimens during mixing, which was required here because of the grain size composition of the clay and the nature of the sludge, higher linear shrinkage occurred during drying. The shrinkage increased from 2.43 to 5.51% or 6.33%. This relatively high change in length can be attributed to the insufficient bonding capacity of the clay minerals, which also explains the reported appearance of the cracks. Shrinkage occurred in all test specimens after firing at 950°C, and at 1050°C a slight linear expansion was recorded. The insufficient volume of "binders" is also apparent in the results for bending strength, which showed that in both specimens containing 20 and 40% sludge, the strength was half that of the clay specimen. As soon as the brick making material is mixed with sludge, the water absorption of the fired ceramic body increases. There is little change in the density. The theoretical porosity displayed a normal increase in the specimens fired at 950°C. This uniform behaviour however could no longer be observed after firing at 1050°C. This is the effect of 100°C difference in heat.

Table 2.18. Important characteristics of dried test specimens fired at various temperatures

<table>
<thead>
<tr>
<th>Properties</th>
<th>Specimen designation</th>
<th>Clay</th>
<th>80% clay + 20% sludge</th>
<th>60% clay + 40% sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear shrinkage % Drying</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 950°C</td>
<td>2.43</td>
<td>5.51</td>
<td>6.33</td>
<td></td>
</tr>
<tr>
<td>at 1050°C</td>
<td>1.30</td>
<td>5.30</td>
<td>6.23</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.63</td>
<td>6.10</td>
<td>7.37</td>
<td></td>
</tr>
<tr>
<td>Compressive strength MPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 950°C</td>
<td>4.73</td>
<td>2.77</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td>at 1050°C</td>
<td>6.36</td>
<td>3.55</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>Water absorption %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 950°C</td>
<td>34.45</td>
<td>38.41</td>
<td>39.58</td>
<td></td>
</tr>
<tr>
<td>at 1050°C</td>
<td>31.31</td>
<td>38.15</td>
<td>37.86</td>
<td></td>
</tr>
<tr>
<td>Density kg/m³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 950°C</td>
<td>2563</td>
<td>2566</td>
<td>2636</td>
<td></td>
</tr>
<tr>
<td>at 1050°C</td>
<td>2615</td>
<td>2480</td>
<td>2534</td>
<td></td>
</tr>
<tr>
<td>Porosity %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 950°C</td>
<td>42.84</td>
<td>43.18</td>
<td>45.07</td>
<td></td>
</tr>
<tr>
<td>at 1050°C</td>
<td>43.13</td>
<td>43.43</td>
<td>40.73</td>
<td></td>
</tr>
</tbody>
</table>
Works operation

Shaping is carried out on a de-airing extruder, the green bricks are intensively dried, and subsequently fired in a coal fired Hoffmann kiln. The mixing of 25% sludge by volume to the so far not yet sufficiently homogeneous clay components was performed according to the mixed bed technique, in which the clay and the sludge are deposited in alternate layers. Discharge by means of multi bucket excavators improved the degree of mixing.

The first positive results in regard to the improvement of the rheological properties of the brick making material indicated that it would be feasible to use a clay body mix containing a specific percentage of sludge from the municipal sewers under operating conditions.

Another positive effect obtained by the use of the sewage sludge was also the reduction in the coal used for firing the kiln. Whereas previously approximately 0.3 kg coal/brick was used for firing, only 0.272 kg coal/brick was required for firing the clay mix containing 25% sewage sludge. This represents an energy saving of 10%.

The quality of the brick specimens produced during the trial period according to the test complies with the requirements of the Yugoslav Standards. With the exception of the compressive strength values, instead of the required compressive strength of 10 MPa the bricks only reached 5 MPa. However, the results indicated that pure Yugoslavia clay brick also under the standard. Allowance should be made for the fact that this reduction is to be attributed to the extremely low values of alumina (7.93%) content and the large quantity of sand in the clay, and also it is attributed to the very high content of organic material (31-61%) and humus (22-47%) in the sludge. Inadequate homogeneity of the mix and the insufficient storage time of the mix have also to be taken into account. This type of raw material can only be used for the production of low strength bricks. However in the region of Subotica, these bricks are widely used for individual buildings, small family houses, and for the restoration of old buildings and as backing bricks for multi storey buildings because of its positive thermal insulating properties.
2.3.2.4 Manufacture of factory bricks using sewage sludge

This work was reported by Slim and Wakefield (1991) of City Engineer’s Department, Port Elizabeth, South Africa.

**Sludge chemical composition**

The average composition of the heat-treated dewatered sludge used by Slim and Wakefield is given in Table 2.19.

This type of sludge is produced by heat treatment using the Zimpro wet air oxidation process in a continuous operation. The sludge in admixture with compressed air is raised to a temperature of 187°C using steam in a reactor operating at a pressure of 2200 kPa. The combination of temperature and pressure sterilises the sludge and greatly improves its dewatering characteristics. Following further gravity thickening, the sludge is transferred to centrifuges for final dewatering, the centrifuges are fitted with in line chemical dosing equipment, with a consumption of polyelectrolyte at 0.6 kg/ton of dry solids processed. A total of 45 tonne of dewatered sludge is produced daily.

<table>
<thead>
<tr>
<th>Components</th>
<th>High</th>
<th>Heat-treated sludge</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids, %</td>
<td>43.0</td>
<td>31.7</td>
<td>35.2</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>35.4</td>
<td>13.6</td>
<td>21.7</td>
</tr>
<tr>
<td>Calorific value, MJ/kg</td>
<td>-</td>
<td>-</td>
<td>16.77</td>
</tr>
<tr>
<td>Total nitrogen N, %</td>
<td>3.6</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Total phosphorus P, %</td>
<td>2.4</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Potassium K, %</td>
<td>0.23</td>
<td>0.09</td>
<td>0.18</td>
</tr>
<tr>
<td>Magnesium Mg, %</td>
<td>0.38</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>Calcium Ca, %</td>
<td>2.38</td>
<td>0.65</td>
<td>1.36</td>
</tr>
<tr>
<td>Sodium Na, %</td>
<td>0.14</td>
<td>0.06</td>
<td>0.09</td>
</tr>
<tr>
<td>Iron Fe, %</td>
<td>1.41</td>
<td>0.45</td>
<td>1.03</td>
</tr>
<tr>
<td>Zinc Zn, mg/kg</td>
<td>1535</td>
<td>651</td>
<td>1153</td>
</tr>
<tr>
<td>Lead Pb, mg/kg</td>
<td>1936</td>
<td>231</td>
<td>750</td>
</tr>
<tr>
<td>Chromium Cr, mg/kg</td>
<td>3141</td>
<td>366</td>
<td>1877</td>
</tr>
<tr>
<td>Copper Cu, mg/kg</td>
<td>287</td>
<td>133</td>
<td>210</td>
</tr>
<tr>
<td>Nickel Ni, mg/kg</td>
<td>48</td>
<td>28</td>
<td>37</td>
</tr>
<tr>
<td>Manganese Mn, mg/kg</td>
<td>165</td>
<td>88</td>
<td>125</td>
</tr>
<tr>
<td>Cadmium Cd, mg/kg</td>
<td>2.8</td>
<td>0.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Cobalt Co, mg/kg</td>
<td>5.0</td>
<td>0.6</td>
<td>2.5</td>
</tr>
</tbody>
</table>

All results, except total solids, are expressed based on dry solids.
Brick making initial trials

Initially small quantities, in the order of 5% by volume of sludge, were mixed with the clay from which batches of bricks were made using the normal production methods. Over a period, the proportion of sludge was gradually increased, but it was found that at levels of sludge above 45% by volume, problems were experienced with both distortion and cracking of the bricks and control of kiln temperatures. However, at approximately 30% sludge by volume, the bricks were of the manufacturer’s normal standard and appearance, temperatures were controllable, and substantial fuel savings were indicated.

Brick production in South Africa

Sludge and clay are blended from variable speed box feeders, equipped with rotating tines, discharging onto a conveyor. Sludge is added at a composition of 30% by volume to the clay for the production of stock bricks, and between 5% and 8% for face bricks. The mixture of clay and sludge is conveyed to the crushing plant where it first passes through a disintegrator which reduces the lumps of clay into fragments of less than 12 mm in diameter. This is followed by a high speed roller mill which further reduces the fragments to a grain size not exceeding 2.5 mm diameter.

The crushed clay and sludge then pass to a double shafted mixer where it is kneaded into a homogeneous mass after the addition of water to give the 20% moisture content required for the extrusion process. The amount of water added is dependent on the original moisture content of the mixture. Without the addition of sludge the water required is in the order of 280 litres per 1000 bricks. When stock bricks are being manufactured, the addition of sludge eliminates the need for any additional water.

The clay mix is then extruded through a metal die to produce a continuous column of the required cross section and pattern. This is guillotined into “slugs”, 1.15 m long, which are in turn sliced by wires to produce 15 bricks of conventional height. These 15 green bricks are then set on laths which are in turn placed in rows of 5 and stacked 10 high on mobile transfer trolleys which transport them to the air drying area. Air drying takes place under cover at ambient temperatures for a period of approximately 2 weeks or by drying in heated chambers where the bricks remain for 48 hours at an average temperature of between 60°C and 65°C. There are 18 chambers, each having capacity for 10000 bricks. The dried, unfired bricks are then removed from the trolley and transferred by conveyor belt to the setting station where they are stacked on tunnel kiln cars ready for firing.
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The tunnel kilns used at this works are straight, ceramic lined chambers of rectangular cross section, 1.8 m high by 2.2 m wide, and approximately 100 m in length having a steel door at each end. From the setting station the loaded kiln cars are pushed on rails through the kiln by means of a hydraulic ram. They first enter a pre heating zone ahead of the kiln door, where they are heated to approximately 100°C by means of hot exhaust air drawn from the kiln. This causes some of the moisture still remaining in the brick to be removed. The trolleys are indexed forward in increments of 1.3 m every hour when using clay alone, at which speed the journey through the kiln takes about 76 h. However, it has been found that the frequency of indexing, and hence the throughput, can be almost doubled when using sludge in the clay. This is directly attributable to the fuel value of the sludge.

With each trolley movement the kiln door automatically opens, allowing one stack of bricks to enter the heating zone which forms the initial stage in the firing process. Here the remaining moisture in the brick is removed and at a temperature of about 150°C the organic matter in the sludge begins to burn. This causes a rapid increase in temperature up to 800°C which is reached at a point some 18 m into the kiln. By this point, the sludge has been completely burnt and the temperature gradient decreases over the next 35 m until the firing zone is reached. Fuel in the form of heavy furnace oil is injected through overhead nozzles over a distance of 5 m in order to raise the temperature to 960°C, required for the vitrification of the clay. When no sludge has been added to the clay, 80 litres of heavy furnace oil are required to provide sufficient heat for the firing of 1000 bricks. The addition of sludge has reduced this requirement to 25 litres per 1000 bricks, and it is anticipated that this figure can be further reduced to 10 litres per 1000 bricks by a small increase in the percentage of sludge added.

After firing, the bricks move into the cooling zone where, over a distance of some 25 m, the temperature is slowly reduced to 600°C to avoid cracking. The rate of cooling is then increased by air which is blown into the kiln and the bricks exit at ambient temperature. Air required for the firing is blown in at the exit end and is drawn out near the inlet end of the kiln. Finally the bricks are removed from the kiln trolleys and conveyed to the stack yard ready for sale.

A temperature profile of the brick firing as undertaken by South African process is shown in Figure 2.5. The solid line illustrates the approximate temperature gradient before the use of sludge when the initial heating depended on the hot air flowing from the firing zone. Figure 2.5 shows the sludge brick firing process adopted by the author, when the
addition of sludge to the clay has considerably altered the temperature profile in the first half of the kiln, as shown by the broken line. This change in the temperature gradient has allowed brick production from the kiln to be increased by almost 100%. The potential energy savings aspect of the sludge brick is clearly illustrated in Figure 2.5.

![Temperature profile for brick making](image)

**Figure 2.5. Kiln temperature profile for brick making**

**Properties of the brick**

It has been reported that the appearance of both face (5-8% sludge) and stock (30% sludge) bricks was excellent, had uniform colour and texture and were free from extensive cracks. They were indistinguishable in both appearance and odour from conventional clay bricks. The bricks conform to the nominal standard dimensions of 220 x 106 x 73 mm. Shrinkage occurred throughout the manufacturing process and allowance for this was made in the extrusion stage. The average weight of the stock brick was 2.36 kg, and the face brick weighed 2.60 kg. This was compared with the conventional stock brick which weighed 3 kg. Hence a stock brick made with sewage sludge is 20% lighter than clay brick. The average compressive strength, measured according to South African Bureau of Standards, was 40.7 MPa for the face bricks and 38.3 MPa for stock bricks. These comply favourably with the standard values of 17.0 MPa and 14.0 MPa respectively for face and stack bricks. The 24-hour water absorption test gave average values of 13.1 % for the face and 14.2 % for the stock bricks. These figures are some 30 % higher than those obtained from similar locally made bricks which do not contain sludge. The higher water absorption can be considered an advantage which may lead to better mortar
adhesion. The properties of sludge brick are shown in Table 2.20. Since full scale production of bricks incorporating sludge began in South Africa 1979, over 120 million sludge bricks were produced up to 1991.

Table 2.20. Properties of Sludge brick

<table>
<thead>
<tr>
<th>Properties</th>
<th>Face bricks</th>
<th>Stock bricks</th>
<th>SABS standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total shrinkage, %</td>
<td>13.7</td>
<td>14.3</td>
<td>-</td>
</tr>
<tr>
<td>Average weight, kg</td>
<td>2.60</td>
<td>2.36</td>
<td>3</td>
</tr>
<tr>
<td>Average compressive strength, MPa</td>
<td>40.7</td>
<td>38.3</td>
<td>17.0- Face Bricks 14.0- Stock Bricks</td>
</tr>
<tr>
<td>Average 24-hour water absorption, %</td>
<td>13.1</td>
<td>14.2</td>
<td>-</td>
</tr>
</tbody>
</table>

SABS : South African Bureau of Standards

Sludge bricks in South Australia

A brick manufacturer in Adelaide, after the initial work at the University of Wollongong in 1991, has produced 250,000 bricks containing 5% sewage sludge in 1992. The process was then tested to ensure that environmental and structural criteria were being met. This was confirmed as both environmentally safe and exceeded the Australian standard, for structural properties. The manufacturer also undertook trials with bricks containing 10% sludge. By 1993, over one million sludge bricks had been produced. The manufacturer indicated that the economic advantages of the sludge brick start in the production process. The sewage sludge contains large concentrations of organic matter that, when mixed with clay and fired, release energy, reducing the amount of fuel needed to vitrify the bricks. The firing process virtually entombs any metal ions, locking them safely away at 1200°C (Janine, 1994).

2.4. “Biofly” brick laboratory method

2.4.1. Introduction

The Biofly brick concept was developed at the Department of Civil and Mining Engineering of the University of Wollongong (Sidrak 1991). The concept involves the addition of two waste materials namely the sewage sludge and fly ash to the clay/shale. The combined product is solidified to make the so called Biofly brick.
2.4.2. Properties of materials

The properties of fly ash, sewage sludge and clay/shale are of prime importance for making Biofly brick. Table 2.21 shows the important characteristics of the three selected materials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fly ash</th>
<th>Dry sludge</th>
<th>Clay/Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (%)</td>
<td>58</td>
<td>21</td>
<td>62</td>
</tr>
<tr>
<td>Alumina (%)</td>
<td>29</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Ferric Oxide (%)</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Loss of Ignition (%)</td>
<td>2</td>
<td>61</td>
<td>6</td>
</tr>
<tr>
<td>Heat value (MJ/kg)</td>
<td>Pre-heated</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.9-2.9</td>
<td>1.1-2.1</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>Particle Size (mm)</td>
<td>0.012</td>
<td>0.15</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Fly ash is comprised of very fine particles, the majority of which are glassy spheres, scoria, iron rich fractions and some crystalline matter and carbon. Due to its size and shape, the characteristics of fly ash is that of a high surface area to volume solid that has agglomerated materials on its surface. The chemical composition of fly ash consists of large quantities of silica, alumina and ferric oxide and smaller quantities of other oxides and alkalies. These properties are very similar to clay. The fly ash varies in colour from light to dark grey depending on the proportion of unburnt coal, iron rich particles and moisture. The fly ash used in this study was from the Munmorah Power Station which is a high silica, low carbon content ash and has a mean particle size of 12 microns.

The wet sludge produced in the municipal treatment plants whether it is primary, secondary or digested sludge contain organic matter and plant nutrients but needs to be dewatered before disposal. However it can also contain chemical contaminants such as heavy metals, toxic organics and pathogenic organisms. High contents of heavy metals are of concern to public health due to their potential to accumulate in the food chain. As such any new proposed disposal options of sludge should overcome these problems. The digested sludge for example has a heat value of about 10 MJ/kg which is considered to be significant in the biofly process.
Clay/shale mixture is not a waste product. The mixture of clay and shale are the primary ingredients used in traditional brick production. This material is used essentially for the purposes of adding plasticity to the other two waste products.

2.4.3. Laboratory method stage I

The digested sludge from the sludge drying beds were collected in drums and sieved through a 600 micron sieve, dried in an oven at 105°C and milled prior to its use. The fly ash was collected dry in pre packaged bags and clay/shale required very little preparation. The laboratory procedures involved with the manufacture of Biofly brick samples are shown in a flow chart in Figure 2.6.

![Flow chart of the Biofly brick process](image)

The fly ash, sludge and the clay/shale were mixed by hand until uniform in appearance. Water is added and mixed again at low speed using a laboratory mixer until optimum moisture content is achieved at about 20%. The mix is extruded in a small pugmill to produce a cylindrical shaped specimen of 25 mm in diameter. The extruded specimens were cut to 75 mm length, weighed, dried initially in air for 48 hours and later in a laboratory oven for 24 hours and reweighed. The dried samples were fired in an electric muffle furnace with temperature stair-stepped from 0°C to 1030°C over a 7 hour period following natural cooling inside the oven. Twenty Biofly brick samples were made for each mixture and clay/brick samples which were used as a control for comparative purposes.
2.4.4. Laboratory results stage I

The fired Biofly brick samples were found to have exactly the same red colour and appearance as the clay/shale brick sample. This is indeed very encouraging particularly from the point of view of customer satisfaction.

The compressive strength of all samples were tested in accordance with the procedures outlined in Australian standard AS 1226.4. The 100% clay/shale brick sample prepared in the laboratory gave an average strength value of 49 MPa which is identical to the Australian standard requirement for Grade A Bricks. The compressive strength of the Biofly brick samples of all waste proportions were consistently higher than the strength of the 100% clay/shale brick samples. This may be primarily attributed to fly ash as well as to greater bonding between all three materials. The average compressive strength of 66 MPa obtained for 70% material replacement include mixing sludge/fly ash indicates that the Biofly bricks are 25% stronger than clay/shale bricks.

The bulk density of the 70% material replacement sludge/fly ash mix were found to be 17 kN/m$^3$ compared to the clay/shale brick sample of 20 kN/m$^3$. This illustrates that the Biofly brick samples are 15% lighter than normal brick samples which is another useful feature of this versatile construction material.

Shrinkage is a function of chemically bound water and volatile constituents. Typical total shrinkage should range from 2.5 to 10 percent. The shrinkage values obtained during all experiments were within the above range. The shrinkage for 70% material replacement mix of sludge/fly ash were found to be 5% compared to the clay brick sample of 4%. This indicates that there is very little difference between shrinkage of biofly brick and normal brick sample.

In brick making, weight loss occurs in two stages. During the drying process, water is evaporated which is the case for the first stage of weight loss. Chemically bound water and volatiles are released during firing causing the second stage weight loss. The total weight loss observed for biofly brick containing 70% material replacement mix of sludge/fly ash was 14% compared to 13% in clay/shale brick samples. Thus the weight loss is found to be almost identical.
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The saturation coefficient was also calculated from laboratory data. For the biofly brick samples, a value of 0.96 was found. The clay/shale brick sample in comparison showed a value of 0.93. They are indeed very similar.

It has been shown in the laboratory using small cylindrical samples that the two waste products namely fly ash and sewage sludge can be conveniently combined with clay/shale and solidified to produce the so called Biofly brick. These waste products have become assets instead of liabilities since the final product is marketable and becomes a resource. The Biofly brick looks similar in colour, is 25% stronger and 15% lighter than the normal brick. These features are indeed very significant.

2.5. Summary:

- Fly ash is comprised of very fine particles, the majority of which are glassy spheres, scoria and some crystalline matter and carbon, containing large quantities of silica, alumina and ferric oxide, and smaller quantities of various other oxides and alkalies. These characteristics producing a superior quality fly ash/clay brick.

- Wastewater sludge characteristics not only depend on the degree of treatment but also on the source of sludge effluent. It is clear that sludge is a very light weight material which also has a significant amount of heat value. These characteristics produce good quality sludge/clay brick.

- It is shown that fly ash bricks of high ash content have properties very similar to those of many other facing and common bricks in general use, though their water absorption amounts are generally very high. The excellent durability in the very severe conditions of the tray exposure test of nearly all the specimens tested would compare favourably with any random selection of ordinary clay bricks. It is not easy to find a satisfactory reason why these fly ash bricks are as good as they are. A possible explanation may be found in their generally uniform pore size.

- The data indicates the firing ranges over which fly ash brick can be fired. The firing range is different for each type of fly ash. From the data it can be seen that the approximate firing temperatures necessary to produce a quality fly ash brick are 1236 °C, 1236 °C, 1197 °C and 1164 °C.
• The date indicates how fly ash brick are affected by different firing temperatures within their firing range. The water absorption of the fly ash brick is relatively changed as the firing temperatures are decreased or increased.

• The saturation coefficient is the ratio of absorption by 24 hour soak to the absorption by 5 hour boil and is an indication of the ratio of easily filled to total fillable pore space. The saturation coefficient of the majority of the fly ash brick tested is within the range of 0.70 to 0.78. The data exhibit a noticeable change in saturation coefficient as the firing temperature is changed. In these instances the saturation coefficient decreases as the firing temperature is increased.

• Although there are no direct ASTM limitations concerning porosity, a brick with low porosity is less likely to become permeated with water and possibly chip and spall if frozen while permeated. The apparent porosity of the majority of the fly ash brick tested is within the range of 20 percent to 30 percent. As indicated the apparent porosity will be decreased by firing the fly ash brick to a higher temperature.

• Bulk density and shrinkage are closely related, in as much as an increase in shrinkage of a fly ash brick causes an increase in bulk density. As can be noticed an increase in firing temperatures causes an increase in bulk density and shrinkage.

• The study shows that there is a different firing range for each fly ash and each fly ash has an optimum firing temperature.

• Structural test results on full-scale sludge bricks/bench scale sludge bricks proved to be encouraging. The compressive strength figures were surprisingly higher than expected and considerably beyond the ASTM standard criteria. Water absorption values were similarly attractive. Although compressive strength is higher than ASTM standard, the addition of sludge to clay reduces the strength and increases the water absorption in general.

• The maximum percentage of dried sludge and sludge ash that could be mixed with clay for brick making were 40% and 50%, respectively. Beyond that, the bonding of the mixtures was poor and extrusion of the bricks results in dog earing of the product. The surface texture of the bricks was found to be uneven, especially for dried sludge bricks.
The degree of surface roughness also increased with the amount of sludge in the brick. This is mainly due to the organic component being burnt off during the firing process.

- The specific gravity of the brick samples decreases as the percentage of dried sludge in the bricks increases. However, the specific gravity of the brick samples increases slightly as the percentage of sludge ash in the bricks increases. This is mainly related to the actual specific gravity of the raw materials.

- It has been reported that the appearance of both face (5-8% sludge) and stock (30% sludge) bricks manufactured in South Africa was excellent, had uniform colour and texture and were free from extensive cracks. They were indistinguishable in both appearance and odour from conventional clay bricks.

- A stock brick made in South Africa with sewage sludge is 20% lighter than clay brick. The average compressive strength, measured according to South African Bureau of Standards, was 40.7 MPa for the face bricks and 38.3 MPa for stock bricks. These comply favourably with the standard values of 17.0 MPa and 14.0 MPa respectively for face and stack bricks. The 24-hour water absorption test gave average values of 13.1% for the face and 14.2% for the stock bricks. These figures are some 30% higher than those obtained from similar locally made bricks which do not contain sludge.

- The addition of dried sludge or sludge ash to clay decreases the compressive strength and increases the water absorption. However addition of fly ash to clay increases the compressive strength and the water absorption but not as much as the sludge addition.

- The small laboratory cylindrical samples of biofly brick with dimensions of 75 mm long, 25 mm diameter were manufactured of two waste materials namely dried sewage sludge and fly ash with the addition of clay. The percentages of dried sludge and fly ash used ranged from 50 to 75%. A control sample of clay brick was prepared as a reference.

- The waste material replacement in this process is up to 75% by weight which is high in comparison with Alleman and Berman results for 0% to 50% sludge by volume. The results of Tay are for 0% to 40% of sludge by weight whereas Slim and Wakefield's results are reported for 30% sludge by volume, which compares well with the biofly brick samples. The firing time is significantly reduced in comparison to conventional processes. The structural properties of biofly brick samples are superior than the clay brick sample.
Chapter Three

Brick Making Processes

3.1. Introduction

Bricks made by shaping a plastic mass of clay and water, which is then hardened by drying and firing, are among the oldest and most enduring work of mankind. Until comparatively recent times the clay was dug, the bricks were made and the kilns set or drawn by human labour with minor help from animal power. About 100 years ago the first effective machines for brick production appeared, and the trend towards mechanisation of clay winning, making and handling operations has continued at an increasing pace to the present day.

Bricks can be made from a wide range of clays and shales, that have one thing in common. They are always composed of secondary or water-containing minerals of extremely fine particle size, that have been produced by the action of weathering agents, water and air, on the felspars and micas of igneous rocks.

It is not always realised that modern brick manufacture involves high speed processing of very large quantities of material. When mixed with water, the clay minerals give a plastic mass which can be shaped by pressure to form a brick, at economically practical temperatures in the range 1000-1200°C. The clay particles can be fused into a cohesive mass of great compressive strength, and controlled evaporation of the free water surrounding the particles in plastic clay should not cause excessive shrinkage or faults in the structure of the brick.

In Australia, the majority of building bricks are made from shales or shaley clays. In Sydney, bricks are made from lightly weathered shales occurring west and south of the city. Since the Second World War there have seen a rapid increase in the production of extruded bricks, which generally require softer material, usually obtained from displaced or secondary clay deposits found near the surface.
3.2. Raw materials and processing

3.2.1 Mining Procedures

In searching for shale deposits, we are likely to come across three types of shales that are visibly alike but minerallogically different, and only one type is suitable as a source of clay for structural clay products. These three types are argillaceous, siliceous, and calcareous. The argillaceous shales contain clay and were probably formed from normal clay sediments. Siliceous shales were formed from silty deposits such as quicksand, and they contain very little clay. These shales can only be used as inert fillers added to a clay to lower excessive shrinkage or to produce an aesthetic texture on bricks. Calcareous shales contain a continuously variable amount of calcite or dolomite, the basic ingredients of limestones. These shales grade from argillaceous shale to limestone. They might be called transitional deposits. Calcareous shales with low percentages of these carbonates can be used in the brick making industry with some special attention, but those with greater amounts are completely unsuitable.

In some locations good clay deposits are below the water table or in areas of slow drainage, the clay is often very wet and sticky and sometimes containing up to 40% water. Such clay pits must be pumped continuously to keep the water out. Drainage ditches dug below the lower level of the mining operation can help in removing the excessive moisture from the clay deposit. Where deposits remain quite damp and sticky, it is impossible to mine the clay with shovels and scrapers, and draglines are used to win the clay. An operation of this kind is shown in Fig. 3.1.

Drier clay deposits containing moisture from 5 to 20% and soft shales can be mined with large earth scrapers or power shovels as seen in Fig. 3.2. Harder shales must be blasted before mining with shovels or front-end loaders. A typical dry fireclay deposit is shown in Fig. 3.3. The readily recognisable sequence of layering from top to bottom is shale, limestone, coal, and fireclay. In this situation the shale, limestone, and coal must be stripped in order to recover uncontaminated fireclay. In all of the preceding figures distinct layering of these sedimentary deposits is visible. Each layer represents a different deposit with respect to time, so mineralogical variations may occur from layer to layer. To mine this type of sedimentary deposit for greatest uniformity, it is necessary to remove the material perpendicular to the bedding planes no matter what the angle of bedding may be in the deposit.
Chapter 3: Brick making processes

Figure 3.1. Mining wet clay with a dragline (Pryor, 1965)

Figure 3.2. Mining soft shale with a power shovel (Pryor, 1965)
A good practice in mining clays and shales to effect greater uniformity is to stockpile the mined material. After first, removing the material perpendicular to the bedding, it is laid down again in thin horizontal layers with scrapers or bulldozers. This stockpile is built, with compaction, to a height convenient for removal with power shovel or front-end loader as pictured in Fig. 3.4. The location of the stockpile should be as close to the plant as possible in an area where good roads can be maintained in poor weather conditions. Another advantage in stockpiling is that the initial mining can easily be completed in the favourable weather months of the year. Somewhat smaller stockpiles can be built under the protection of a shed to keep the material more uniformly dry. This procedure can also be used for wet clay as a means of air drying it to a more satisfactory water content for the forming operation.

A caution should be interjected here concerning a danger in stockpiling that must be avoided. If pyrite is present in the raw material and especially if calcite or dolomite is also present, the stockpile cannot be held longer than two months either inside or outside. This is because pyrite oxidises to iron oxide and sulfuric acid upon exposure to air. This surely takes place after mining or even blasting a deposit open. The sulfuric acid immediately
attacks the other minerals present to produce sulphates which can be troublesome and can make the whole stockpile completely useless.

![Remining a stockpile with a front-end loader](image)

**Figure 3.4. Remining a stockpile with a front-end loader (Pryor, 1965)**

### 3.2.2 Raw Material Processing

Wet clay must be dried to a water content below that required for forming, since mixers, such as pug mills, are designed to mix while water is added, even in small amounts. They do not work well when attempting to temper a too-wet material with a dry material to bring about the proper consistency. Some factories use rotary, fuel-fired dryers or stockpile-and-turnover procedures for air drying.

Damp clays that cannot be screened are put through smooth rolls to break up big lumps, to crush pebbles, and to start the mixing process. The output of the rolls will be irregular slabs of clay about 25 mm thick, and these will go directly to a pug mill where additives such as barium carbonate, soda ash, bentonite are made and water is added to produce the desired consistency. In the past such damp clays were used exclusively for soft-mud bricks moulded in sand-coated boxes, but in recent times extruded products are also made, even
though it may be necessary to add a relatively dry shale, clay, or calcined raw material to control the moisture content and plasticity.

A different process is used for preparing dry clays and shales. The equipment is similar for both materials, but there are differences in the details of the machinery when going from dry clay to a hard shale. The problem is to grind the clay-containing materials to fine particle size, and this requires several separate operations as the feed becomes smaller and smaller.

Fig. 3.5. presents a typical flow diagram for such a comminution process. The fixed path primary crusher is placed in series with the secondary crusher, so that they both must have the same capacity for continuous operation. Sometimes a surge bin is placed between these operations so that they do not have to have equal capacities. In other cases there may be two or more secondary crushers receiving the feed from the primary crusher. The secondary crushing operation and the screening is a closed-circuit system. The material being ground passes continuously through the machines to the screens where the fine particles are removed for production, and the coarse particles are cycled back to the secondary crusher.

Figure 3.5. Flow diagram for processing dry clays and shales previous to forming (Taggart, 1945)
Chapter 3: Brick making processes

The shale part of the material which does not pass through the screens is sometimes fed into a pulveriser where the output is all of sub screen size. This increases the amount of fine particles in the final distribution which, in turn, increases plasticity in production.

The primary crusher is designed to take the material as mined, which may be in lumps or pieces up to 300 mm in diameter. The machinery to break down such large pieces needs to be especially strong and powerful. For this purpose, jaw, double-roll, or single-roll crushers are used. The roll crushers are not smooth rolls as used with damp clays. They often have knobs or teeth to pull the odd shaped chunks into the roll mechanism and assist in breaking them. The double roll crushers feed between the rolls which are set apart to control the size of pieces passing, and at least one or both rolls are strongly spring loaded so that they will not become jammed if a particularly tough piece is forced into the mechanism. A single roll crusher crushes between the roll and a perforated plate, as shown in Fig. 3.6.

A dry clay crusher is more apt to have teeth instead of knobs on the rolls. The distribution of particle sizes after primary crushing is from about 50 mm down to a fine powder, however, the amount of fines will not be extremely small, since this machinery is not designed to produce small particles.

The product from the primary crusher feeds the secondary crusher which may be a dry pan, rim-discharge grinder, hammer mill, or chain mill. All of these machines are designed to grind the 50 mm material down to the size of the screen openings and finer. The hammer and chain mills use rotating and swinging objects to beat the material against a perforated plate to reduce the particle size. The dry pans and rim discharge grinders use two large, rotating and turning, steel wheels to crush the charge against a circular bottom plate. The dry pan has a perforated bottom plate for the particles to pass when they are reduced to about 10 mm in diameter. The rim-discharge grinder discharges the ground material over the side of an adjustable height pan resting on a rotating base plate. A pair of rim discharge grinders is shown in Fig. 3.7. They are receiving fireclay from a surge bin which holds the output from a single primary crusher.

All of these secondary crushers are designed to discharge when only part of the charge is fine enough to pass the screen openings. This is done to prevent accumulation of material in the crusher which will pass the screens and reduce grinding efficiency. The amount of material ground fine enough to go through the screens before discharge varies from 25% to
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Figure 3.6. Single roll crusher receiving a charge of shale as mined (Taggart, 1945)

Figure 3.7. Two rim discharge grinders with a fireclay feed (Taggart, 1945)
75% depending on the material being ground and the size of the openings in the screen. The finer screens send more oversize material back to the crusher. The feed rate to these crushers must be constant, therefore, the feed from the primary crusher must be regulated to just compensate for the amount of material passing the screens. This is usually done by monitoring the electric power required by the secondary crusher. As the level of material builds up in the crusher, more power is required for operating the machine. An increase in amperage to the motor cuts off the feed from the primary crusher. Conversely, when the amperage falls to a preset value, the feeder puts more primary material into the crusher (Pryor, 1965).

Each secondary crusher requires a set of screens to remove the material ground fine enough for production requirements. All screens may have the same size openings or they may be different in order to obtain the desired particle-size distribution. In any case sufficient screening capacity must be installed to receive the continuous output from the secondary crusher. As can be seen in Fig 3.5, the oversize from the screens is returned to the secondary crusher for continued grinding while the material passing is delivered to bins in order to keep a constant supply for production.

Clay materials, as used in the structural clay products industry, require definite screen characteristics. The screens are inclined, so that the material will flow continuously over the openings. This inclination is fixed, together with the feed rate. The feed to each screen must be uniform across the screen and the thickness of the bed held constant as it falls on the screen. A bank of screens in operation is shown in Fig. 3. 8. The flow of feed down the screen is from left to right. The electrical vibrating mechanisms are located on the bridge over each screen, and the electrical heating mechanisms are visible on the lower left sides. The capacity of these screens is more related to width than to length. The efficiency improves with the length as the load lightens, and fine particles are more free to move and find an opening.

Because of the flat particle shape, even though the ground particles are aggregates of much smaller particles, oblong meshes are often used as screens with the width of the slot being the factor determining size. Since clay materials tend to block or “blind” the screens, the long axes of the meshes are set in the direction of flow of the feed. The minimum size of openings for this type of dry screening is 20 mesh (0.841 mm). Below this size, the screening efficiency falls so low that the screen capacity will not keep up with production.
requirements (Taggart, 1945). Some structural clay products factories use screens up to 9.51 mm, however, it is quite normal to have screens of 8 mesh or 2.38 mm.

Figure 3.8. Bank of screens in a structural clay products plant (Taggart, 1945)

In the brick making industry, it is uneconomical to dry the raw materials to a constant state before grinding and screening, therefore, variations in moisture, due to the vagaries of the weather and the hygroscopic nature of the clay minerals, cause efficiency to vary in grinding and screening. This not only requires enough screening capacity for the more adverse conditions, but the particle-size distribution in the product is altered according to the moisture content. The amount of fines increase with moisture content because the damp particles tend to aggregate together and do not pass the screen as they should. In this situation many fine particles are cycled back to the cruscher for further comminution.

These variations in the particle-size distribution are, for the most, absorbed in production without great difficulty, however, there are times and places where these moisture variations cause such disruptive effects as off-grade ware.
3.2.3 Blending and Additives

Dry ground clay materials ready for processing are stored in large surge bins that may contain enough material for several days production. The purpose of storage at this point is to prevent production delays when mechanical failures or adverse weather conditions might otherwise cause the entire plant to be shut down. Separate bins are required for each different material or different particle-size distributions of the same material. Such bins may take the form of an open stockpile or closed vertical bins fed from the top. Front-end loaders or conveyor belts under a grating in the floor are the most common ways of bringing the open-stockpile materials into production. Mechanical feeders are used at the bottoms of closed bins to transfer the ground materials to conveyor belts leading to the forming machinery. Considerable engineering design must go into the closed bins to ensure positive, uninterrupted gravity feed. The feed from most closed bins is automatically and continuously weighed as it passes onto a conveyor belt. This ensures the correct proportions of the various materials being blended into the desired composition (Johanson, 1965).

Small additions of materials to the main clay blend are referred to as additives. Dry additives are fed from a hopper onto the conveyor belt taking the final blend to the mixing equipment, which is usually a pug mill. Each hopper is equipped with a calibrated and synchronised feeding device to give exactly the right amount of the additive. Fig. 3. 9. is a photograph of such a feeder. Some of the dry materials considered as additives to the clay batch are barium carbonate, soda ash, bentonite, colorants, and binders to increase the dry strength of the formed product. The white chemical such as barium carbonate is added to the material on the conveyor belt by means of a disk feeder at the bottom of a hopper. There are other types of feeders also available and in use in this industry.

Solutions or water suspension additives are fed from a liquid storage tank directly to the pug mill as part of the water added to obtain plasticity. Calcium chloride solutions, barium carbonate suspensions, and water-soluble binders are examples of materials added in liquid form. The proportions must be carefully controlled by means of automated valves and constant concentrations.
3.3 Forming of Structural Clay Products

3.3.1 Plastic Forming Methods

3.3.1.1 Soft-Mud Process

In the soft-mud brick manufacturing process, plasticity is not as much of a factor as workability and consistency. Soft wet clay must be packed into damp wooden moulds that have been previously dusted with sand. It is necessary for the clay to flow easily into the shape of the mould with low-pressure packing. In the soft-mud process, the bricks are not
stacked in the wet condition, but the moulds are emptied onto pallets where the bricks stay until dried. The properties of workability and consistency are achieved by adding water beyond the amount required for maximum consistency, thus, the term "soft mud" is quite appropriate.

The soft-mud process is an automation of the old technique of hand-moulding bricks. An automatic brick machine of this type is shown in Fig. 3.10. The mixing and tempering tub or pug mill is visible on the right-hand side just forward of the main drive mechanism. The soft plastic clay is pushed from the pug mill into the main part of the machine where it is proportioned and pressed into the mould boxes. The mould boxes are tied together in a gang of between 8 to 12 units. As the mould boxes emerge from the machine, the excess clay is scraped off the top. The gang moulds are tipped over and tapped to release the bricks onto a waiting pallet. As the loaded pallet goes to a dryer rack, the empty moulds move below the machine where they are washed with a water spray and resanded. They are then elevated into the machine ready to be filled again.

![Figure 3.10. Soft-mud brick machine (Sharp, 1993)](image)

The sand used for lining the moulds serves two purposes. It allows for easy release of the sticky clay from the moulds, and it is a decorative feature. The basic sand is usually fine
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grained, perhaps 40 mesh, but sometimes sands as coarse as 10 mesh are used. The fired colour of the sand and the texture it imposes on the bricks determine the appearance of the finished product. The mould sands work best in this machinery if they are thoroughly dry. Therefore, a soft-mud brick plant has a sand preparation section where the sands are dried, screened, and mixed in preparation for delivery to the brickmaking machine.

Soft-mud facing bricks have a distinctive appearance. They are coated with sand on five sides, and the sixth side shows where the clay was scraped off. This scraping action always leaves a burr along the edge of the bricks. These burrs are along the face of the bricks, so they can be observed even when placed in a wall. In dumping the bricks out of the moulds onto the pallets, the unsanded side is down, and this action sometimes causes the soft clay piece to slump slightly. This makes the area of the unsanded side larger than its opposite sanded side. The shape of the whole brick is, then, somewhat truncated. These deviations from true shape are aesthetically desirable for soft-mud products. The bricks not only appear to be antique, but the lack of perfection produces an interesting wall which might otherwise be monotonous. There is nothing about the forming of these bricks which detracts from their serviceability. Durability is related to the raw materials and the firing operation. Figure 3.11 illustrates the various procedures involved in the preparation of a soft mud brick (Sharp, 1993).

3.3.1.2 Stiff-Mud Process

The shapes of structural clay products made by the stiff-mud process are precise and uniform, and the standards for the products made by this process require them to be so. For these reasons, stiff-mud forming demands the greatest application of the fundamentals of clay-water systems, to optimise the process with regard to product tolerances and economics. The plastic state or plasticity of clay water systems is the key to understanding the process well enough to produce the best results. One must be able to regulate the degree of plasticity through the secondary factors while recognising the requirements for the primary factors. Figure 3.12 illustrates the various procedures involved in the preparation of stiff-mud brick (Sharp, 1993).

Most structural clay products, including bricks, are made by the extrusion process. Machinery for extrusion is adaptable to automation and high speed production. Extrusion machines are available in several sizes. Some are capable of producing products at the rate of 150,000 standard brick equivalents per day, and they require electric motors ranging
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**SOFT MUD BRICK PLANT**

**Extruding at 13% to 14% water content**

**Stockpile open layered, 30000 to 40000 tonnes, 1 year production**

- 14 tonne bucket loader
- Box feeder with slat conveyor
- Toothed roll crusher
- Conveyor with magnet
- Belt weight
- 100 tonne box feeder with level sensor & slat conveyor
- Conveyor
- Wet pan product size 12 mm
- Conveyor
- Synchronised smooth rolls: product 2 mm to 6 mm
- Conveyor
- Tipper cars
- 1 of 5 x 1500 tonne bunkers with level sensors
- Chain bucket dredger
- Conveyor
- 100 tonne box feeder with level sensor
- BaCO3 Hopper & screw feeder
- Belt weigher
- Single shaft mixer
- Extruder

Figure 3.11. Outline of clay preparation procedures for soft mud brick
(Sharp, 1993)

from 55 kW to 260 kW. Typical extrusion machines as supplied to the structural clay products industry are shown in Figs. 3.13 and 3.14.
The machines in Fig 3.13 & Fig 3.14 show pug mill tubs to the left in which the clay materials and additives are blended and mixture tempered with water to the desired consistency. A view into a pug mill during operation is given in Fig. 3.15, where the mixing knives can be seen. Different types of knives are available to suit various raw materials, and the knives have variable pitches for the purpose of varying the time that the clay remains in the mill. The additives that may affect plasticity are binders, internal lubricants, and wetting agents. Lignosulfonate binders are commonly used to increase the strength of the product after drying, but they usually act to lower the plastic by acting as a deflocculant. Water-soluble or emulsified internal lubricants allow for easier extrusion but reduce plasticity by interfering with the structured water hulls. Wetting agents act to reduce the surface tension of the water, which allows less water to be added, reduces the power necessary for extrusion, and speeds up the drying time, but all of these advantages are gained at the expense of plasticity. Wetting agents reduce capillary attractive forces and often act as deflocculants. In most factories, the use of a lignosulfonate binder as a pug-mill additive is found to be beneficial overall in spite of its effect on plasticity (Hogue, 1970).

Although theoretically products should be extruded at the optimum water content for maximum plastic strength, some plants extrude a somewhat drier mixture. Mixtures with water contents lower than the optimum can be extruded only when more plastic strength is available than is necessary to prevent cracking.

It may be economically desirable to extrude as dry as possible and sacrifice some plastic strength. The economics are questionable, however, when one observes the extra power required to extrude a drier column. The advantages to a fairly dry extrusion were reported by Hodgkinson (1970) as:

1. The harder product is more amenable to automatic handling.
2. The lower water content saves fuel on drying.
3. Better quality and shape of product is obtained.
4. The ware can be stacked on cars for drying so that pallet drying is not required.

Usually water is added with material manually. Some operators have used a wattmeter or an ammeter connected to the motor driving the extrusion machine as a guide to consistency. Others used only their feel of the stiffness of the extruded column as a guide. Such manual control of water content has been monitored, and it was found that differences
in water contents were negligible from 10 or 15 minute period to the next, but a large sinusoidal variation with a wave length of 2 to 3 hours went through a day’s production. For example, shortly after starting up in the morning, the water content was correct. As the morning proceeded, the clay column became wetter until just before lunch a soft column would be recognised and the proper correction applied. Towards midafternoon, the column became obviously too dry, and steps were taken to get more water into the mill. At the
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Figure 3.13. Stiff-mud extrusion machine showing auger which forces clay through a die (Connor, 1966)

Figure 3.14. Stiff-mud extrusion machine showing arrangement for quick change dies (Connor, 1966)
day's end, the extruded product was headed towards a too-wet condition. The total variation was respectively, 4%, 2% above and 2% below the desired water content.

Tatnall (1962) has published information on various devices to automatically control moisture content in the pugging process, and all devices produced smaller variations than manual control. Tatnall (1962) placed a load cell on the tie rod of the auger section of the extrusion machine to transmit a hydraulic signal, based on the force required to extrude the clay, to a proportional controller that operated a pneumatic control valve on the water supply. In order to make this system operate properly, the raw material fed to the pug mill was volumetrically controlled, with a pneumatic gate valve regulating the flow to a
constant-speed conveyor belt. It was also necessary to have a constant-pressure water supply. A control system based on the electrical resistance across the pugged clay in the mill was perfected by Connor (1966). The controls were actuated by the amount of electrical imbalance around a control point detected by the instrument. Proportional control was used to regulate up to 20% of the total water input. The bulk of the water was fed continuously into the mill at a constant rate.

To control water content in extrusion machines, a system was developed to allow employees to force detectors to “feel” the clay consistency by direct contact with the pugged clay. Probes with strain gauges at their bases are installed through the sealing-die case directly into the flow of plastic clay at the downstream end of the auger. The detectors react to the stiffness by transmitting signals by way of a proportional controller to a mechanised valve.

After the mixed and tempered clay leaves the pug mill, the clay is forced through a sealing ring into a vacuum-auger chamber as shown just to the right of the pug in Figs 3.13 and 3.14. The vacuum chamber is needed to deair the mixed clay during the extrusion process. A high-capacity vacuum pump must be hooked up to this part of the extrusion machine. The sealing ring acts to close the upper vacuum chamber, and the die full of clay becomes the lower vacuum seal. As the plastic clay enters the vacuum chamber, it encounters the shredder which breaks up the compacted column to facilitate the deairing process. The lumps of clay from the shredder fall on the lower main extrusion auger. This auger is visible at the right end of the machine as shown in Fig. 3.13.

The auger screw is the driving force to push the deaired clay through the forming die. The helix angle has been found to be best at 20° to 25°. Some augers are single wing and others are double. The double-wing screw moves the clay more rapidly per revolution and keeps a more uniform pressure on the die. At the downward end of the auger screw, a propeller is sometimes mounted to break up the continuity of the smooth cuts in the clay mass coming off the auger flights.

One of the problems with auger extrusion is that the die puts a great deal of back pressure on the auger, so some of the clay tends to be forced backward off the ends of the auger screw. These extrusion pressures vary from 3.5 to 10.5 MPa, and the actual operating pressure is determined by the auger feed and the cross-section of the extruded shape formed by the die. Both of these extremes in pressure are undesirable, and probably the optimum
extrusion pressure is around 5.5 MPa, achieved with a proper auger-feed: die-size ratio. A good arrangement is to have the volume of clay extruded equal to or slightly greater than 50% of the total auger capacity. It has been recommended by the equipment manufacturers that the auger be operated at 40% to 60% of capacity. In the brick making industry this is called a slightly starved auger. Backflow is also retarded by making the inside of the auger barrel rough, even to the extent of adding ridges to increase the resistance to flow as reported by Blume (1972).

In these machines there is an optimum extruded-column speed which is also related to the auger feed and die cross-section, as far as auger pressure and backflow is concerned. Column speeds of around 6 m/min are considered too slow, and 21 m/min too fast. Obviously, this places the optimum column speed around 12 m/min. for the best balance of all these factors.

As the plastic clay leaves the auger it enters the throat, or spacer, which leads the plastic clay into the die. The spacer can be seen just behind the mounted die shown in Fig. 3.14. The proper length and taper of the spacer seem to depend on the plastic characteristics of the clay material. To obtain the best product at the lowest power requirement, however, quantitative specifications for this part of the machine would require a throat section about twice as long as a double-wing (Blume, 1972).

A brick die can be seen mounted on the front of the extrusion machine in Fig. 3.14. The mounted die is hinged on the left-hand side and another die can be mounted on the collar hinged to the right. This is a quick-change die arrangement. During production a different-shaped die can be installed in a matter of minutes by unbolting the die and swinging it aside, allowing the new die to be swung into place and bolted. The unused die can then be removed from the collar for cleaning and storage. The next die to be used can be mounted on the collar while the machine is in production. The length of the die for all extruded products should not be any longer than necessary for obtaining a well-formed column. A rule of thumb for die length is 1.5 to 2 times the greatest distance across the die or 3 to 4 times the wall thickness of the piece being extruded (Blume, 1972).

One of the jobs of the plant engineer is to make certain that the die is centred on the auger and balanced. The flow of plastic clay must be uniform through the die, side-to-side, top-to-bottom, and outside-to-inside. The flow through the die can be checked by cutting off the extruded column even with the outer edge of the die and running out a short column
for observation. A die off centre to the right will extrude a circular column to the right. A more detailed analysis of the column flow can be made by placing vertical and horizontal cutting wires in front of the die so that the extruded test column will be cut into four parts. The four separate columns will give more information on the places where the column is moving faster or slower. When alignment is good, further adjustments may be made by increasing the frictional resistance in that part of the die through which the clay is moving fastest and decreasing the resistance where the clay is moving too slowly.

Most structural clay products are made with a core in the die to produce hollow parts, such as cored facing bricks. The cores are placed in the die by means of a bridge at the back of the die, which allows the plastic clay to flow around it. Fig. 3.16 shows the back of a die with a bridge holding ten coring fingers that protrude into the die. These fingers can be seen in Fig. 3.17. from the front end of a die used for forming 10 holes cored bricks. When cores are used in a die, the flow of material around the core bridge and the coring elements must also be balanced in all directions. The first consideration in obtaining a balanced flow is to make sure the cores are centred in the die, and all well thicknesses of the extruded column are uniform.

Figure 3.16. Bridge at the back of the die holding ten coring fingers for cored face bricks (Blume, 1972)
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Figure 3.17. Extrusion die for a ten-hole cored brick (Blume, 1972)

To reduce the frictional resistance against the sides of the die, lubrication is used. Oils, emulsions, or steam are used for die lubrication by introducing the lubricant under high pressure into an annular groove around the back end of the die. Kerosene lubricating oil mixtures are frequently used. A mixture of 20% kerosene and 80% oil is recommended for clays with low plasticity, and for highly plastic clays the mixture could be 40% kerosene and 60% oil. Wax emulsions, mineral oil and water emulsified with diamide, and emulsions of castor and peanut oils have been used for die lubrication. Die lubrication improves die balance, reduces power required for extrusion, and improves the surface of the extruded column. The major problem in the auger-extrusion method of forming is the inherent introduction of laminations or inhomogeneous texture in the extruded column. The auger flights are primarily responsible for this, but there are also slip planes created in the spacer and the die as reported by Hodgkinson (1962).

Clay particles become aligned when pressure is applied to a plastic clay mass. The pressure exerted on the clay by the rotating auger flights orients the clay grains as they push the deaired clay into the die. This orientation puts spiral laminations into the extruded column, consisting of localised concentrations of clay particles all oriented parallel to the
auger flights. The new directions of applied forces, as the clay moves through the throat of the die, causes slip planes to develop, which also result in planes of preferred orientation. The pressure on the clay column exerted by the walls of the die causes alignment of clay particles parallel to these walls. This puts an oriented skin on the column, consisting almost entirely of clay-mineral particles. In addition, if there is considerable friction or imbalance as the clay flows through the die, slip planes and fractures can be created in the interior of the product being formed.

If these areas of preferred orientation are not properly dealt with in the extrusion process, they result in laminations that open up as internal cracks during drying and firing of the product. When this kind of internal structure persists into the final product, failures by spalling and disintegration occur in service, especially where freezing temperatures are encountered and where there are soluble salts that tend to crystallise in these open flaws. It might seem at this point that all is lost in trying to make durable structural clay products by the auger-extrusion method, however, such is not the case, because there are a number of things that can be done to heal these inherent lamination into a coherent body.

The most important procedure in the extrusion process to deal with the problem of laminations, is deairing the pugged clay. When air is present where the extrusion auger is acting to push the clay through the die, the cuts of the auger flights entrap air between the oriented clay planes, and these air pockets prevent the oriented surfaces from coming into intimate contact. As the auger forces the plastic mass into the die, the pressure compresses the enclosed gases, causing the air pockets to become smaller in volume, however, as the compressed column moves out of the die, the pressure is released and the compressed gases expand to open the laminations again. This expansion caused by the release of internal pressure can create additional cracks within the product. All of this action is eliminated by applying an adequate vacuum in the deairing chamber.

In order for the vacuum chamber to do its job properly, a vacuum of 660 mm to 690 mm of Hg is required. 610 mm of Hg vacuum is not sufficient, and 510 mm of Hg is no better than no vacuum at all. It must be understood that the high vacuum does not eliminate the planes of preferred orientation but allows the laminations to be knit together under the extrusion pressure. In fact when the compressible gases are absent, the extrusion pressure becomes greater because of the incompressibility of the clay-water mass. The importance of a proper vacuum in extrusion cannot be overestimated, and a word of caution should be introduced here. Some factories have been known to lower the vacuum on their machines
when producing certain product lines, for the purpose of creating special texturing effects on the surface of the ware. Such a procedure should never be resorted to, as history has proven over and over again that durability must never be sacrificed for decorative effects. It would be better to invent an alternative procedure to apply the desired texture to a well-formed column or discontinue the line entirely.

A second consideration for the elimination of the problem of laminations has to do with the raw materials. The texture and filler particles, tend to interfere with the development of continuous layers of oriented clay grains. The particles do not contribute to the orientation when they are more equidimensional in shape, and they disrupt the preferred orientation when the clay grains have to pack around them. The interrupting action of the texture-filler fraction assists the vacuum in knitting together the auger and slip-plane laminations.

Other factors in reducing the disturbing effects of laminations are incorporated into auger design and operation. One of the reasons for the somewhat starved auger during operation is to reduce the orientation of clay planes introduced by the auger flights, consequently, the laminations are smaller and more randomly distributed throughout the extruded column. The propeller at the end of the auger screw helps to chop up the laminations just before the plastic clay moves into the die throat. The proper helix angle on the auger and the correct ratio between the auger feed and the cross-section of the die are other factors which tend to minimise the undesirable effects of laminations. The water content is another possible variable in the control of laminations. The amount of water necessary for maximum plasticity is conducive to the introduction of layers of preferred particle orientation. This is another case where a reduction in water content is advantageous if there is already sufficient plastic strength.

Usually die lubrication has little or no effect on the development or healing of laminations from the auger, but it does help to reduce slip planes in the column as it passes through the die. The use of an internal lubricant seems to reduce the severity of laminations, but there will be an accompanying loss of plasticity.

**Cutting of Extruded Columns**

For brick production, the continuously extruded column must be cut in units of the proper size. A common machine for cutting the moving column is the reel-type wire cutter shown in Fig. 3. 18. The extruded column can be seen running through the cutter with the
cut column emerging to the right. This machine moves back and forth in synchronisation with the column speed. The cycle starts in a position with the reel closest to the die, and as the column passes through the cutter, a limit switch activates the horizontal movement of the cutter when the column reaches the end of the machine. It then follows the column at the column speed, and during this travel, the reel rotates spring-loaded cutting wires through the column. The synchronisation of the rates of travel of the column and cutter allows the cuts to be made straight and true. With the equipment shown in Fig. 3.18, twenty-one bricks are cut at a time without stopping the extrusion process. After cutting, the forward motion of the cutter stops, and it returns to its original position until the extruded column again fills the cutting machine.

![Reel-type wire cutter for brick production](image)

**Figure 3.18. Reel-type wire cutter for brick production (Hodgkinson, 1970)**

Although the reel-type cutting process has been adapted to automatic setting of plastic ware on kiln cars, the method is used mostly when the ware is picked off from the conveyor belt and stacked on kiln cars by hand labour. In practice this process is known as “hacking”, whether it is done manually or automatically. A photograph of the manual process is presented as Fig. 3.19. Note that the kiln cars are resting on elevators to make the workmen’s job easier and faster.
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The automatic hacking machines used in brick factories employ a somewhat different method of cutting the extruded column, which is designed to fit the automated process. The column is cut roughly into 1.2 to 1.8 m lengths by a guillotine. Depending on the thickness of the product, the machine sometimes places two of these column sections together before final cutting. The column section is moved to the automatic hacking machine where it is pushed through fixed wires that complete the forming operation. Such a cutting operation is shown in Fig. 3.20. The scrap pieces at the ends of the rough-cut section will be returned to the pug mill for reuse. The precisely cut bricks are moved immediately to a spacing table where they are arranged for automatic pick-up and transfer to kiln cars.

Automatic Hacking of Bricks

The driving force for the development of automatic hacking was the cost and unavailability of the semiskilled labour required for manual handling. Careless workmanship has caused breakage and kiln wrecks when the stacks were not set properly. The economics of the setting process have been improved by the introduction of these machines, however, there was more flexibility in the hacking of different shapes and in the
design of the setting when manual labour was used. Each automatic setting machine has reduced the labour force from about eight semiskilled workmen to one skilled technician.

![Figure 3.20. Column section being wire cut for automatic hacking of large bricks (Hodgkinson, 1970)](image)

Automatic hacking machines in operation are shown on Figs 3.21 and 3.22. The plastic, extruded bricks in Fig. 3.21. have just been placed on a kiln-car deck in one operation by the lifting and transporting mechanism overhead. The inflatable bags that grip the bricks can be seen in the photograph. This machine is setting the hack shown in Fig. 3.22. Soft-mud bricks, having been dried on pallets, are being automatically set on a kiln car in Fig. 3.23. Note the different setting pattern which is more appropriate to this type of brick. The setting head of this machine is holding one course of bricks just previous to adding them to the stack on the car.

### 3.3.2 Dry-Press Forming

Dry-pressing is really a damp-pressing operation where the clay-containing materials are tempered with 6% to 8% water before forming. Clay materials with this water content are granular rather than plastic. The dampened materials are put through a rather
Figure 3.21. Automatic setting of stiff-mud face bricks on a kiln car deck (Tatnall, 1962)

Figure 3.22. Automatic setting of soft-mud face bricks after drying (Tatnall, 1962)
coarse screen to make the granular aggregates of particles fairly uniform. In this state the material can be poured into a press mould like salt. Hydraulic rams are used to compact the damp charge under pressures between 34.5 and 68.9 MPa. The compressed piece is ejected from the mould by the lower ram and at this time has enough strength to be handled-carefully. Binders are usually added to the mix to add dry strength and to facilitate pressing by internal lubrication. Figure 3.24 illustrates the various procedures involved in the preparation of dry pressing brick (Sharp, 1993).

Dry-pressing of face bricks was a fairly common practice 70 to 80 years ago, but it was superseded by the extrusion process, which gave greater production rates. Now it may be time to reconsider the dry-pressing process for the manufacture of face bricks. During this lapse of time, presses have become bigger and faster, and it is possible to make bricks economically. There are certain advantages to be gained by reintroducing the dry-press method. To start with, the problems and cost of drying would be eliminated, and the dependence of the industry on clay minerals would be overcome. Products could be made more uniform in size and shape because only firing shrinkage would be encountered, and this need not be appreciable if materials other than clay are
Figure 3.24. Outline of clay preparation procedures for dry pressing brick
(Sharp, 1993)

used. Figure 3.25 illustrates the various procedures involved in the preparation of brickworks (Sharp, 1993).

3.4. Biofly brick manufacture

3.4.1. Introduction

Solidification/Stabilisation are two of the most widely techniques used in waste management. Solidification/Stabilisation processes have different goals. Solidification systems attempt to convert the waste into an easily handled mass with reduced hazard from volatilisation, leaching, or spillage. Stabilisation systems attempt to reduce the solubility or chemical reactivity of waste by changing its chemical state or by physical entrapment like micro encapsulation. The two are often considered together because they have the common purpose of improving the containment of potential pollutants in treated wastes. Combined processes are often termed waste fixation or encapsulation.

The Biofly brick process is an innovative process which involves the solidification of two materials namely, sewage sludge and fly ash with clay/shale as an additive to manufacture face building bricks. This process has the potential to convert two waste products into assets instead of liabilities.
**EXAMPLE OF AUSTRALIAN BRICKWORKS**

**Bucket loader to storage**

**Pre-crushing rolls 600 mm dia. x 1200 mm long**

**Slat conveyor**

**Wet pan with plasticity regulator**
rolls 1800 mm dia. x 700 mm wide, 8000 kg & 9400 gk

**Belt conveyor with metal detector**

**Differential smooth rolls**
rolls 1000 mm dia. x 1000 mm long, speed 135/110 rpm, gap 2 mm

**Secondary synchronised smooth rolls**
speed 250 rpm, gap 0.7 to 0.8 mm

**Transfer cars**

**Two de-airing double shaft mixers with steamers**

**Sealed insulated silos, 350 m3 capacity with rotating base & auger discharge**

**Conveyor belt**

**Differential smooth rolls 1000 mm dia. x 1000 mm wide, speed 246/238 rpm, gap 2.0 mm**

**Double shaft mixer**

**Vacuum extruder switchable to 1 of 2 speeds, with an 8 column hinged die**

---

Figure 3.25. Outline of Australian brickworks clay preparation procedures (Sharp, 1993)
3.4.2. Brick manufacturing process

The raw materials for Biofly brick are fly ash and sewage sludge which are the by-products of coal fired power stations and sewage treatment plants respectively and they do not require any preparation.

All raw materials were weighed and mixed using an electric mixer until the required consistency was obtained. Water was added carefully until the required consistency was achieved.

3.4.2.1. Extruding

Biofly materials with a 26-33% water content is forced by an auger into a horizontal cone shaped tube which tapers down to the die. Two compaction stages are commonly incorporated, with a vacuum chamber between them to remove any air in the material which might otherwise reduce the strength with which the particles join together. A continuous column of material, approximately the plan size of two or three bricks required in section, is forced from the die and picked up on a table. The material column is cut into brick sized pieces by an arrangement of saw. Extruded bricks, although often smooth, may be mechanically patterned or textured. In the case of biofly brick material, surface treatment was not added. Extruded Biofly bricks have no perforation. Most conventional clay bricks have 30% perforations, which by increasing the surface area speed up the drying, firing, and cooling times. Any internal stresses are also simultaneously relieved thus preventing distortion of the bricks during firing.

3.4.2.2. Drying

Dryness Stages

The methods by which ceramics are formed depend on the workability that is developed when finely granulated solid material is intimately mixed with a suitable proportion of water. Products formed by extrusion commonly contain a certain amount of moisture to assist with the forming process. In the brick manufacturing industry, the object of drying is to remove water from bricks in order to avoid disruption by the evolution of steam during the initial stages of firing. A thorough understanding of the mechanism of drying clay wares requires careful examination of the relationship existing between the solid particles and the
water in the system. The drying of nearly all wet granular materials can be divided into several stages.

**Dryness No. 1**

Drying is probably one of the most important stages associated with brick making. The problem is that each stage in the production of a ceramic piece has a dryness factor. Workable clay will contain from 12 to 20% physically attached moisture. The moisture content may vary depending on the clay, sludge usually with high moisture content depending on the degree of treatment (20-95%) and fly ash with very little moisture (2-5%). The green brick made from these materials is very soft and must be left to harden to leather hard for finishing off.

**Dryness No. 2**

The water at this stage will usually be up to 30%. The brick is still in a stage where it is normally considered to be too wet to put into a kiln. So now we have a brick which has been formed, dried, and now requires to be air dried to a state where it can be put into the kiln.

**Dryness No. 3**

By now the brick has moisture in the range 8-12%, and if scraped, will come away as dust. It is quite air dried, but, perversely, it is still what might be referred to as kiln wet. The brick is now put into the kiln and very low heat has to be applied to drive off the last remaining physical water. The brick must therefore be kept at low temperature until it is kiln dry, the kiln temperature should be kept around 150°C.

**Dryness No. 4**

At this stage, we have removed all the physically attached water but is the brick dry? Yes! it is physically dry but No! it is not chemically dry. When material and water are mixed, some of the water simply stays around as a separate entity, giving softness and workability, but quite a percentage of the water is actually absorbed chemically by the material, and the only way to remove this is by subjecting it to a very considerable heat. This is the chemically bonded water and the brick has to be heated to 600-700°C before all this water is removed.
3.4.2.3. Firing

The process of firing ceramics ordinarily involves gradually heating the kiln up to the degree needed to do the desired work on the ware, then cooling it, again gradually, to room temperature.

Firing consists of several stages namely, water smoking, dehydration, oxidation, vitrification and cooling. A typical firing curve for the manufacture of biofly brick is shown in Fig. 3.26. The firing curve used was a stepped temperature curve. The temperature inside the kiln was increased in steps to 1100 °C and was held at that temperature for two and half hours. Then the kiln was turned off and allowed to cool naturally. The firing curve was maintained using a programmable controller connected to the kiln. The stair stepping was an attempt to mimic the continuous temperature profile achieved in commercial applications. This was developed by a trial and error process and final mixing and firing schedule is given later in Fig. 4.1.

![Firing Curve](image)

**Figure 3.26. Biofly Brick Firing Curve**

Water smoking removes the residual free water from the drying operation. Water smoking raises the temperature of the brick to approximately 200 °C. The temperature of the kiln is gradually raised to 400 °C. This begins the dehydration phase. During dehydration, the temperature is raised from the initial 400 °C to 550 °C, driving off all chemically bound water. For kaolinite, the following decomposition occurs.
3. Chapter 3: Brick making processes

\[ \text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 \stackrel{550 \text{oC}}{\longrightarrow} \text{Al}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O} \]

Kaolinite \hspace{1cm} Meta-Kaolin

During the oxidation process (540 °C-980 °C) air is introduced into the kiln, causing combustion of all volatile materials. Iron pyrite (FeS2) which is present in the materials decomposes, producing gaseous sulfur dioxide and ferric iron. Further reduction reduces the ferric iron to ferrous iron.

Vitrification is a two step operation, incipient and complete. Incipient vitrification occurs when the material is heated enough to begin fusion, usually between 980 °C to 1200 °C. Particles begin to flow at this point, but individual particles are still recognizable. Most building bricks are fired to this stage of vitrification. Complete vitrification is the total fusion of all particles into a solid impervious mass. As an example, paving bricks are fired to complete vitrification.

The vitrification stages for kaolinite can be represented by the following equations.

\[ 2(\text{Al}_2\text{O}_3.2\text{Si}_2\text{O}_5) \stackrel{930 \text{oC}}{\longrightarrow} 2\text{Al}_2\text{O}_3.3\text{Si}_2\text{O}_2 + \text{Si}_2\text{O}_3 \]

Metakaolin \hspace{1cm} Silicon Spinel

\[ 2(\text{Al}_2\text{O}_3.3\text{Si}_2\text{O}_2) \stackrel{1090 \text{oC}}{\longrightarrow} 2(\text{Al}_2\text{O}_3.2\text{Si}_2\text{O}_5) + \text{Si}_2\text{O}_3 \]

Silicon Spinel \hspace{1cm} Pseudo-Mollite

\[ 3(\text{Al}_2\text{O}_3.\text{Si}_2\text{O}_2) \stackrel{1200 \text{oC}}{\longrightarrow} 3\text{Al}_2\text{O}_3.2\text{Si}_2\text{O}_2 + \text{Si}_2\text{O}_3 \]

Pseudo-Melllite \hspace{1cm} Mellite \hspace{1cm} Cristobalite

Cooling is the final step in the burning process. This is a carefully controlled operation, which is essential to prevent cracking.

3.5. Summary

- The overall purpose of clay preparation is to supply a uniform body to the final forming operation. It should, ideally, be uniform with respect to the following properties:

  1. Chemical and mineralogical composition.
2. Particle size distribution.
3. Moisture content.
4. Degree of ageing.

All these properties can be affected by the choice of equipment used to store, crush, transport, and mix the clay body. In addition to the choice of equipment, the way the equipment is used can also affect the uniformity of the clay in the body.

- Each piece of plant used in clay preparation gives optimum performance when supplied with feed materials at a constant rate somewhere within the equipment manufacturer's design limit. If the feed rate is constantly changing, then the output from crushers, for example, will be of variable particle size distribution. This will affect the performance and production rate of any subsequent grinding and mixing stages.

- Roll crushers are commonly used in the first stage of crushing. They are commonly fitted with a paddle above the rolls to prevent large pieces of feed "bridging" or blocking the entrance to the crusher. They produce a minimum of fines and virtually no oversize.

- Particle size distribution has an important effect in the development of plasticity for extrusion and in development of good pressing characteristics. Effective screening is important in the control of particle size distribution. An indicator of screen efficiency is the presence of screenable fines in the screen tailings.

- Continuous mixing of dry powders is readily performed in a single shafted ribbon mixer, more commonly the dry materials would be blended either prior to primary crushing or just after. It is generally easier to get good mixing of finely ground dry materials than it is mix wet clays. With plastic clays when water is to be added, the double shafted mixer with blades is a practical choice.

- The various stages in clay preparation, has been examined in this chapter. The examination considered features of equipment which determine the initial choice, and also the general operating principles influencing performance.

- After preparation of the raw materials with regard to composition and particle size, structural clay products are usually formed in the plastic state. Bricks are formed or moulded by one of three processes:
1. Soft-mud process.
2. Stiff-mud or stiff-plastic process.
3. Dry press process.

- Preliminary mixing processes are the same except that the water content varies from a considerable amount in the soft-mud (16% to 23%) process to a small amount in the dry press (5% to 7%) process.

- Stiff-mud or stiff-plastic process use a limited amount of water, which is added until the clay is plastic. Moisture content vary from 13% to 14% for this process. Clay is extruded through a die by either a screw or auger form in a clay ribbon.

- Stiff-mud process, clay forced by an auger into a horizontal cone shaped tube which tapers down to the die. Two compaction stages are commonly incorporated, with a vacuum chamber between them to remove any air in the material which might otherwise reduce the strength with which the particles join together. A continuous column of material, approximately the plan size of ten bricks required in section, is forced from the die and picked up on conveyor. The material column is cut into brick sized pieces by an arrangement of reel type wire cutter.

- Dry or dust process use dry clay, shale at water content ranging from 5 to 7 percent. Clay used is relatively non-plastic and the brick unit is formed at pressure between 34.5 to 68.9 MPa. This process is primarily employed to manufacture facing bricks and tiles.

- The various stages of the Biofly brick making process such as, mixing, extruding, drying and firing processes are discussed, further discussion in detail are follow in the thesis.
Chapter Four

Research Methods

4.1. Introduction

Various tests were carried out on the raw materials sewage sludge, fly ash and clay/shale as well as on the green and burnt bricks. The tests were primarily concerned with identifying similarities or discrepancies between the brick types, together with determining physical/chemical and material properties of the raw materials as well as the burnt bricks.

Tests carried on the raw materials sewage sludge, fly ash and clay/shale include:

- Sieve analysis
- Linear shrinkage
- Loss on ignition
- Leachability
- Chemical analysis
- Density
- X-ray diffractometry
- Water content

Tests carried on the biofly and clay/shale bricks are:

- General features and composition
- Transverse strength
- Efflorescence
- Water absorption properties
- Linear shrinkage
- Thin sectioning
- Gas emission
- Measurement of dimensions
- Compressive strength
- Initial rate of absorption (suction)
- Resistance to salt attack
- X-ray diffractometry
- Leachability

Sources of raw materials

The source of the raw materials namely, fly ash, sewage sludge and clay/shale have been obtained from a number of sources and their details are given in Table 4.1.
Table 4.1 Sources of Fly ash, Sludge and Clay/Shale

<table>
<thead>
<tr>
<th>Materials</th>
<th>Source, NSW</th>
<th>Treatment and availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>Eraring Power Station</td>
<td>25 kg Bags supplied by Boral</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>Bellambi STP</td>
<td>From sludge drying beds after primary treatment and anaerobic digestion</td>
</tr>
<tr>
<td></td>
<td>Wollongong STP</td>
<td>Dewatered sludge from anaerobic digestion after secondary treatment</td>
</tr>
<tr>
<td></td>
<td>Shellharbour STP</td>
<td>Dewatered sludge from anaerobic digestion after secondary treatment</td>
</tr>
<tr>
<td></td>
<td>Port Kembla STP</td>
<td>Dewatered sludge from primary treatment and anaerobic digestion</td>
</tr>
<tr>
<td>Clay/Shale</td>
<td>Badgery’s Creek</td>
<td>Crushed to size 2-5 mm at Badgery’s Creek brick plant</td>
</tr>
</tbody>
</table>

- **Fly ash** obtained from Eraring power station. Since Boral is a major supplier of fine grade fly ash, it is readily available at Boral laboratories and delivered to University of Wollongong laboratory in 25 kg sacks. The fly ash was comprised of high alumina, silica and iron with low carbon content of 4%.

- **Sewage sludge** there are 4 sewage treatment plants in various parts of Wollongong which produce sludge as a by-product. The type and quality of the sludge varies with the degree and extent of the wastewater treatment processes used. Secondary treatment, digested dewatered sludge from Wollongong and Shellharbour treatment plants were used. Primary treatment, digested dewatered sludge from Port Kembla treatment plant was used however primary treatment, digested sludge from sand drying beds which are one year old from Bellambi treatment plant was also used. Average water content of the sewage sludges from Shellharbour, Port Kembla, Bellambi, and Wollongong were found to be 80.2, 79.3, 79, and 80.4% respectively.

- **Clay/Shale** from Badgery’s Creek quarrying operations was used. It was chosen from four types of clay (Badgery’s Creek red, Badgery’s Creek yellow, Greystanes and
Woonona) using the plasticity index which were found to be 15.74, 13.17, 11.65 and 9.97% respectively. The highest plastic clay of Badgery’s Creek red was chosen.

4.2. Tests on raw materials

4.2.1. Fly ash investigation

Particle size analysis

Particle size determination of fly ash, was carried out using Mastersizer S from Malvern instruments Ltd. To check repeatability of results, two samples from the same batch were tested. Detailed report on the particle size analysis is given in Volume 2, Appendix 4. However, the summary results of particle size analysis shown in Table 4.2 illustrates that the readings are very repeatable. It is seen that fly ash particles were very small and varied in size between 0.1 μm to 878.67 μm. The volume weighted mean diameter $D(4,3)$, Surface weighted or Sauter mean diameter $D(3,2)$ and median diameter $D(\nu,0.5)$ are 29.745, 2.705 and 14.39 μm respectively. Since the fly ash characteristics may vary considerably even within the same power plant, adequate ash was collected in one batch so that the entire experimental program could be undertaken with one batch.

<table>
<thead>
<tr>
<th>Fly ash</th>
<th>Size range (μm)</th>
<th>Particle diameters range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eraring 1</td>
<td>0.11-878.67</td>
<td>D(4,3) = 29.16</td>
</tr>
<tr>
<td>Eraring 2</td>
<td>0.09-878.67</td>
<td>D(3,2) = 2.61</td>
</tr>
<tr>
<td>Average</td>
<td>0.1-878.67</td>
<td>D(\nu,0.5) = 14.39</td>
</tr>
</tbody>
</table>

Chemical analysis

The fly ash sample was oven dried and fused with lithium metaborate at 1050°C for 15 minutes, then dissolved in acid and the resulting solution analysed by atomic absorption spectrophotometry. The important chemical characteristics of Eraring fly ash are shown in Table 4.3 and the data indicated are from an average of two samples. It shows that the fly ash is rich in silica, alumina and iron totalling about 92.9% by weight and the other constituents included are calcium, magnesium, sodium, potassium, titanium oxides totalling around 5%. Alkalies in the material is 1.43%. Loss on ignition is 1.2%
which provides an indication of the unburnt carbon present in the ash. The similarity between the chemical analysis for both clay/shale and fly ash will make it easy to replace the clay/shale and use the fly ash as a filler material in biofly brick.

**Density**

Density was determined for ground materials, passing 425 mm sieve using the method specified in AS 1289 C5.1. Kerosene was used as a replacement for the specified amount of distilled water in order to provide improved permeation through the fine particles. Fly ash particle density was determined as 2157 kg/m³.

**Water content**

Water content was determined using the method specified in AS 1289 B1.1. Average water content of the fly ash found to be less than 2%.

**Table 4.3. Chemical composition of Eraring fly ash**

<table>
<thead>
<tr>
<th>Sample compound</th>
<th>% by weight</th>
<th>AS 1129 F</th>
<th>ASTM N</th>
<th>Requirements</th>
<th>C618-1974 S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>67.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂+Al₂O₃+Fe₂O₃</td>
<td>92.9</td>
<td>Not Specified</td>
<td>70.0 min</td>
<td>70.0 min</td>
<td>70.0 min</td>
</tr>
<tr>
<td>MgO</td>
<td>0.7</td>
<td>Not Specified</td>
<td>5.0 max</td>
<td>Not Specified</td>
<td>5.0 max</td>
</tr>
<tr>
<td>CaO</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃*</td>
<td>0.2</td>
<td>2.5 max</td>
<td>4.0 max</td>
<td>5.0 max</td>
<td>4.0 max</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Available alkalies**</td>
<td>1.43</td>
<td>Not specified</td>
<td>Not specified</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.08</td>
<td></td>
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<tr>
<td>P₂O₅</td>
<td>0.04</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>0.0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.0016</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.003</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.008</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.0017</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.000002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L.O.I.***</td>
<td>1.2 ( @ 550°C)</td>
<td>8.0 max</td>
<td>10.0 max</td>
<td>12.0 max</td>
<td>10.0 max</td>
</tr>
</tbody>
</table>

N Raw or calcined naturally occurring pozzolans
F Fly ashes;
Any other material of suitable type

- In accordance with AS 1129 the SO₃ content of fly ash should not exceed 1.5 per cent if the ratio of cement to fly ash in concrete is less than 1.0 by mass
- Loss on ignition done to Australian Standard. ASTM method includes free moisture, Australian Standard does not. Loss on Ignition to Australian Standard may be taken as an accurate indication of carbon content.

4.2.2. Sludge investigation

Particle size analysis

Particle size determination, was carried out on the dry milled sludge using Mastersizer S from Malvern instruments Ltd. The results for the four types of sludges are summarised in Table 4.4 however the detailed results are given in Volume 2, appendix 4. It is evident that the sludge particles were very fine and vary in size between 0.06-443.23, 0.065-601.56, 0.06-615.065 and 0.065-326.57 μm for Shellharbour, Port Kembla, Bellambi and Wollongong respectively. The four types of sludge exhibit different grading, the finest overall sludge being that from Shellharbour (25.22 μm), followed by Bellambi (28.48 μm), Wollongong (31.49 μm) and Port Kembla (32.37 μm) in order of increasing coarseness based on volumetric diameter. Since sludge characteristics may vary considerably even within the same sewage plant, an adequate amount of sludge was collected at one time to last for the entire experimental program.

<table>
<thead>
<tr>
<th>Sludge type</th>
<th>Size range (μm)</th>
<th>Particle diameters range (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D(4,3)</td>
</tr>
<tr>
<td>Shellharbour 1</td>
<td>0.06-409.45</td>
<td>27.70</td>
</tr>
<tr>
<td>Shellharbour 2</td>
<td>0.06-477.01</td>
<td>22.74</td>
</tr>
<tr>
<td>Average</td>
<td>0.06-443.23</td>
<td>25.22</td>
</tr>
<tr>
<td>Port Kembla 1</td>
<td>0.07-555.71</td>
<td>38.80</td>
</tr>
<tr>
<td>Port Kembla 2</td>
<td>0.06-647.41</td>
<td>25.95</td>
</tr>
<tr>
<td>Average</td>
<td>0.065-601.56</td>
<td>32.375</td>
</tr>
<tr>
<td>Bellambi 1</td>
<td>0.06-878.67</td>
<td>30.09</td>
</tr>
<tr>
<td>Bellambi 2</td>
<td>0.06-351.46</td>
<td>26.87</td>
</tr>
<tr>
<td>Average</td>
<td>0.06-615.065</td>
<td>28.48</td>
</tr>
<tr>
<td>Wollongong 1</td>
<td>0.07-351.46</td>
<td>30.09</td>
</tr>
<tr>
<td>Wollongong 2</td>
<td>0.06-301.68</td>
<td>32.90</td>
</tr>
<tr>
<td>Average</td>
<td>0.065-326.57</td>
<td>31.495</td>
</tr>
<tr>
<td>Total average</td>
<td>0.0625-496.606</td>
<td>29.392</td>
</tr>
</tbody>
</table>
The surface weighted or Sauter, mean diameter for the four types of sludge are 2.005 μm for Port Kembla, 2.17 μm for Bellambi, 2.755 μm for Shellharbour and 3.37 μm for Wollongong.

**Chemical analysis**

Digested sludge from Bellambi treatment plant which had been on the drying bed for more than one year was used. The Wollongong, Shellharbour and Port Kembla sludges were collected fresh straight from the dewatering equipment. A sample of the sludge was oven dried in the laboratory looked very much like a very peaty type soil. The sample was sieved through a 600 micron sieve with the sludge retained being ground in a mortar and pestle and passed through 600 micron. Loss on ignition test at 550°C was conducted to determine the level of organic matter present. A separate oven dried sample was taken and dissolved in HCl and HNO₃ acids in 1:1 proportion. The sludge was resampled from the oven dried pile and fused with Lithium Metaborate (LiBO₂) in a graphite crucible and fused at 1050°C.

**Table 4.5. Chemical composition of dried sewage sludge**

<table>
<thead>
<tr>
<th>Sample compound</th>
<th>Bellambi %</th>
<th>Wollongong %</th>
<th>Shellharbour %</th>
<th>Port Kembla %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>30.6</td>
<td>11.5</td>
<td>12.6</td>
<td>9.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.0</td>
<td>3.6</td>
<td>4.1</td>
<td>2.9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.0</td>
<td>5.1</td>
<td>9.3</td>
<td>11.9</td>
</tr>
<tr>
<td>MgO</td>
<td>0.9</td>
<td>0.8</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>CaO</td>
<td>2.4</td>
<td>5.0</td>
<td>3.5</td>
<td>4.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.5</td>
<td>4.9</td>
<td>4.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Trace metals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.048</td>
<td>0.034</td>
<td>0.054</td>
<td>0.048</td>
</tr>
<tr>
<td>Zn</td>
<td>0.084</td>
<td>0.105</td>
<td>0.440</td>
<td>0.267</td>
</tr>
<tr>
<td>Cu</td>
<td>0.044</td>
<td>0.083</td>
<td>0.063</td>
<td>0.076</td>
</tr>
<tr>
<td>Cr</td>
<td>0.010</td>
<td>0.041</td>
<td>0.006</td>
<td>0.008</td>
</tr>
<tr>
<td>Pb</td>
<td>0.004</td>
<td>&lt;0.001</td>
<td>0.016</td>
<td>0.004</td>
</tr>
<tr>
<td>Ni</td>
<td>0.005</td>
<td>0.007</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>Cd</td>
<td>0.021</td>
<td>0.06</td>
<td>0.08</td>
<td>0.06</td>
</tr>
<tr>
<td>L.O.I. (at 550°C)</td>
<td>44.9</td>
<td>67.0</td>
<td>63.3</td>
<td>64.8</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>2005</td>
<td>1974</td>
<td>1915</td>
<td>1916</td>
</tr>
</tbody>
</table>

L.O.I. : Loss Of Ignition
Immediately after fusion, the molten mass was poured directly into stirred dilute HNO₃ solution, dissolved, filtered, and made to appropriate volume for subsequent analysis using Atomic Absorption Spectrophotometer for the determination of heavy metal concentration. All the results of the above mentioned tests appear on Table 4.5. Chemical analysis shows that SiO₂ + Al₂O₃ + Fe₂O₃ content for Wollongong, Shellharbour and Port Kembla sludges are 20.1, 26 and 24.6%, respectively. However for Bellambi sludge the SiO₂ + Al₂O₃ + Fe₂O₃ content is 43.6% which is nearly twice the amount of the other sludges. This may be associated with the amount of sand/silt which may be present in the sludge from the drying bed. Other constituents such as magnesium, calcium, sulphur, sodium, and potassium are 11.2, 9.5 and 8.8%, respectively, however Bellambi sludge shows these constituents as 4.2% which is less than a half of most of the sludges. Loss on ignition provides an indication of the organic and volatile matter present in the sludge ash, and this is found to be about 65% for most of the sludges however in Bellambi sludge it is the least at 45%. This is expected as the Bellambi sludge has been in the drying bed for over a year and it is expected that the active biomass which contributes to the organics content would have reduced.

Density

Density was determined using the same procedure described in section 4.2.1 and the values for the four sludges are shown in Table 4.5. The different sludge densities being comparable except Bellabi was higher due to the sand content of the sludge from drying beds.

Water content

Water content were determined using the method specified in AS 1289 B1.1. Average water content of the sewage sludges were found to be 80.2, 79.3, 79, and 80.4% for Shellharbour, Port Kembla, Bellambi, and Wollongong respectively.

4.2.3. Clay/Shale investigation

Preliminary laboratory investigation were conducted using different types of clay/shale from four sources to evaluate liquid limit, plastic limit and plasticity index in
order to choose the highest plasticity clay/shale for the biofly process. Badgery’s Creek red clay/shale was chosen as it had the highest plasticity index.

**Particle size analysis**

The dry clay/shale material, as supplied consisted of a considerable proportion of the coarse clay/shale fraction consists of relatively large, compressed plate like particles. These ranged in size, length to width ratio ranging from 1:1 to 3.1. Thickness of the coarse particles was normally 1 to 2 mm. It was considered that the inclusion of such particles in a grading analysis would be non representative of a true grading at time of extrusion. Likewise, drying of the particles would produce a product which might contain particles of an artificial size. Consequently it was decided to simply remove the large, flat compressed clay/shale particles from the sample used for particle size determination. It is likely, therefore, that a true grading of the clay/shale would yield a larger proportion of material passing 75μm sieve. Fine particle size determination was carried out using Mastersizer S from Malvern instruments Ltd. The summary results of the grain size distribution analysis is shown in Table 4.6 and detailed information can be found in Volume 2, appendix 4. It is clear that the clay/shale fine particles vary in size between 0.065 μm to 615 μm. The volumetric mean particle size was about 21.23 μm.

<table>
<thead>
<tr>
<th>Clay/Shale</th>
<th>Size range (μm)</th>
<th>Particle diameters range (μm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D(4,3)</td>
<td>D(3,2)</td>
</tr>
<tr>
<td>Badgery’s Creek 1</td>
<td>0.07-351</td>
<td>14.75</td>
<td>1.57</td>
</tr>
<tr>
<td>Badgery’s Creek 2</td>
<td>0.06-878</td>
<td>27.71</td>
<td>1.65</td>
</tr>
<tr>
<td>Average</td>
<td>0.065-615</td>
<td>21.23</td>
<td>1.61</td>
</tr>
</tbody>
</table>

**Chemical analysis**

The clay/shale sample was oven dried, ground in a vibrating disc mill to pass 150 microns, fused with Lithium Metaborate (LiBO2) at 1050°C for 15 minutes, dissolved in acid and the resulting solution analysed by Atomic Absorption spectrophotometry. The results of the analysis are shown in Table 4.7. The analysis shows that SiO2 + Al2O3 + Fe2O3 content about 93% and the other constituents includes magnesium, calcium, sodium, and potassium about 5.6%. It is noted that chemical analysis of clay/shale and fly ash are similar except in the quantity of Fe2O3 which was 5.8% in the clay/shale
compared to 3.1% in fly ash. This similarity is a useful feature when replacing fly ash instead of the clay/shale in the biofly brick process.

**Density**

Density was determined using the same procedure described in section 4.2.1 and the value for the clay/shale particle density was determined as 2327 kg/m$^3$.

**Water content**

Water content were determined using the method specified in AS 1289 B1.1. The average water content of the clay/shale found to be 17.5%.

**Table 4.7. Chemical composition of Badgery’s Creek clay/shale**

<table>
<thead>
<tr>
<th>Sample compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>60.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>17.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.8</td>
</tr>
<tr>
<td>MgO</td>
<td>1.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.9</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.04</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.6</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.1</td>
</tr>
</tbody>
</table>

**Trace Metals**

<table>
<thead>
<tr>
<th>Trace Metals</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.059</td>
</tr>
<tr>
<td>Zn</td>
<td>0.011</td>
</tr>
<tr>
<td>Cu</td>
<td>0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>0.007</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>0.006</td>
</tr>
<tr>
<td>Cd</td>
<td>0.045</td>
</tr>
</tbody>
</table>

| L.O.I.        | 8.6 (@550°C) |

**Atterberg limits**

Liquid limit, plastic limit and plasticity index for four types of clay/shale were determined in accordance with AS 1289 C1.1, AS 1289 C2.1 and AS 1289 C3.1 as shown in Table 4.8. Raw materials were riffled to obtain a homogeneous sample and then ground with a mortar and pestle to produce a sample of material passing 425 mm sieve. The clay with the highest plasticity was chosen out of the four types.
Table 4.8. Summary of the results for Atterberg limits

<table>
<thead>
<tr>
<th>Clay/Shale type</th>
<th>Liquid Limit %</th>
<th>Plastic Limit %</th>
<th>Plasticity Index %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Badgery's Creek red</td>
<td>32.00</td>
<td>16.26</td>
<td>15.74</td>
</tr>
<tr>
<td>Badgery's Creek yellow</td>
<td>31.00</td>
<td>17.83</td>
<td>13.17</td>
</tr>
<tr>
<td>Greystanes</td>
<td>28.50</td>
<td>16.85</td>
<td>11.65</td>
</tr>
<tr>
<td>Woonona</td>
<td>32.00</td>
<td>22.03</td>
<td>9.97</td>
</tr>
</tbody>
</table>

**Linear shrinkage**

Linear shrinkage of the clay was determined in accordance with AS. 1289. C4.1. The material as-received was ground to produce a sample passing 425 mm sieve. Sufficient water was added to the sample to bring it to a consistency similar to the liquid limit. Shrinkage sample was prepared using a linear shrinkage mould of 125 mm length. After air-drying and subsequent oven-drying, a value of 8% was estimated as the linear shrinkage for Badgery’s Creek.

It is concluded that the particle size for fly ash, the four types of sludges and clay/shale showed that the volumetric mean diameter can be classified as equivalent to the category of medium silt. The particle sizes are similar hence good and uniform mixing can be achieved with clay/shale act as a binder for sewage sludge and fly ash waste materials to make the biofly brick. It is expected that with increasing the quantity of the fly ash that the structural properties related to the durability and strength can also be increased. This can be attributed to the physical/chemical properties of the fly ash. The fly ash is considered to be glassy spheres, scoria and some crystalline matter and carbon, contain large quantities of SiO$_2$, alumina Al$_2$O$_3$ and ferric oxide Fe$_2$O$_3$, and smaller quantities of various other oxides and alkalies. The percentage content of the silica, alumina and iron in both fly ash and clay/shale is nearly the same, and hence the fly ash can be combined easily with the clay/shale to make the actual size biofly brick.

**4.3. Laboratory manufacture of full size bricks**

**4.3.1 Experimental procedure**

The experimental procedure for making actual size biofly bricks is summarised in Figure 4.1 in the form of a flow chart. The details of each of the processes are described below.
Clay/Shale + Fresh Sludge + Fly Ash
as is condition

Electrical mixer
The admixture was kneaded with an electrical mixer (600 kg/batch). Water is added to achieve the desired plasticity

Pilot scale extruder
Extruded bricks, water content 18-25% forced by augers through a die in a continuous column, cut off to size

Air drying 3 days.
Additional kiln drying at 180 degree C for 48 hrs.

Firing at 1100 degree C maximum in gas kiln for 20.5 hrs.

Exhaust gas analysis
Natural cooling

100 "Biofly" Bricks  ready for testing

Figure 4.1. Pilot scale manufacture of biofly brick

Batching

The Biofly Stage I, bricks were made with dry raw materials. However in this project (Biofly) Stage II, the three raw materials, fly ash, sludge and clay/shale, were mixed in “as is” condition of different proportions, and bricks were made with each of these mixtures. All mixes were batched by weight. Initially the water content of each raw material is determined. The clay/shale was in a fine granular form and its water content ranged between 14-18%. The sewage sludge water content ranged between 77-80%. The fly ash was essentially dry and its water content is <2%. The optimum water
content of the mixture was obtained using AS 1289 B1.1 and it was found to be between 24-33% as shown in Table 4.9.

Table 4.9. Water addition for different mixes (kg)

<table>
<thead>
<tr>
<th>Material Proportions % &quot;as is&quot;</th>
<th>Mix</th>
<th>Sludge water (kg)</th>
<th>Clay/Shale water (kg)</th>
<th>Workable moisture content (kg)</th>
<th>Water to be added for a 100 kg mix, (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 SS/50 FA/30 C/S</td>
<td>70 S</td>
<td>15.94</td>
<td>4.14</td>
<td>28.5</td>
<td>8.42</td>
</tr>
<tr>
<td>15 SS/50 FA/35 C/S</td>
<td>65 S</td>
<td>12.00</td>
<td>5.21</td>
<td>29.7</td>
<td>12.48</td>
</tr>
<tr>
<td>20 SS/40 FA/40 C/S</td>
<td>60 S</td>
<td>15.88</td>
<td>6.52</td>
<td>26.6</td>
<td>4.20</td>
</tr>
<tr>
<td>25 SS/30 FA/45 C/S</td>
<td>55 S</td>
<td>20.12</td>
<td>7.42</td>
<td>33.5</td>
<td>5.95</td>
</tr>
<tr>
<td>20 SS/30 FA/50 C/S</td>
<td>50 S</td>
<td>16.26</td>
<td>8.80</td>
<td>31.3</td>
<td>6.24</td>
</tr>
<tr>
<td>20 PS/50 FA/30 C/S</td>
<td>70 P</td>
<td>15.86</td>
<td>4.83</td>
<td>26.5</td>
<td>5.81</td>
</tr>
<tr>
<td>15 PS/50 FA/35 C/S</td>
<td>65 P</td>
<td>12.04</td>
<td>5.49</td>
<td>26.7</td>
<td>9.16</td>
</tr>
<tr>
<td>20 PS/40 FA/40 C/S</td>
<td>60 P</td>
<td>15.88</td>
<td>6.04</td>
<td>26.1</td>
<td>4.18</td>
</tr>
<tr>
<td>25 PS/30 FA/45 C/S</td>
<td>55 P</td>
<td>19.35</td>
<td>7.42</td>
<td>24.8</td>
<td>-</td>
</tr>
<tr>
<td>20 PS/30 FA/50 C/S</td>
<td>50 P</td>
<td>16.02</td>
<td>7.20</td>
<td>31.3</td>
<td>8.08</td>
</tr>
<tr>
<td>20 BS/50 FA/30 C/S</td>
<td>70 B</td>
<td>15.48</td>
<td>4.14</td>
<td>24.5</td>
<td>4.88</td>
</tr>
<tr>
<td>15 BS/50 FA/35 C/S</td>
<td>65 B</td>
<td>11.89</td>
<td>5.04</td>
<td>24.8</td>
<td>7.86</td>
</tr>
<tr>
<td>20 BS/40 FA/40 C/S</td>
<td>60 B</td>
<td>15.88</td>
<td>5.96</td>
<td>24.5</td>
<td>2.66</td>
</tr>
<tr>
<td>25 BS/30 FA/45 C/S</td>
<td>55 B</td>
<td>19.85</td>
<td>7.06</td>
<td>25.3</td>
<td>-</td>
</tr>
<tr>
<td>20 BS/30 FA/50 C/S</td>
<td>50 B</td>
<td>15.94</td>
<td>7.55</td>
<td>26.7</td>
<td>3.21</td>
</tr>
<tr>
<td>20 WS/50 FA/30 C/S</td>
<td>70 W</td>
<td>16.06</td>
<td>4.95</td>
<td>24.5</td>
<td>3.49</td>
</tr>
<tr>
<td>15 WS/50 FA/35 C/S</td>
<td>65 W</td>
<td>12.19</td>
<td>5.77</td>
<td>23.6</td>
<td>5.63</td>
</tr>
<tr>
<td>20 WS/40 FA/40 C/S</td>
<td>60 W</td>
<td>16.10</td>
<td>7.04</td>
<td>25.6</td>
<td>2.46</td>
</tr>
<tr>
<td>25 WS/30 FA/45 C/S</td>
<td>55 W</td>
<td>20.00</td>
<td>7.33</td>
<td>27.0</td>
<td>-</td>
</tr>
<tr>
<td>20 WS/30 FA/50 C/S</td>
<td>50 W</td>
<td>16.02</td>
<td>8.25</td>
<td>24.5</td>
<td>-</td>
</tr>
</tbody>
</table>

| Clay/Shale Laboratory Brick | LB  | -                | 21.6                 | 21.6                          | -                                    |

S: Shellharbour  P: Port Kembla  B: Bellambi  W: Wollongong

All raw materials were weighed and mixed using a rotating blade electric mixer made by Bennett Engineering South Australia, capacity 50 kg as shown in Figure 4.2. Water was added carefully until the required water content was achieved. For a typical mix of 100 kg of raw material, the procedure adopted is as follows.

i) Sludge was placed in the mixer first, then fly ash was added followed by clay/shale. They were mixed for (8-10 minutes) until a uniform mix is obtained.

ii) Water was added gradually to produce the desired "workable" water content as shown in Table 4.9. During the addition of water, mixing was carried out continuously for a period of (20-22 minutes). The total time taken for items (i) and (ii) is about 30 minutes.
Figure 4.2. A rotating blade electric mixer used for mixing biofly brick raw materials

Sludge was added first and then fly ash followed by clay/shale, so that the fine fly ash powder gets “glued” together with the raw sludge material which also has a higher water content. This has avoided fine fly ash particles from escaping from the top of the mixer. Several precautions and measures have been taken to ensure that these materials are handled safely. Wearing of hand gloves and face mask during mixing and transport is important. Details description regarding health and material handling precautions are described in Chapter 10.
Extruding

A special de-airing extruder was custom built by Venco West Australia using specification supplied by Dr. Sivakumar from the University of Wollongong. The extruder rotating in 1430/20 rpm, 5.50 kW, 415 volt and 0.60 amp. During the commissioning period of the extruder, it was not possible to make either biofly or clay/shale bricks. After a number of attempts the problem was identified that the die supplied by Venco was not suitable to compact the material in the form of a brick. A new die was designed and manufactured within the Department of Civil and Mining Engineering of the University of Wollongong. After a few trials, the modified die together with the extruder produced bricks to a satisfactory standard. The extruder also had a stop/start facility whereby extrusion can be stopped and started for brick cutting.

Having obtained the correct water content and consistency, the material was extruded using the above de-airing extruder rotating in 1430/20 r/min. The raw material mixture was pushed into the pugmill end where an auger moved it along the pipe and through a shredder. This has helped to de-air and densify the mix via the vacuum chamber using a Clisby Series 1000 compressor which has a maximum pressure of 100 kPa vacuum. As the mix travelled along the auger it was kneaded further and condensed at the end to a densely packed and massive material that was finally extruded through the die and on to a cutting table. The samples were then cut from the extruded column using a hand saw to the desired length of 230 mm as shown in Figure 4.3.

Drying

The drying stage of the process can be hampered with serious problems if a thorough understanding of the mechanism of drying is not clear in mind. While it is desired to keep the formed brick as near to its original size and shape as possible, the shrinkage characteristic of material-water systems on drying can cause distortion, warping, and even cracking if the process is not carried out with a full appreciation of the mechanism. Inadequate drying of the raw brick can cause problems in the kiln including explosion of the raw material, fissures and bloating. Some kind of energy, conventionally heat, is necessary to bring the moisture out of the brick and an efficient use of this energy is a significant economic factor. The rate of drying is also an important consideration.
Drying of the brick is the reverse of adding water to develop plasticity, and the mechanisms of drying can be related to those of plasticity development. The molecules involved in these processes will be the last to be removed in drying. Plasticity was developed when a little free water was present, so the removal of this unbound water will be the first stage of drying.

First stage: The extruded samples were marked, measured, weighed and left to air-dry for three days at room temperature. By now the brick has moisture in the range 8-12%, and if scraped, will come away as dust. It is air dried well, but, perversely, it is still what might be referred to as kiln wet. The brick is now put into the kiln and very low heat has to be applied to drive off the last remaining physical water. The brick must therefore be kept at low temperature until it is kiln dry, the kiln temperature should be kept around 180°C.

Second stage: The samples were placed in the gas kiln at 180°C for 48 hours for additional drying to drive off the last remaining physical water as shown in Figure 4.4.
The samples were once again measured and reweighed following kiln drying. At this point, the “dry” samples are ready to be fired.

![Image of biofly brick drying in a kiln at 180°C for 48 hours](image)

**Figure 4.4. Drying of biofly brick in the gas kiln at 180°C for 48 hours**

**Odour problem and control**

Odours from biofly brick processing originate during sludge storage, mixing, extruding and drying. Odour is primarily caused by the presence of sewage sludge which decompose and produce a variety of odourous compounds. This is one of the significant problem faced during the biofly Stage II. The bricks were made in a laboratory with inadequate ventilation and the odour problem created concerns to nearby offices within the University and at some point we received a significant number of written and verbal complaints and we have to shut the operation down. After a few months of negotiations, an alternative location in Coniston was found which is further away from the University. The bricks were mixed and extruded in an open area and hence odour was minimised. The drying of the bricks took place within a scrubber system which operated on the absorption and neutralisation principle using...
NaOH solution. This has worked reasonably well. Further details regarding odour control is given in Chapter 10.

**Firing**

Two firing curves have been developed. One for the clay/shale and the other for Biofly brick. A significant amount of time has been spent in the development of such curves and this is discussed in detail in Chapter 5. A short summary is given below.

The dried bricks were fired in a computer controlled kiln Port.O.Kiln Model SNG 80 H using natural gas which was specially piped into the biofly laboratory. The kiln had a cavity space of 1.4 m³ which was heated by two burners and they were located on one side of the cavity as shown in Fig. 4.5. Each burner is rated to produce a flow rate between 0.4-4.8 m³/h. When the kiln was originally purchased, it was felt that about 50 full size bricks could be fired. During the firing trials, it has been found that the cavity received unequal distribution of heat from the burner. The distribution of heat was made uniform by creating a baffle and shelf arrangement from which only a batch of 24 bricks can be fired at any time. By this method, the progress in the firing of bricks has been slowed by half the time. In fact to mix, extrude, dry and fire a batch of 100 bricks, it has taken more than a month of full time work. This does not include time for measuring of any of the properties analysed.

The kiln was controlled by digital program with built-in microprocessor model REX-P100 as shown in Figure 4.6. There are no fixed firing baffles or bagwalls which was supplied with this kiln, however it has been found that a bagwall system is necessary to prevent flame impingement during firing of the bricks which is positioned between the burner ports and the setting shelves.

For the Biofly brick, firing was done for a period 20.5 hours in comparison to clay/shale which took 48 hours. The temperature in the kiln was raised from room temperature to 200°C in about 3 hours and it was maintained at 200°C for about 15 minutes. Subsequently the temperature was raised to 400°C in about 3 hours and maintained at that temperature for about 15 minutes. Again the temperature was raised to 600°C in 3 hours and maintained at that temperature for about 15 minutes. Then the temperature was raised to 800°C in 3 hours and maintained for about 15 minutes, followed by the temperature being raised to 1100°C in 5 hours and maintained at this
temperature for about two and half hours. The kiln was then turned off and allowed to cool naturally. Figure 4.7 and 4.8 illustrates firing curves for Biofly and clay/shale bricks, respectively. Detail development of firing curves for biofly and clay/shale bricks are illustrated in Chapter 5.

Figure 4.5. Firing of biofly brick in Port.O.Kiln Model SNG 80 H
The firing curve was maintained using a digital programmable logic controller connected to the kiln. The digital program was an attempt to mimic the continuous temperature profile achieved in commercial applications. This was developed by a trial and error process. Following natural cooling, the specimens were removed from the kiln for testing.
Figure 4.7 Firing Curve to produce full size Biofly brick

Figure 4.8. Firing Curve to produce full size clay/shale brick
Chapter 4: Research Methods

4.4 Methods of sampling and testing

4.4.1 Methods of sampling and testing clay building bricks

Testing Procedures

All standard structural tests followed procedures in accordance with Table 4.10. The following tests outline the major requirements by the Australian standard.

Table 4.10 Standard Test Requirements for Fired Clay Bricks

<table>
<thead>
<tr>
<th>Test</th>
<th>Method</th>
<th>Specification AS-1226-1984</th>
<th>No. of bricks required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension (mm)-20 bricks</td>
<td>AS 1226.2</td>
<td>4510-4690</td>
<td>20</td>
</tr>
<tr>
<td>Length</td>
<td></td>
<td>2150-2250</td>
<td></td>
</tr>
<tr>
<td>Width</td>
<td></td>
<td>1470-1570</td>
<td></td>
</tr>
<tr>
<td>Depth</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse strength (MPa)</td>
<td>AS 1226.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Minimum T.S.</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Average T.S.</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Characteristic T.S.</td>
<td></td>
<td>Not less than 1.0 MPa</td>
<td>10</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>AS 1226.4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Average C.S.</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Characteristic C.S.</td>
<td></td>
<td>Not less than 7.0 MPa</td>
<td>10</td>
</tr>
<tr>
<td>Characteristic expansion (mm/m)</td>
<td>AS 1226.5</td>
<td>No specified limits</td>
<td></td>
</tr>
<tr>
<td>Pitting due to lime particles</td>
<td>AS 1226.7</td>
<td>Internal(Covered)-No limits.”</td>
<td></td>
</tr>
<tr>
<td>Initial rate of absorption (Suction), kg/m²/min</td>
<td>AS 1226.8</td>
<td>“Gen. Purpose” Above d.p.c. &amp; Internal (Not covered)-Not worse than Moderate Liability. “Exposure”-No liability</td>
<td>5</td>
</tr>
<tr>
<td>Water absorption prop. %</td>
<td>AS 1226.9</td>
<td>No specified limits</td>
<td></td>
</tr>
<tr>
<td>Cold water absorption, 24 hrs</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Boiling water absorp., 5 hrs</td>
<td></td>
<td></td>
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<tr>
<td>Saturation coefficient</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistance to salt attack</td>
<td>AS 1226.10</td>
<td>40 cycles</td>
<td>5</td>
</tr>
</tbody>
</table>

Measurement of dimensions

Twenty bricks from each batch were selected and tested in accordance with AS 1226.2. Any blisters or other small projections, together with any loose particles which might have adhered to the surfaces of the bricks, were removed and all the twenty bricks
were assembled in a straight line on a smooth concrete surface. Standard lengths were determined as shown in Figure 4.9 using a tape measure and is given below.

<table>
<thead>
<tr>
<th>No of bricks tested: 20</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total length (in mm)</td>
<td>4510-4690</td>
</tr>
<tr>
<td>Total width (in mm)</td>
<td>2150-2250</td>
</tr>
<tr>
<td>Total depth (in mm)</td>
<td>1470-1570</td>
</tr>
</tbody>
</table>

Figure 4.9. Arrangements for measurement of dimensions of biofly brick

**Transverse strength**

The transverse strengths of samples of ten bricks from each batch were determined in accordance with AS 1226.3. The bricks were tested as simply supported beams with a test load applied midway between supports. The ten bricks were placed with their bedding faces supported by a roller at each end, the load being applied through a third roller on the centre of the top face as shown in Figure 4.10. Specimens were supported over a span length of 180 mm. All specimens were fully immersed in water at room temperature for a period of not less than two hours immediately prior to testing.
The bricks were tested, without shock, by a gradually increasing the load in an Avery universal hydraulic testing machine with a full scale loading of 15 kN. A typical table showing the observations to be undertaken to determine the transverse strength testing is shown in Table 4.11.

**Calculations:**

1. \( T = \text{Transverse Strength (MPa)} \)
   \[ T = \frac{3 \times W \times L}{2 \times B \times D^2} \]

2. \( T_c = \text{Characteristic Transverse (MPa)} \)
   \[ T_c = \bar{T} - 1.65 \ s' \]

3. \( \text{S.D.} = \text{Standard Deviation} \)
   \[ s' = \text{S.D.} = \sqrt{\frac{\sum (T - \bar{T})^2}{N - 1}} \]

**Figure 4.10. Method of loading biofly brick test specimen for determining transverse strength**

where:

- \( L = \text{Span (mm)} \)
- \( \bar{B} = \text{Average width of the specimen (mm)} \)
- \( \bar{D} = \text{Average height of the specimen (mm)} \)
- \( N = \text{No. of specimens} \)
- \( s' = \text{The unbiased standard deviation (MPa)} \)
- \( \bar{T} = \text{The average of the individual transverse strengths of the specimens (MPa)} \)
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Table 4.11. Typical observation table for the measurement of transverse strength

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Length mm</th>
<th>Breadth mm</th>
<th>Depth mm</th>
<th>Max load W</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L₁</td>
<td>L₂</td>
<td>B₁</td>
<td>B₂</td>
<td>D₁</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>Average</td>
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</tbody>
</table>

**Compressive strength**

The compressive strengths of samples of ten bricks from each batch were determined in accordance with AS 1226.4. Compressive strength tests were performed on full size bricks. An Avery universal testing machine of 1800 kN capacity was used to apply a gradually increasing compressive force at the rate of 360 kN per minute. The bricks were placed on their bedding faces between two pieces of 11 mm steel board prior to loading in the testing machine as shown in Figure 4.11. All specimens were immersed in water for not less than two hours prior to testing. A typical table showing the observations to be undertaken to determine the compressive strength testing is shown in Table 4.12.

**Calculations:**

1. \( C = \text{Compressive Strength (MPa)} \)
2. \( \text{ASS. } C = \text{Assessed Compressive Strength (MPa)} \)
3. \( \bar{C}_c = \text{Characteristic Compressive Strength (MPa)} \)
4. \( S.D. = \text{Standard Deviation} \)

\[
C = \frac{W}{(L \times B)}
\]
\[
\text{ASS. } C = 1.33 \text{ } C_1 \text{ or } \bar{C} - 0.38 \text{ } R
\]
\[
R = \frac{(H - L_1)}{2}
\]
\[
\bar{C}_c = \bar{C} - 1.65 \text{ } s'
\]
\[
s' = \text{S.D.} = \sqrt{\frac{\sum (C - \bar{C})^2}{N - 1}}
\]

**where:**

\( C_1 = \text{Lowest } C \)
\( \bar{C} = \text{Average } C \)
\( H = \text{Sum of 2 highest } C \)
\( L_1 = \text{Sum of 2 lowest } C \)
R = Range \hspace{1cm} N = \text{No. of specimens}

s' = The unbiased standard deviation (MPa)

Figure 4.11. Method of loading biofly brick test specimen for determining compressive strength

Table 4.12. Typical observation table for the measurement of compressive strength

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Breadth mm</th>
<th>Length mm</th>
<th>Max load W kN</th>
<th>C MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B_1</td>
<td>L_1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B_2</td>
<td>L_2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average
Characteristic expansion

The characteristic expansion of the bricks was determined in accordance with AS 1226.5 as shown in Figure 4.12. A sample of five bricks representing the range of the firing treatments of the product is taken from the kiln. Their temperature is allowed to equilibrate, reference points are established at the ends of the bricks and the distances between the points are measured between 24 h and 32 h after the bricks are drawn from the kiln. The bricks are then exposed to saturated steam at 100°C for 4 h, after which they are cooled and remeasured when their temperature is within 2°C of the temperature at which they were first measured and within 100 h of taking of that first measurement.

Figure 4.12. Measuring frame and reference bar used in determination of biofly brick characteristic expansion

The difference in length multiplied by an appropriate factor gives the characteristic expansion-the “e” value.

A typical table showing the observations to be undertaken to determine the characteristic expansion testing is shown in Table 4.13.
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Z1= First initial length of the reference bar mm
Z2= Second initial length of the reference bar mm
Z3= First Final length of the reference bar mm
Z4= Second Final length of the reference bar mm

\[ Z_i = \frac{(Z_1 + Z_2)}{2} \]
\[ Z_F = \frac{(Z_3 + Z_4)}{2} \]
\[ d_Z = Z_i - Z_F \]
L = Length of Reference Bar (mm)

**Table 4.13. Typical observation table for the measurement of characteristic expansion**

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Length of Brick L mm</th>
<th>Yi</th>
<th>Yf</th>
<th>[ \Delta L = \frac{[(Y_f + d_Z) - Y_i]}{L} ]</th>
<th>[ \bar{\Delta L} ]</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

where:

\[ d_Z = \text{Difference between final and initial gauge readings of the reference bar (mm)} \]
\[ Z_i = \text{Initial gauge reading of the reference bar (mm)} \]
\[ Z_F = \text{Final gauge reading of the reference bar (mm)} \]
\[ Y_i = \text{Initial gauge reading of brick before steaming (mm)} \]
\[ Y_f = \text{Final gauge reading of brick after steaming (mm)} \]
\[ d_L = (Y_f + d_Z) - Y_i \]
\[ \Delta L = dL/L = \text{Change in length of each brick due to steaming} \]
\[ \bar{\Delta L} = \frac{\sum \Delta L}{5} = \text{Average change in length of the samples due to steaming} \]
\[ e = \text{The characteristic expansion} = 1000 \ k \ \bar{\Delta}L \ mm/m \text{ where } k \text{ is a value corresponding to } \bar{\Delta}L \text{ obtained from Table 1 AS 1226.5}. \]

**Efflorescence**

The liability to efflorescence of the bricks was determined in accordance with AS 1226.6. Five bricks from each batch were sampled. Each brick was placed with one end partially submerged in a dish of distilled water which was allowed to soak up into the
brick for a period of seven days as shown in Figure 4.13. Bricks were then removed from the water and air dried for two days, followed by oven drying at 100°C until constant mass was attained.

![Figure 4.13. Efflorescence test of biofly brick](image)

All faces of the bricks were then visually examined and the development of efflorescence assessed. A typical table showing the observations to be undertaken to determine the efflorescence testing is shown in Table 4.14.

In the assessment of efflorescence, the following criteria were used:

- Nil: no observable efflorescence
- Slight: not more than 10% of any surface of the specimen covered by a thin deposit of salt
- Moderate: more than 10% of one surface but not more than 50% of the total specimen surface covered by a thin deposit of salt
- Heavy: a deposit of salts covering more than 50% of the total brick surface
- Serious: any efflorescence that is accompanied by powdering and/or flaking of the surface of the specimen
Table 4.14. Typical observation table for the measurement of efflorescence

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Area covered %</th>
<th>Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
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<td>2</td>
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</tbody>
</table>

Pitting due to lime particles

Pitting due to lime particles of the bricks was determined in accordance with AS 1226.7. Five typical bricks from each batch were taken, and placed in the humidity room for 48 hours as shown in Figure 4.14.

Figure 4.14. Examination for pitting due to lime particles of biofly brick in the humidity room
The specimen were examined later for pitting. The development of pitting on each face examined was described as “nil”, “moderate” or “appreciable” in accordance with the following Table 4.15.

Table 4.15. Typical observation table for the measurement of Pitting due to lime particles

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>No of pits</th>
<th>Less than 3 mm</th>
<th>Between 3-5 mm</th>
<th>Greater than 5 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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</tbody>
</table>

Interpretation of Results:

The development of pitting on each face examined shall be described, in accordance with the following definitions:

Nil No pitting
Moderate Not more than five small pits, none exceeding 3 mm in diameter
Appreciable More than five small lime pits, one or more pits exceeding 3 mm in diameter

Initial rate of absorption (Suction)

The initial rate of absorption (suction) of the bricks was determined in accordance with AS. 1226.8. The initial rate of absorption (IRA) is the amount of water absorbed in one minute through the bed face of the brick. It is a measure of the “suction” of the brick and is an important factor in the design of mortars to bond strongly with the bricks. It is not an absolute measure of bond strength.

Eleven bricks were sampled from each batch. One was used to set up the test and adjust the water level to the appropriate value. The ten test bricks from each batch were dried for a period of forty eight hours in an oven at 105°C and then cooled to room temperature. The mass and average dimensions of the bed face to the immersed area were determined. The bricks were tested individually by placing them on a support
system within a large tank of water so that the brick was immersed in the water to a depth of 3 ± 0.25 mm as shown in Figure 4.15.

The brick was placed and allowed to remain partially immersed for a period of sixty seconds. On removal from the tank the brick was wiped with a damp cloth and its mass determined. A typical table showing the observations to be undertaken to determine the initial rate of absorption testing is shown in Table 4.16.

**Calculation:**

\[
IRA = 1000 \times \frac{(M_2 - M_1)}{(L \times B)} = \text{kg/m}^2/\text{min}
\]

where:

- IRA = Initial rate of absorption in kg/m^2/min
- M_1 = Mass of specimen oven dry (g)
- M_2 = Mass of specimen after 1 min. absorption (g)
- L = Length of the bed surface (mm)
- B = Breadth of the bed surface (mm)
Table 4.16. Typical observation table for the measurement of initial rate of absorption

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Dry weight M₁ (g)</th>
<th>Wet weight M₂ (g)</th>
<th>Length L mm</th>
<th>Breadth B mm</th>
<th>IRA kg/m²/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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Water absorption properties

The water absorption properties of the bricks were determined in accordance with AS 1226.9. Ten bricks were sampled from each batch. The bricks were oven dried at 105°C for a period of 72 hours to attain constant mass. When cooled, the mass of each brick was determined and then the bricks were completely immersed in clean water at ambient temperature for a period of 24 hours as shown in Figure 4.16.

On removal from the water, surface moisture on the bricks was removed with a damp cloth and the mass determined. The bricks were immediately returned to the water tank, the water was heated to boiling point and allowed to boil continuously for five hours as shown in Figure 4.19. On removal from the water, surface moisture on the bricks was removed with damp cloth and the mass determined.

Results were calculated for both the cold water absorption test and the boiling water absorption test. A typical table showing the observations to be undertaken to determine the water absorption and saturation coefficient testing is shown in Table 4.17.

Calculation:

1. Cold water absorption test - 24 hrs (%)

\[ Ac = 100 \times \frac{(M₂ - M₁)}{M₁} \]

Average \[ \overline{Ac} = \frac{\sum A_c}{10} \]

2. Boiling absorption test - 5 hrs (%)

\[ Ab = 100 \times \frac{(M₃ - M₁)}{M₁} \]

Average \[ \overline{Ab} = \frac{\sum A_b}{10} \]
Figure 4.16. Water tank used for determining water absorption properties of biofly brick

Table 4.17. Typical observation table for the measurement of water absorption and saturation coefficient

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Dry mass $M_1$ (g)</th>
<th>Saturated Mass after 24 hrs immersion $M_2$ (g)</th>
<th>Saturated Mass after 5 hrs boiling $M_3$ (g)</th>
<th>Cold water absorption test for each specimen (%) $A_c$</th>
<th>Boiling absorption test for each specimen (%) $A_b$</th>
<th>Sat coeff for each specimen ASTM C67 SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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</tbody>
</table>
3. Calculation of saturation coefficient (ASTM, C67)

$$SC = \frac{(M_2-M_1)}{(M_3-M_1)}$$  
Average $\overline{SC} = \frac{\sum SC}{10}$

**Resistance to salt attack**

A sample of five bricks from every batch, were selected in accordance with the recommended sampling procedure given in the test method AS 1226.10. Specimens of dimensions 55mm long, 25mm wide and 25mm thick were cut with a diamond saw from each of the bricks. Each specimen contained one long face which was cut from the face of the brick that would normally be exposed in a wall as shown in Figure 4.17. Sodium sulphate was selected for the salt cycling. The salt solution was prepared from Na$_2$SO$_4$. 10 H$_2$O at 14 percent m/m concentration.

The following procedure for the salt cycling was devised. The dried samples are washed in duplicate and exposed to cycles of soaking for one hour in 150 mL of the salt solution followed by subsequent oven drying for two hours at 110 °C. The cycle number at which the deterioration of the samples began was accepted as the first of three consecutive cycles in each of which there was a significant weight loss. The examination of each test specimen by rubbing was carried out by holding the specimen directly above the cup in which it was soaked, to ensure that all particles dislodged during the examination were collected in the cup. The oven dried mass of each test specimen, determined to the nearest 10 mg was recorded. Their performance was studied by the following method.

The test specimens were rubbed down after each cycle of drying and soaking and the result was assessed on the basis of the number of particles lost. In addition, the mass of particles which was considered to be the result of a significant loss, equals or exceeds 0.4 g (excluding pieces that weight more than 0.3 g), was determined by filtration.

- Filter the salt solution with the aid of vacuum through 0.45 µm filter paper, transferring all particles by washing from the cup to the paper.
- Wash the residue with liberal amounts of hot water three more times.
- Suck the residue dry, remove the filter paper from the funnel and transfer the residue to a watch glass with the aid of a brush.
- Dry it for at least 30 minutes at 110 °C and cool it in air to room temperature.
- Reject particles heavier than 0.3 g and weight the remaining residue.
• Discard the filtrate collected in the vacuum flask.
• Continue cycling in a fresh solution of sodium sulphate.

The test specimens were weighed after each overnight drying. At the completion of 40 cycles, the extent of any surface damage was noted. This test was performed manually without any automation. For completion of all the 22 batches, it took over six months of full time work focused on this test.

Figure 4.17. Determining resistance to salt attack of biofly brick using specimens of dimensions 55mm long, 25mm wide and 25mm thick

4.4.2 Methods of sampling and analysis for leaching

Concerns have been raised in regard to the fate of hazardous contaminants which might be introduced either to the brick manufacturing operation or the finished products through the addition of fly ash and sewage sludge wastes. The fate of toxic and hazardous inorganics, and particularly heavy metals, represents a considerably significant concern.
Hence, the fate of metal contaminants introduced into biofly brick by fly ash and sewage sludge additions are examined. One such "fate" will be specifically addressed, particularly metal losses due to natural weathering of an exposed biofly brick surface using an appropriate leaching test.

Samples of burnt brick were prepared to test leaching properties of nine metals, including 7 heavy metals (Cd, Cr, Cu, Fe, Pb, Ni and Zn). Five of these metals (Cd, Cr, Cu, Pb and Mn) are associated with the USEPA’S criteria for classifying hazardous wastes via the extraction test procedure and two of these metals (Cd and Zn) have elemental boiling points (765 and 906°C) below the vitrification temperature and five of these metals (Cr, Cu, Fe and Pb) have melting points (660, 320, 1083, 327 and 419°C) below the vitrification temperature used with brick production.

Three particle size ranges are selected in accordance with previous work undertaken by Bishop (1988). The pulverised samples sieved through a sieve series which included (9.5-4.75 mm) sieve, (0.2-0.6 mm) sieve and (75 μm) sieve. In all cases, the samples were pulverised with a mortar and pestle and mechanically sieved as a complete series in order to accumulate the required amount of material for each test (200 g). The three different particle sizes of each sample were then subjected to leachability tests to determine the extent to which metals would leach from the brick.

The USEPA Toxic Characteristic Leaching Procedure (TCLP, 1990), were used to evaluate the leaching potential of the brick. A sample weighing 200 g was taken from each size and was placed in 0.5 N acetic acid and diluted up to 1000 mL using demineralised water. The diluted samples were then placed in a PVC extractor vessel, and rotated at 50 rpm using a shaker over 24 hours as shown in Figure 4.18. The samples were then removed and filtered through a 0.45 μm millepore filter using a vacuum pump. The filtrate was placed in 200 mL PVC bottles in quadruplicate for the three different particle sizes of each sample.

Analysis

Preliminary digestion for metals

The sample solutions had to be digested before analysing for heavy metals in order to reduce the interference by organic matter and to convert the metals associated with other elements to a form that can be determined by atomic absorption spectrophotometry.
For this, the sample is mixed well and 100 mL of it is transferred to a beaker. 5 mL of concentrated nitric acid is added to the beaker. The solution is then brought to a slow boil and evaporated on a hot plate to about 15 mL. Another 5 mL of nitric acid is added and the beaker is covered with a watch glass. The solution is again heated to obtain a refluxing action. This is continued till the digestion is complete as shown by a light coloured, clear solution. The sample is not allowed to dry during digestion in accordance with Standard Methods (APHA, AWWA, WEP: 1993) standard method. A further 2 mL of nitric acid is added and the solution is warmed to dissolve any remaining residue. The beaker walls and watch glass are washed with deionised water. The solution and the rinse water are transferred to 100 mL volumetric flask and is allowed to cool. Then the solution is diluted using demineralised water to the 100 mL mark and mixed thoroughly.

*Determination of metals by atomic absorption spectrophotometry*

*Principle*

A portion of the sample solution is aspirated into a flame and atomised. A light beam is directed through the flame, into a monochromator, and on to a detector that measures
the amount of light absorbed by the atomised element in the flame as shown in Figure 4.19. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample.

Figure 4.19. Determination of metals by atomic absorption spectrophotometry

Interference

Many metals can be determined by direct aspiration of sample into an air acetylene flame. The most troublesome type of interference is the chemical interference. This results from the lack of absorption by atoms bound in molecular combination in the flame. This can also occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidised immediately to a compound that will not dissociate further at the flame temperature. Such interference may be eliminated by the addition of specific elements or compounds to the sample solution. In the case of magnesium determination, the interference of phosphate is eliminated by the addition of lanthanum.
**Sensitivity, detection limits and optimum concentration ranges for determination**

The sensitivity of flame atomic absorption spectrophotometry is defined as the metal concentration that produces an absorption of 1%. The detection limit is defined as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection limits vary with the instrument, the element determined, and the technique selected. The optimum concentration range usually starts from the concentration of several times the sensitivity and extends to the concentration at which the calibration curve starts to flatten. To achieve best results, it is always better to use concentrations of samples and standards within the optimum concentration range of the spectrophotometer. Table 4.18 gives the concentration ranges of different metals that can be measured with conventional atomisation.

*Determination of Al, Cd, Cr, Cu, Mn, Pb, Fe, Ni and Zn by direct aspiration using an air acetylene flame:*

**Apparatus**

Atomic absorption spectrophotometer and associated equipment

**Reagents**

Air: Commercially bottled clean air

Acetylene: Standard commercial grade

Nitrous oxide: Standard commercial grade

Metal free water: Deionised water

**Standard metal solutions:**

Aluminium, Cadmium, Chromium, Copper, Manganese, Lead, Iron, Nickel and Zinc

**Procedure**

Blank and three standard metal solutions are used to calibrate the atomic absorption spectrophotometer. Then the sample solution is aspirated through the flame and the metal concentration obtained directly. The leaching tests have taken a significant amount of time to complete. For example, for a single batch (consisting of 4 samples for each particle size) the procedure involved include crushing, sieving to three particle size, adding acid and shaking took more than two days to complete. The digestion and analysis took a further three days full time work. The total number of metal (9 metals for each
sample) samples analysed is 2376. In addition leachability of the three raw materials were also undertaken which consisted of a total of 648 samples. Overall the leaching tests took more than five months of full time work.

Table 4.18 Atomic absorption concentration ranges with direct aspiration

<table>
<thead>
<tr>
<th>Element</th>
<th>Wavelength nm</th>
<th>Flame gases</th>
<th>Detection limit mg/L</th>
<th>Sensitivity mg/L</th>
<th>Optimum conc. range mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>328.1</td>
<td>A-Ac</td>
<td>0.01</td>
<td>0.06</td>
<td>0.1-4</td>
</tr>
<tr>
<td>Al</td>
<td>309.3</td>
<td>N-Ac</td>
<td>0.1</td>
<td>1</td>
<td>5-100</td>
</tr>
<tr>
<td>As</td>
<td>193.7</td>
<td>N-H</td>
<td>0.002</td>
<td>-</td>
<td>0.002-0.02</td>
</tr>
<tr>
<td>Au</td>
<td>242.8</td>
<td>A-Ac</td>
<td>0.01</td>
<td>0.25</td>
<td>0.5-20</td>
</tr>
<tr>
<td>Ba</td>
<td>553.6</td>
<td>N-Ac</td>
<td>0.03</td>
<td>0.4</td>
<td>1-20</td>
</tr>
<tr>
<td>Be</td>
<td>234.9</td>
<td>N-Ac</td>
<td>0.005</td>
<td>0.03</td>
<td>0.05-2</td>
</tr>
<tr>
<td>Bi</td>
<td>223.1</td>
<td>A-Ac</td>
<td>0.06</td>
<td>0.4</td>
<td>1-50</td>
</tr>
<tr>
<td>Ca</td>
<td>422.7</td>
<td>A-Ac</td>
<td>0.003</td>
<td>0.08</td>
<td>0.2-20</td>
</tr>
<tr>
<td>Cd</td>
<td>228.8</td>
<td>A-Ac</td>
<td>0.002</td>
<td>0.025</td>
<td>0.05-2</td>
</tr>
<tr>
<td>Co</td>
<td>240.7</td>
<td>A-Ac</td>
<td>0.03</td>
<td>0.2</td>
<td>0.5-10</td>
</tr>
<tr>
<td>Cr</td>
<td>357.9</td>
<td>A-Ac</td>
<td>0.02</td>
<td>0.1</td>
<td>0.2-10</td>
</tr>
<tr>
<td>Cs</td>
<td>852.1</td>
<td>A-Ac</td>
<td>0.02</td>
<td>0.3</td>
<td>0.5-15</td>
</tr>
<tr>
<td>Cu</td>
<td>324.7</td>
<td>A-Ac</td>
<td>0.01</td>
<td>0.1</td>
<td>0.2-10</td>
</tr>
<tr>
<td>Fe</td>
<td>248.3</td>
<td>A-Ac</td>
<td>0.02</td>
<td>0.12</td>
<td>0.3-10</td>
</tr>
<tr>
<td>Hg</td>
<td>253.6</td>
<td>A-Ac</td>
<td>0.2</td>
<td>7.5</td>
<td>10-300</td>
</tr>
<tr>
<td>Ir</td>
<td>264.0</td>
<td>A-Ac</td>
<td>0.6</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>766.5</td>
<td>A-Ac</td>
<td>0.005</td>
<td>0.04</td>
<td>0.1-2</td>
</tr>
<tr>
<td>Li</td>
<td>670.8</td>
<td>A-Ac</td>
<td>0.002</td>
<td>0.04</td>
<td>0.1-2</td>
</tr>
<tr>
<td>Mg</td>
<td>285.2</td>
<td>A-Ac</td>
<td>0.0005</td>
<td>0.007</td>
<td>0.02-2</td>
</tr>
<tr>
<td>Mn</td>
<td>279.5</td>
<td>A-Ac</td>
<td>0.01</td>
<td>0.05</td>
<td>0.1-10</td>
</tr>
<tr>
<td>Mo</td>
<td>313.3</td>
<td>N-Ac</td>
<td>0.1</td>
<td>0.5</td>
<td>1-20</td>
</tr>
<tr>
<td>Na</td>
<td>589.0</td>
<td>A-Ac</td>
<td>0.002</td>
<td>0.015</td>
<td>0.03-1</td>
</tr>
<tr>
<td>Ni</td>
<td>232.0</td>
<td>A-Ac</td>
<td>0.02</td>
<td>0.15</td>
<td>0.3-10</td>
</tr>
<tr>
<td>Os</td>
<td>290.9</td>
<td>N-Ac</td>
<td>0.08</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>283.3</td>
<td>A-Ac</td>
<td>0.05</td>
<td>0.5</td>
<td>1-20</td>
</tr>
<tr>
<td>Pt</td>
<td>265.9</td>
<td>A-Ac</td>
<td>0.1</td>
<td>2</td>
<td>5-75</td>
</tr>
<tr>
<td>Rh</td>
<td>343.5</td>
<td>A-Ac</td>
<td>0.5</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Ru</td>
<td>349.9</td>
<td>A-Ac</td>
<td>0.07</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Sb</td>
<td>217.6</td>
<td>A-Ac</td>
<td>0.07</td>
<td>0.5</td>
<td>1-4</td>
</tr>
<tr>
<td>Se</td>
<td>196.0</td>
<td>N-H</td>
<td>0.002</td>
<td>-</td>
<td>0.002-0.02</td>
</tr>
<tr>
<td>Si</td>
<td>251.6</td>
<td>N-Ac</td>
<td>0.3</td>
<td>2</td>
<td>5-150</td>
</tr>
<tr>
<td>Sn</td>
<td>224.6</td>
<td>A-Ac</td>
<td>0.8</td>
<td>4</td>
<td>10-200</td>
</tr>
<tr>
<td>Sr</td>
<td>460.7</td>
<td>A-Ac</td>
<td>0.03</td>
<td>0.15</td>
<td>0.3-5</td>
</tr>
<tr>
<td>Ti</td>
<td>365.3</td>
<td>N-Ac</td>
<td>0.3</td>
<td>2</td>
<td>5-100</td>
</tr>
<tr>
<td>V</td>
<td>318.4</td>
<td>N-Ac</td>
<td>0.2</td>
<td>1.5</td>
<td>2-100</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>A-Ac</td>
<td>0.005</td>
<td>0.02</td>
<td>0.05-2</td>
</tr>
</tbody>
</table>

° A-Ac = air-acetylene, N-Ac = nitrous oxide-acetylene, N-H = nitrogen-hydrogen
4.4.3 Methods of sampling and analysis for air pollution

The two waste materials contain varying compositions of pollutants and there is no data available on the characteristic of pollutants that could be emitted during the firing of biofly brick. Concerns have been raised in regard to the fate of hazardous contaminants which may be present in sewage sludge and fly ash.

On one hand, it might be reasonable to expect thorough combustion of the sludge's constitutive organics due to the extreme firing temperature of 1100°C which may yield an exothermic heat release and, consequently, reduce the energy required for firing of the biofly brick. However, the fate of toxic and hazardous inorganics, particularly heavy metals, represents a considerably more significant concern. In addition, in some countries there have been concerns of fluorine emissions from brick manufacturing plants. Fluorine is a cumulative pollutant. Three batches were selected for gas analysis. They are:

(I) 25 S/30 FA/45 C/S Shellharbour mix, provides information on biofly brick made from uncontaminated sewage sludge from Shellharbour.

(II) 25 S/30 FA/45 C/S Port Kembla mix is chosen to provide information on biofly brick made from industry contaminated sewage sludge from Port Kembla.

(III) Laboratory clay/shale mix is chosen to obtain base line data on flue gas emitted from ordinary brick manufacturing.

For each batch, 24 bricks made of the same proportion of raw materials were fired in the kiln. The sampling was carried out with the intention of determining the concentration of the following pollutants namely, heavy metals, fluorides, chlorides and acid gases. These pollutants were selected based on the literature review. Since the firing temperature used in a batch process changed with time, it was decided to determine the concentration of the pollutants at each stage of firing. Hence, the firing process was divided into five different temperature ranges and gas samples were collected continuously within each temperature range.

The five temperature ranges are: 0 to 200°C; 200 to 400°C; 400 to 600°C; 600 to 800°C and 800 to 1100°C. Gas samples were collected for 3.25 hours per range for the first four ranges, and for 7.50 hours for the last range for biofly bricks. For the clay/shale
brick the first four temperature ranges were the same and the fifth was between 800 to 1030°C. The time ranges however were different and they are 4.25 hours, followed by 21.25, 11.75, 3.25 and 7.50 hours, respectively. The kiln flue arrangement is shown Fig. 4.20. The flue gas leaving the kiln gets diluted from incoming atmospheric air and gets discharged into the cylindrical flue gas pipe above the knobby. Hence an estimate of dilution factor is obtained by determining the concentration of CO₂ and O₂ in the flue gas within the kiln exit and within the cylindrical flue pipe. A dilution factor of 10% has been calculated which has been used throughout the entire sample run.

Figure 4.20. The firing kiln and the knobby with a gap of 200 mm in between
4.4.3.1 Determination of fluoride emission

**Principle**

A gas sample for the duration of 20.5 and 48 hours, for Biofly and clay/shale bricks, respectively, is extracted from the sampling point in the stack through an absorbing solution (0.1 N NaOH) in a series of impingers connected as shown in Figures 4.21, 4.22, 2.23 and 2.24.

The gas flow rate was maintained constant at 0.023 m$^3$/min during the sampling period for all the pollutants. Readings were taken throughout the entire sampling run for the temperature and pressure of the gas sample illustrated in Figures 4.21, 4.22, 2.23 and 2.24. The fluoride ion concentration is then determined by using a fluoride ion selective electrode. The test is performed according to Australian standard requirements reported by Ferrari et al., (1988).

**Reagents**

**Water**: demineralised water is used in the preparation of all the reagents.

**Sodium hydroxide solution (200 g/L)**: Dissolve 200 g of sodium hydroxide in water, cool and dilute with water to 1 L.

**Total ionic strength adjustment buffer (TISAB)**: Add 57 mL of acetic acid (1048 kg/m$^3$), 58 g of sodium chloride and 4 g of (1,2-cyclohexylene-dinitrilo)-tetraacetic acid (CDTA) to 500 mL of water. Stir to dissolve then add sodium hydroxide solution until the pH is between 5.0 and 5.5. Cool the solution to room temperature and dilute with water to 1 L.

**TISAB (1+1)**: Dilute 500 mL of TISAB to 1 L with water.

**Alcoholic citric acid solution (21 g/L)**: Dissolve 4.2 g of citric acid monohydrate in 200 mL of ethanol (950 mL/L).

**Alcoholic sodium hydroxide-glycerol solution (20 g/L)**: Dissolve 4 g of sodium hydroxide in 200 mL of solution consisting of 190 mL of ethanol (950 mL/L) and 10 mL of glycerol.
Figure 4.21. Stack gas sampling train-schematic
Sulphuric acid (28 mL/L): Cautiously add, with continuous stirring, 28 mL of sulphuric acid (1840 kg/m$^3$), to 500 mL of water. Cool and dilute with water to 1 L.

Sodium hydroxide solution (40 g/L): Dissolve 40 g of sodium hydroxide in water, cool and dilute with water to 1 L.
Figure 4.23. Impingers used for stack gas sampling collection

Figure 4.24. Gas meters used for stack gas sampling collection
**Standard solutions**

Stock sodium fluoride solution (1000 μg HF/mL): Dissolve 1.050 g of pure, dry sodium fluoride in 250 mL of water and dilute to 500 mL with TISAB in a volumetric flask. Mix well and transfer to a plastic bottle.

Standard sodium fluoride solution (20 μg HF/mL): Pipette 10 mL of sodium fluoride solution into a volumetric flask and dilute to 500 mL with TISAB (1+1).

Working standard sodium fluoride solutions: Pipette 1.0, 5.0, 50.0 mL of the standard 20 μg HF/mL solution into 100 mL volumetric flasks and dilute to volume with TISAB (1+1) for working standards equivalent to 0.2, 1.0 and 10.0 μg HF/mL respectively.

**Procedure**

Transfer each fluoride working standard into a plastic beaker containing a coated magnetic stirring bar and place on the magnetic stirrer. Insert the fluoride ion selective electrode and stir the solution until a steady response is indicated on the meter.

Standardise the readout of the selective ion meter for each of the working standards or, if the reading is in millivolts, prepare a calibration curve by plotting the concentration of fluoride in micrograms of hydrogen fluoride per millilitre (μg HF/mL) against potential in millivolts.

Measure the concentration of the solution of each sample of blank and determine the concentration of fluoride in micrograms of hydrogen fluoride per millilitre (μg HF/mL).

Measure the concentration of the solution of each sample for gaseous fluoride and, with reference to the calibration curve, determine the concentration of fluoride in micrograms of hydrogen fluoride per millilitre (μg HF/mL) for the solution of each sample.

Taking account of the volume of solution of each sample and the concentration of fluoride, calculate the amount of fluoride in each sample (C_s), in micrograms of hydrogen fluoride.

Taking account of the volume of solution of each sample and the concentration of fluoride, calculate the amount of fluoride in each blank (C_b), in micrograms of hydrogen fluoride, corresponding to each sample.
**Calculation and expression of results**

Air volume: Calculate the air volume from the following formula:

\[ V_0 = (V_f - V_i) \times \frac{273}{T_c} \times \frac{P_c}{101.3} \]  

(4.1)

where

\( V_0 \) = air volume sampled, at 0°C and 101.3 kPa, in cubic meters

\( V_i \) = initial gas meter reading, in litres

\( V_f \) = final gas meter reading, in litres

\( T_c \) = estimated mean ambient temperature near the meter at time of sampling, in °K

\( P_c \) = estimated mean ambient pressure near the meter at the time of sampling, in kPa.

Fluoride concentrations: Calculate the fluoride concentration from the following formula:

\[ C_g = \frac{(C_s - C_b)}{V_0} \]  

(4.2)

where

\( C_g \) = gaseous fluoride concentration expressed as micrograms of hydrogen fluoride per cubic metre of air at 0°C and 101.3 kPa

\( C_s \) = amount of hydrogen fluoride (HF) per sample, in micrograms

\( C_b \) = amount of hydrogen fluoride (HF) in the blank, in micrograms

### 4.4.3.2 Determination of chloride emission

**Principle**

A gas sample for the duration of 20.5 and 48 hours, for Biofly and clay/shale bricks, respectively, is extracted from the sampling point in the stack through an absorbing solution (0.1 N NaOH) in a series of impingers connected as shown in Figures 4.21, 4.22, 2.23 and 2.24. The gas flow rate was maintained constant at 0.023 m³/min during the sampling period for all the pollutants. Readings were taken throughout the entire sampling run for the temperature and pressure of the gas sample illustrated in Figures 4.21, 4.22, 2.23 and 2.24. The chloride concentration is then determined by titrating against silver nitrate solution, using potassium chromate as indicator. Principally in a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed. The test is performed according to (APHA 4500-C1-B, 1993).
Reagents

Potassium chromate indicator solution: Dissolve 50 g K₂CrO₄ in a little distilled water. Add AgNO₃ solution until a definite red precipitate is formed. Let it stand for 12 h, filter, and dilute to 1 L with distilled water.

Standard silver nitrate titrant, 0.0141 M (0.0141 N): Dissolve 2.395 g AgNO₃ in distilled water and dilute to 1000 mL. Store in a brown bottle.

Standard sodium chloride, 0.0141 M (0.0141 N): Dissolve 824.0 mg NaCl (dried at 140°C) in distilled water and dilute to 1000 mL.

Procedure

Sample Preparation: Use a 100 mL sample or a suitable portion diluted to 100 mL.

Titration: Directly titrate sample in the pH range 7 to 10. Adjust sample pH to 7 to 10, with H₂SO₄ or NaOH if it is not in this range. Add 1.0 mL K₂CrO₄ indicator solution. Titrate with standard AgNO₃ titrant to a pinkish yellow end point.

Standardise AgNO₃ titrant and establish reagent blank value by the titration method outlined above.

Calculation

\[
mg \, Cl^-/L = (A-B) \times N \times 35450/\, mL \, sample
\]  
(4.3)

where:

\[
A = \text{titration for sample, (mL)}
\]

\[
B = \text{titration for blank, (mL) and}
\]

\[
N = \text{normality of AgNO}_3
\]

\[
mg \, NaCl/L = (mg \, Cl^-/L) \times 1.65
\]  
(4.4)

4.4.3.3 Determination of acid gases emission

Principle

A gas sample 20.5 and 48 hours, for Biofly and clay/shale bricks, respectively, is extracted from the sampling point in the stack through demineralised water as an
absorbing solution in a series of impingers connected as shown in Figures 4.21, 4.22, 2.23 and 2.24. The gas flow rate was maintained constant at 0.023 m$^3$/min during the sampling period for all the pollutants. Readings were taken throughout the entire sampling run for the temperature and pressure of the gas sample illustrated in Figures 4.21, 4.22, 2.23 and 2.24. The absorption solution is heated, cooled and diluted to a practical volume (500 mL). An aliquot is titrated against sodium tetraborate solution and the subsequent calculation yields concentration of acid gas as grams of hydrochloric acid per cubic meter of gas at normal temperature and pressure. The test is performed according to Australian standard requirements reported by Ferrari et al., (1988).

**Procedure**

Transfer sample quantitatively to a beaker, boil, cool and transfer to an appropriate sized volumetric flask. Make up to the mark with demineralised water, typically 500 mL. If the volume is greater than 100 mL, for example 500 mL, take a 100 mL aliquot and transfer to a 300 mL conical beaker. If the volume collected is less than 500 mL, take a smaller aliquot and dilute to 100 mL in a 300 mL conical beaker. For example, volume of 100 mL, aliquot of 20 mL diluted to 100 mL in a 300 mL conical beaker. Titrate with 0.1N Na$_2$B$_4$O$_7$ solution using 1 mL methyl red-methylene blue indicator solution. A sample of the water used to absorb the stack gas is treated the same way as the samples to provide a reagent blank to be subtracted from the sample titrations. Average of three titrations have been used.

**Calculations**

Acid gas (as g HCl) = \[(\text{sample} - \text{blank}) \times N.(\text{Na}_2\text{B}_4\text{O}_7) \times 36.5 \times V_1/1000 \times V_2\] \hspace{1cm} (4.5)

where

- \(\text{sample titre}\) = average of three sample titrations (mL)
- \(\text{blank titre}\) = average of three blank titrations (mL)
- 36.5 = molecular weight of HCl
- \(V_1\) = volume of sample diluted
- \(V_2\) = volume of aliquot used in titration

Volume of gas sampled at normal temperature and pressure (NTP)

\[E = \left[\frac{273}{(273+C)}\right] \times \left[\frac{101.3}{(101.3+D)}\right] \times B\] \hspace{1cm} (4.6)
where

\[
\begin{align*}
B &= \text{volume of gas sampled in m}^3 \text{ at sampling conditions} \\
C &= \text{testing apparatus temperature (°C)} \\
D &= \text{testing apparatus pressure (kPa)} \\
E &= \text{volume of gas at NTP (m}^3) \\
\end{align*}
\]

Finally, acid gas as hydrochloric acid at NTP in g/m^3 = Acid gas (as g HCl)/E

### 4.4.3.4 Determination of heavy metals emission

**Principle and applicability**

Principle: A gas sample was taken for the duration of 20.5 and 48 hours, for Biofly and clay/shale bricks, respectively, is extracted from the sampling point in the stack through an absorbing solution (0.1 N NaOH) in a series of impingers connected as shown in Figures 4.21, 4.22, 2.23 and 2.24. The gas flow rate was maintained constant at 0.023 m^3/min during the sampling period for all the pollutants. Readings were taken throughout the entire sampling run for the temperature and pressure of the gas sample illustrated in Figures 4.21, 4.22, 2.23 and 2.24. The heavy metal concentration is then determined by digesting the sample and using atomic absorption spectrophotometry. The test is performed according to Australian standard requirements reported by (Ferrari et al., 1988).

Applicability: This method is applicable for the determination of heavy metals present in the stack gases of stationary sources. Even very low concentrations can be determined by this method.

### Reagents

Water: Deionised water is used in the preparation of all the reagents

Absorbing solution: Distilled water and 0.1 N nitric acid are used as the absorbing solution. 64 ml of concentrated nitric acid is dissolved in deionised water and diluted to 1 litre in a volumetric flask
Procedure

Blank and three standard metal solutions are used to calibrate the atomic absorption spectrometer. Then the sample solution is aspirated through the flame and the metal concentration obtained directly.

4.4.3.5. Determination of carbon monoxide, carbon dioxide, combustible gases, oxides of nitrogen and sulfur dioxide emissions

A gas sample for the duration of 20.5 and 48 hours, for Biofly and clay/shale bricks, respectively, is extracted from the sampling point in the stack through portable gas analyser ENERAC MODEL 2000 as shown in Figure 4.25. Readings were taken throughout the entire sampling run for carbon monoxide, carbon dioxide, combustible gases, oxides of nitrogen and sulfur dioxide every 15 minutes in a paper record. The gas flow rate was maintained constant at 0.023 m$^3$/min during the sampling period for all the pollutants. Readings were taken throughout the entire sampling run for the temperature and pressure of the gas sample on a chart record.

Figure 4.25. Portable gas analyser ENERAC MODEL 2000 used for the determination of carbon monoxide, carbon dioxide, combustible gases, oxides of nitrogen and sulfur dioxide emissions
Chapter 4: Research Methods

4.5. X-Ray diffractometry

The object of firing the biofly materials is to convert a fairly loosely compacted blend of various minerals into a strong, hard, and stable product. To achieve this conversion many chemical and physical processes come into play. The properties of the final product such as strength, porosity, stability against the action of moisture and chemicals, thermal expansion, thermal conductivity, and hardness are determined by the kind and amounts of the various phases resulting from the firing process.

It is important to review the reactions that take place on heating some of the important disilicate minerals. The raw materials for the biofly brick contain between 40% to 80% of these minerals, therefore, they are bound to have important influences on the final product and on the way that the final phases are achieved. It has been found that a single disilicate mineral may break down on heating to provide as many as four new compounds, to serve as reactants with each other and other minerals present. In many cases, one or more of these decomposition products remains in the final product and exerts its influence on the properties, this is likely to be the case in biofly bricks. To determine phase changes during a high temperature firing process such as in the Biofly process, the X-Ray diffraction technique is used.

X-Ray diffraction patterns were determined for raw materials as well as for dry and fired bricks as follows:

1. X-Ray diffraction patterns were made for the biofly raw materials namely the Shellharbour sludge, Eraring fly ash and Badgery's creek clay/shale to determine and compare the mineralogical characteristics of the raw materials of the biofly brick.

2. Samples for X-Ray diffraction were taken from dry and fired brick of Shellharbour mix consisting of 15% Sludge + 50% Fly Ash + 35% Clay/Shale.


The material was pulverised with a mortar and pestle to produce a powdered material suitable for placing in aluminium mounts (2 g). The pulverised material was lightly compacted in the mount ready for powder X-Ray diffractometry.
4.6. Thin sectioning microscope analysis

Identification of biofly brick minerals often requires the application of a number of auxiliary techniques, such as chemical, differential thermal analysis, and others. A chemical analysis gives only the amount of chemical elements that are present, it does not give information about how these elements are combined with one another. Thin sectioning using polarized light microscopy gives principal crystallographic pattern, and hence, gives the actual minerals that are presented in a mixture and how they combined together.

Dry and fired samples for thin sectioning microscope were cut from selected bricks from two batches, 15% S/50% FA/35% C/S Shellharbour biofly brick and clay/shale brick. Specimens from each of the two types of bricks were prepared for thin sectioning analysis. Two 10 mm thick slabs were sliced, using a diamond saw, from each brick. Slices were taken at a position approximately midway along the longitudinal face. The “open” porosity cut face of each slice was impregnated with a low viscosity, blue coloured epoxy resin. Approximately 2 mm from the face of each sample was ground off using coarse carborundum powders. A slice, measuring approximately 50 mm by 25 mm, was cut from each slab, glued to a glass slide and ground down to a thickness of 30 \( \mu \text{m} \) (0.030 mm). A coverglass was attached to the thin section with Canadian balsam. For observation and analysis, the thin section was mounted in a Leitz orthoplan microscope and observed in transmitted light at a nominal microscope magnification of 1 x 2.5 x and 10 x.

4.7. Summary

• Various tests have been described on the raw materials sewage sludge, fly ash and clay/shale as well as on the dry and burnt bricks. The tests were primarily concerned with identifying similarities or discrepancies between the brick types, together with determining physical and material properties of the raw materials as well as the burnt bricks. The tests undertaken on the raw materials are:

• Sieve analysis
• Linear shrinkage
• Loss on ignition
• Leachability
• Chemical analysis
• Density
• X-ray diffractometry
• Water content
• It is concluded that the particle size for fly ash, the four types of sludges and clay/shale showed that the volumetric mean diameter can be classified as equivalent to the category of medium silt. The particle sizes are similar hence good and uniform mixing can be achieved with clay/shale act as a binder for sewage sludge and fly ash waste materials to make the biofly brick.

• Fly ash exhibited the finest range of particle size which may likely to enhance the durability and strength of the biofly brick.

• The percentage content of the silica, alumina and iron in both fly ash and clay/shale is nearly the same, and hence fly ash can replace or combine other materials readily to make biofly brick.

• Tests carried out on the bricks are in accordance with Australian Standard 1226 (1984), TCLP (1990) and Australian Standard for air pollution (1988). The Australian Standard 1226 provides the methods of Sampling and Testing for Clay Building Bricks. TCLP Standard provides the methods of sampling and analysis for leachability test, and the Australian Standard for air pollution provides the methods of sampling and analysis for air test. The tests undertaken for the burnt bricks have been itemised and summarised as:

(i) Physical and structural tests

• General features and composition
• Transverse strength
• Efflorescence
• Water absorption properties
• Linear shrinkage
• Measurement of dimensions
• Compressive strength
• Initial rate of absorption (suction)
• Resistance to salt attack

(ii) X-ray diffractometry

• X-Ray diffraction patterns were determined both on the raw materials as well as for dry and fired bricks. The Shellharbour sludge, Eraring fly ash and Badgery’s creek clay/shale have been chosen. Samples for X-Ray diffraction were also taken from dry and fired brick of Shellharbour mix consisting of 15% S + 50% FA + 35% C/S and compare with clay/shale fired brick.
(iii) Thin sectioning

• Dry and fired samples for thin sectioning microscope were cut from selected bricks from two batches, 15% S/50% FA/35% C/S Shellharbour biofly brick and compare with clay/shale brick.

(iv) Leachability tests

• Leachability tests were determined for raw materials as well as for fired bricks in accordance with TCLP. Three particle size ranges from fired bricks are selected in accordance with previous work undertaken by Bishop et al. (1988). The pulverised samples were sieved through (9.5-4.75 mm), (0.2-0.6 mm) and (75 μm) sieves, 200 g of samples were used in each leaching test to determine the concentration of 9 heavy metals.

(v) Gas emission

• Three batches were selected for gas analysis. They are:

  • 25 S/30 FA/ 45 C/S Shellharbour mix, provides information on biofly brick made from uncontaminated sewage sludge from Shellharbour.

  • 25 S/30 FA/45 C/S Port Kembla mix is chosen to provide information on biofly brick made from industry contaminated sewage sludge from Port Kembla.

  • Laboratory clay/shale mix is chosen to obtain base line data on flue gas emitted from ordinary brick manufacturing.

• For each batch, 24 bricks made of the same proportion of raw materials were fired in the kiln. The sampling was carried out with the intention of determining the concentration of the following pollutants namely, heavy metals (Al, Cd, Cr, Cu, Mn, Pb, Fe, Ni and Zn), fluorides, chlorides and acid gases. These pollutants were selected based on the literature review. Since the firing temperature used in a batch process changed with time, it was decided to determine the concentration of the pollutants at each stage of firing. Hence, the firing process was divided into five different temperature ranges and gas samples were collected continuously within each temperature range.
Chapter Five

Development of Firing Curve

5.1. Introduction

Development of a suitable firing curve is a crucial step for any high temperature solidification process. Improvement in reducing firing schedules can also result in substantial cost savings in fuel. There is obviously a maximum firing rate for any ceramic that allows thermal reactions to go far enough to produce acceptable fired properties. Certainly, firing at a slower-than-maximum rate but with an ideal firing profile lends a certain margin of safety to the firing process, but the practical limit may be set by:

(i) The kiln furniture or by the kiln design itself.
(ii) The clay/shale type.
(iii) The mix proportion.
(iv) The amount of material replacement.

The firing schedule of a brick body may be divided into three parts (Prokopovich, 1993a), representing structural changes that occur with temperature, and which determine the body’s ability to absorb elastic strain energy:

1. During heating, the green body is a rather fragile, and brittle compact.

2. Above 900 °C, a glass phase begins to develop and increase in volume while decreasing in viscosity to the final maturation temperature. These temperatures may be called the pyroplastic range, which extends into the cooling period until the glass phase loses its viscous character at its transition temperature. Throughout this range the body cannot store any elastic strain energy permanently, although at the beginning and at the end of the range it is possible to apply stresses faster than the viscous component can relieve, which may cause fracture.
3. The third range is the final portion of the cooling curve below the glass transition temperature, where the body is a relatively strong, elastic, and brittle ceramic.

Thermal shock causing fracture can occur in any of the above three divisions, but it is most dangerous during heating and cooling when the body is brittle. During heating, the biofly body is fragile because of the relatively low interparticle bond strengths that may be compounded by residual strains from the forming process. During cooling, the biofly body is relatively strong but is subject to brittle fracture as a result of strains set up by the α-β quartz inversion at 573 °C.

5.2. Development of firing curve

The aim of the work is to develop two firing curves, one for biofly brick and the other one for clay/shale brick using a trial and error approach. The industrial firing curve was modified by shortening the time during different stages. The sequence of events such as water smoking, followed by dehydration and oxidation, ending by vitrification which occurs during the firing of the brick presented as well as colour development and cooling stresses are discussed below.

A schematic diagram of the firing procedure is shown in Fig. 5.1. Firing takes place in Port.O.Kiln Model SNG 80 H with two burners in one side capacity between 0.4-4.8 m³/h/burner as shown in Figure 5.2. The kiln controlled by digital program with built-in microprocessor model REX-P100. There are no fixed firing baffles or bagwalls with this kiln. Trials undertaken without a baffle produced completely burnt bricks when they were placed adjacent to the “naked” flame. It has been found that a bagwall system is necessary to prevent flame impingement during firing of the bricks which is positioned as shown in Figure 5.2 between the burner ports and the setting shelves.

The burner arrangement is shown in Fig. 5.3. The primary air opening is easily adjusted by turning the metal primary air disc. In the early stages of the firing the primary air opening will be completely closed, but will need to be opened later before starting oxidation stage at 550°C, sequence of procedure as follow:

1. Open damper to increase gas flow.
2. Then open primary air to full on both burners.
Chapter 5: Development of Firing Curve

Firing trials

Clay/Shale brick

Trials of temp. range from
0 deg C to 1030 deg C
passed by 200, 400, 600 and 800 deg C

Biofly brick

Trials of temp. range from
0 deg C to 1100 deg C
passed by 200, 400, 600 and 800 deg C

Figure 5.1. A schematic diagram of the firing procedure

When primary air valve is fully opened, it provides a highly oxidising conditions and this is essential for biofly brick firing procedure.

Firing consists of several stages namely, water smoking, dehydration, oxidation, vitrification and cooling as shown in the industrial firing curve in Fig. 5.4. This process lasts from 60 to 100 hours depending upon the types of clay used and the type of brick to be manufactured through the tunnel kiln. The tunnel kiln is a device for carrying out continuous heat exchange between gases and clay within the tunnel in a controlled way.
Chapter 5: Development of Firing Curve

Dry clay bricks which have been set in packs on kiln cars travel through the kiln tunnel while kiln gases are made to travel through the kiln in the opposite direction. During the passage of the bricks through the kiln their temperature is raised from ambient to the maximum desired temperature and cooled again back to ambient temperature in a controlled manner so that the maximum possible percentage of first quality bricks are recovered while using the minimum amount of energy. Energy in the form of fuel and electric power is supplied to the kiln in order to heat up the kiln gases and to provide a dynamic force to cause the gases to flow in the required directions within the kiln tunnel. The fuel is consumed in burners and electric power in various fans and controls.

Biofly Stage I

In biofly stage I, (1990-1991) small cylindrical samples 75 mm x 10 mm were fired in an electrical muffle furnace with a small cavity. This firing curve developed in 1991 using the electric muffle furnace with temperature stair-stepped from room temperature to 1030 °C over a 7 hour period and is shown in Fig 5.5. The firing curve was maintained using a programmable controller connected to the kiln. The stair-stepping
was an attempt to mimic the continuous temperature profile achieved in commercial applications. The curve shown in Fig. 5.5 has several limitations. The curve was obtained in a small electric furnace and for very small samples. In practice, bigger gas kiln is used. Hence this curve can not be used for stage II.

**Biofly Stage II**

For biofly stage II, the firing curve was developed in a gas kiln and is shown in Figure 5.6. The industrial firing curve, was significantly modified since the nature of the body is substantially different, and hence the rates in each level determined by a trial and error process, followed by natural cooling. It has been found that it is possible to make biofly brick in twenty and half hours. A total of 8 firing curve trials were carried out to develop and select a suitable firing curve for the manufacture of full size biofly brick in the laboratory and a detailed description is given in section 5.5.

Clay/shale brick firing curve shown in Figure 5.7 was developed in a similar manner. The curve indicated that it requires forty eight hours to make the full size clay/shale brick. A total of 10 firing curve trials were carried out to develop and select a suitable firing curve for the manufacture of clay/shale brick in the laboratory.
Chapter 5: Development of Firing Curve

![Figure 5.5. Biofly Brick Firing Curve - Stage I (Small sample)](image)

![Figure 5.6. Biofly Brick Firing Curve - Stage II (Actual size)](image)
Chapter 5: Development of Firing Curve

5.3. The action of heat on ceramic bodies

The changes that take place in ceramic materials on heating are of vital importance to a thorough understanding of the firing operation. The principal chemical and physical changes which occur during firing are reported by Prokopovich (1993a) as:

1. The removal of residual moisture in the ware.
2. Decomposition of the ware minerals with evolution of steam.
3. Oxidation and decomposition reactions.
4. Vitrification or sintering.
5. Polymorphic transformations.

5.3.1. The removal of residual moisture in the ware

Ideally, the ware should enter the kiln with no free moisture present, as most kilns are not suitable dryers. However, it is often not desirable to increase the temperature faster than is suitable for drying, which may cause strains, uneven shrinkage and cracks. Bricks can explode if they contain more than 2% of free moisture. Also the water evaporated from the hotter part of the setting easily condenses out on the cooler part making it moist, causing first expansion and then shrinkage.
The mechanical or uncombined water is generally driven off by the time the goods have attained 150 °C. The appearance of the smoke in the temperature range 150-165°C in the old coal-fired kilns led to this stage being known as the “water-smoking period” (Prokopovich, 1993a).

5.3.2. Decomposition of ware minerals

After the mechanical water has been removed there still remains the chemically combined water. Between 450-550 °C kaolinite decomposes with the loss of about 14% of its weight as steam (Prokopovich, 1993a).

Biofly brick loses 7 to 8% of its weight on firing and since the bulk of this loss is due to the breakdown of the ware mineral, and about 25 m³ of steam is released for every 100 kg of ware fired. Although traces of combined water may continue to be given off until a temperature of 850-900 °C is reached, almost all water would have been driven off by 650 °C. Hence the temperature range from 150 °C to 650 °C is known as the “combined-water-smoking period”. From the above it can be readily appreciated why the rate of temperature rise during the “water-smoking” periods must be relatively slow. If it were not so, the rapid evolution of steam might disrupt the Biofly bricks.

5.3.3. Oxidation and decomposition reactions

Biofly brick contains organic matter which is oxidized during firing. Apart from the organic or carbonaceous matter, the brick also contains sulphur compounds, such as the sulphides of iron and ferrous compounds which are oxidized to a ferric condition.

The oxidizing period in the firing of biofly, although not very definite, may be considered as extending from 350 °C to 850 °C. It overlaps at the lower end of the range with the period when the ware is decomposing and the combined water is being evolved, the rapid evolution of steam may exclude the air or oxygen required to affect the oxidizing reactions. At the upper end it may extend into the vitrification period causing bloating. The oxidation of free carbon is governed by the following three important conditions as reported by Prokopovich (1993a).
(i) **Availability of oxygen.** Sufficient oxygen should be present in the atmosphere surrounding the article. This is not the case if the ware is in the process of decomposing, whereby the evaluation of water vapour excludes the oxygen.

(ii) **Permeability of the product.** The available oxygen should readily penetrate through the system of pores to the carbonaceous matter beneath the surface. This requires high permeability and long periods of time, particularly for articles several centimetres thick. Permeability of bricks is highest at the conclusion of the decomposition process of biofly. The presence of sludge increases the permeability of the brick in comparison to clay brick.

(iii) **Temperature** is another important factor. The higher the temperature the more readily any particular form of carbon will react with oxygen. If, however the oxygen has poor access to the carbon and the products of combustion cannot readily escape from the site within the brick mass where they are formed, then oxidation cannot proceed and the effect of rising temperature will be to convert carbon into a form more closely resembling graphite, which is not so readily oxidizable.

Under some conditions it may happen that the carbonaceous residue is still incompletely oxidized in the centre of the product by the time the surface has become vitrified. This accounts for one possible mechanism of formation of ‘black core’ in fired bricks. Since the vitrification of bricks becomes significant at 850 °C-900 °C, it is clear that the oxidation of carbonaceous matter must be completed before this temperature range is reached. Keeping in mind the three factors discussed above, Prokopovich (1993a) has indicated that the optimum temperature for the combustion of carbonaceous material lies in the range 750 °C to 900 °C with 100% to 150% excess air.

The oxidation of sulphides is perhaps best exemplified by considering the behaviour of iron pyrites. Sulphides in general react with oxygen in the temperature range of 350 °C to 800 °C, forming SO2 gas which escapes through open pores. A variety of reactions could take place including formation of ferrous and ferric sulphates.

Many impurities in the biofly brick are in the form of hydrates, carbonates and sulphates. Depending on the composition, hydrates and carbonates decompose over a wide temperature range between 100 °C and 1000 °C, and 400 °C to 1000 °C, respectively. Calcium carbonate, CaCO3 decomposes at about 900 °C.
The presence of CaCO₃ in the brick body may cause the following problems. If the dissociation reaction with evolution of gaseous CO₂ occurs after the surface of the brick started to vitrify, bloating may occur. Calcium carbonate may also cause 'Lime Blowing' - the falling away of small pieces from the face of the brick as a result of the expansion of nodules of lime present in the fired brick.

Sulphates create a particular problem in firing because they do not decompose until a very high temperature is reached, as shown below:

<table>
<thead>
<tr>
<th>Sulphate</th>
<th>Decomposition begins at (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO₄</td>
<td>890</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>1200</td>
</tr>
<tr>
<td>BaSO₄</td>
<td>1510</td>
</tr>
</tbody>
</table>

Calcium sulphate is often present as an impurity and may also be formed by reaction of calcium carbonate or calcium oxide with sulphur trioxide or sulphur dioxide and oxygen in the kiln atmosphere.

Apart from the reactions mentioned above a variety of other reactions depending on the composition of a body as well as polymorphic phase transformations could take place.

5.3.4. Vitrification and sintering

Although most of the processes that take place during the initial firing stages are of general importance and frequently cause the main problems during firing, they are only secondary phenomena. The primary processes which occur on heating, and are important in connection with the firing behaviour of all ceramic compositions, are grain growth and densification, associated with sintering or vitrification stated by Prokopovich (1993a).

Sintering is a process by which fine particles in contact with each other agglomerate on heating to produce an increase in bulk density and a decrease in the porosity of the mass. Solid-state reactions or intercrystallization occurring during sintering result in the
formation of crystalline bonds which give strength to the fired body. It is convenient to distinguish between:

1. the solid-state sintering and
2. the vitrification or sintering in the presence of a liquid phase.

Vitrification is the principal process responsible for development of strength of the fired brick. Vitrification may be defined as the progressive partial fusion of biofly body as a result of a firing process. The onset of vitrification, produced by the appearance of a liquid phase, may occur at remarkably low temperatures in ceramic bodies, because of their polyphase character. During the vitrification period, fluxes start to melt and the ware shrinks. The amount and viscosity of the liquid phase must be such that densification is produced in a reasonable time without excessive shrinkage, or deformation under the pressure of overlying bodies.

The vitrification range is the temperature interval between the beginning of vitrification of a ceramic body and the temperature at which the body begins to deform. The range can be either long or short, the latter giving rise to difficulties in production. There is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at the firing temperature to develop the desired properties. For biofly brick, this maximum temperature was found to be 1100°C however for clay/shale brick it was 1030°C.

The melt formed during the vitrification solidifies upon cooling, resulting in a glassy bond which gives the fired brick its strength, and as the amount of glass increases, the porosity of the brick decreases. Prokopovich (1993a) has indicated that firing shrinkage and porosity of the brick are two important parameters that may be used to control the firing process.

In practice, vitrification is greatly affected by the composition of raw materials, their purity, and grain size. Generally, sewage sludge and fly ash added to the clay alter the intrinsic properties such as:

1. Reduce shrinkage.
2. Reduce plasticity.
3. Reduce energy requirements during the firing process.
Firing characteristics of the clay bricks are altered by the addition of sludge and fly ash. Energy required to fire the brick is indeed reduced due to the increase of volatile organics contained within the sludge as well as the nature of the pre-fired material fly ash. Therefore biofly brick is fired in less than a half the time required for firing clay/shale brick.

5.3.5. Polymorphic transformation

Polymorphism may be defined as the property possessed by some substances existing in a number of different crystalline forms depending upon the temperature, pressure, and the presence of impurities. All forms being of the same chemical composition, but differing in crystalline structure and physical properties, and yielding identical liquid or gaseous phases on melting or evaporating (Prokopovich, 1993a).

Polymorphs change into one another and this process is known as a polymorphic transformation. The rate at which transformation occurs is a function of the type of structural change involved. All polymorphic transformations can be classified (Prokopovich, 1993a) into two general types depending on the type of structural change necessary:

(i) Displacive transformations or Inversions - fast

This transformation involves a slight change of bond angles and a slight adjustment of interatomic distance, without breaking bonds. The essential characteristics may be summarized as follows:

a) transformation occurs promptly when the inversion temperature is reached
b) transformation is completed in a few seconds
c) transformation is readily reversible
d) transformation does not proceed from nuclei, but occurs throughout the whole crystal at once, provided it is entirely at the appropriate temperature.
(ii) **Reconstructive transformations or Conversions - slow**

Here the change in structure cannot be arrived at simply by displacing atoms, but interatomic bonds must be broken and reconstructed. These transformations are characterised by the following:

a) transformation is often spread over a temperature range  
b) transformation is sluggish, and it is necessary to maintain the temperature near the transformation point for a considerable length of time  
c) transformation is not readily reversible  
d) transformation proceeds from nuclei in the solid state, usually inward from a free surface on the crystal  
e) a mineralizer catalyst may be necessary for the transformation to take place.

5.4. **Firing problems and faults**

In the case of biofly bricks, the type of polymorphic transformation which occur during firing have not been investigated in detail. Although the type of transformation affect the physico-chemical properties, such detail investigation is beyond the scope of this project.

(i) **Disruption and Spoiling:** Disruption of bricks is cause by rapid removal of water during water-smoking period, and spoiling of the surface of other pieces by impurity-laden condensation.

(ii) **Bloating:** Bloating occurs due to vitrification before various gas-evolving reactions are completed, caused by gases being trapped in the vitreous body. A typical example of such a reaction is the decomposition of calcium carbonate with evolution of carbon dioxide. Bloating is generally caused by a too rapid firing cycle.

(iii) **Black Cores:** Formation of black cores due to incomplete burning out of carbon and/or incomplete oxidation of iron. The black core is principally associated with the ferrous state of the iron present. The FeO present during firing acts as a flux, readily forming black ferrous silicate glasses in the centre of the brick.
(iv) **Cracking:** This may occur during the water-smoking period, and during periods of rapid volume changes. It is during rapid expansion or contraction of pieces that strains are set up that may cause cracking. Successful cooling of fired bricks entails consideration of any physico-chemical changes that may occur. For instance, the quartz inversion involves a considerable volume change-2% volume change-and cooling should be very slow at this point. It should also be noted that the cooling rate should be slow when passing through the glass transition point which occurs at about 760 °C, and below this temperature the glassy phase becomes a rigid, elastic solid. Too rapid cooling contraction may set up strains that cause cracking either immediately or in the first few days after removal from the kiln.

(v) **Scumming:** This is caused by the deposition of magnesium and calcium sulphates on the exposed surfaces of the brick during the drying operations. The scumming salts typically have high melting points, are soluble in water, and react with the clays to form white refractory silicates and aluminosilicates. During firing, calcium scum forms anorthite, and magnesium forms forsterite or enstatite. The literature introduced in the section has been adopted from course notes by (Prokopovich, 1993a).

### 5.5. Firing curve and visual inspection

A total of 17 firing curve trials were carried out to develop a suitable firing curve for the manufacture of biofly and clay/shale bricks in the laboratory. A trial and error approach was adopted. Variables studied include the rate of firing, total firing time, brick composition, position and arrangement within the kiln. The fired bricks were checked visually for efflorescence at the surface as well as for structural deficiencies such as cracks, fissures or missing pieces, surface texture and rectangularity.

A summary of the firing trials consisting of total firing time, brick composition and the number of bricks used as well as successful firings are summarised in Table 5.1. This table provides the 8 and 10 trials undertaken respectively for biofly and clay/shale bricks.

Process details including soak time, rate of firing at different levels and maximum firing temperature are summarised in Table 5.2
### Table 5.1. Summary of total firing time and brick composition

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Total firing time</th>
<th>Brick Type*</th>
<th>Number of Bricks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hours</td>
<td>minutes</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>00</td>
<td>20/40/40</td>
</tr>
<tr>
<td>2</td>
<td>38</td>
<td>00</td>
<td>25/30/45</td>
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<td>16</td>
<td>00</td>
<td>20/40/40</td>
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<tr>
<td>4</td>
<td>18</td>
<td>25</td>
<td>20/50/30</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>36</td>
<td>20/30/50; 25/30/45; 15/50/35; 20/50/30; 20/40/40</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>30</td>
<td>20/40/40; 25/30/45; 20/30/50; 15/50/35; 20/50/30</td>
</tr>
<tr>
<td>7</td>
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<td>20</td>
<td>30</td>
<td>%/100; L. C/S</td>
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<td>10</td>
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<td>%/100; L. C/S</td>
</tr>
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<td>11</td>
<td>24</td>
<td>00</td>
<td>%/100; L. C/S</td>
</tr>
<tr>
<td>12</td>
<td>50</td>
<td>00</td>
<td>%/100; L. C/S</td>
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<td>32</td>
<td>00</td>
<td>%/100; L. C/S</td>
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<td>20</td>
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<td>%/100; F. C/S</td>
</tr>
<tr>
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<td>48</td>
<td>00</td>
<td>%/100; F. C/S</td>
</tr>
<tr>
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<td>48</td>
<td>00</td>
<td>%/100; F. C/S</td>
</tr>
<tr>
<td>17</td>
<td>48</td>
<td>00</td>
<td>%/100; F. C/S</td>
</tr>
<tr>
<td>18</td>
<td>48</td>
<td>00</td>
<td>%/100; L. C/S</td>
</tr>
</tbody>
</table>

* The proportions refer to % sludge, % fly ash and % clay/shale respectively. The percentage refer to relative weights of materials as received condition which indicates moisture content

(1) - No. of good bricks

L. C/S - Laboratory clay/shale

F. C/S - Factory clay/shale
## Table 5.2. Process observation of laboratory bricks

<table>
<thead>
<tr>
<th>Remarks</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
<th>Trial 4</th>
<th>Trial 5</th>
<th>Trial 6</th>
<th>Trial 7</th>
<th>Trial 8</th>
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<td>Soak time, h. min.</td>
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<td>1.11; 1.11; 1.11; 1.67</td>
<td>1.11; 1.11; 1.11; 1.00</td>
<td>1.11; 1.11; 1.11; 1.07</td>
<td>1.11; 1.11; 1.11; 1.00</td>
<td>1.11; 1.11; 1.11; 1.00</td>
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<td>1100</td>
<td>1100</td>
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<table>
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<th>Trial 11</th>
<th>Trial 12</th>
<th>Trial 13</th>
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<td>Soak time, h. min.</td>
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<td>Max. Temp. °C</td>
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<table>
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<th>Trial 15</th>
<th>Trial 16</th>
<th>Trial 17</th>
<th>Trial 18</th>
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</thead>
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<tr>
<td>Soak time, h. min.</td>
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<td>0.15; 0.15; 0.15; 2.30</td>
<td>0.15; 0.15; 0.15; 2.30</td>
<td>0.15; 0.15; 2.30</td>
<td>0.15; 0.15; 2.30</td>
</tr>
<tr>
<td>Rate of firing at different levels °C/min</td>
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<td>0.13; 0.37; 0.83; 0.76</td>
<td>0.20; 0.23; 0.47; 0.76</td>
<td>0.83; 0.15; 0.27; 0.76</td>
<td>0.83; 0.15; 0.27; 0.76</td>
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Table 5.3. Firing curve observation of laboratory bricks

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<td>13</td>
<td>18</td>
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<td>3.15</td>
<td>6.15</td>
<td>6.24</td>
<td>9.24</td>
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<td>9.45</td>
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<td>18</td>
<td>20.30</td>
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<td>3.15</td>
<td>6.15</td>
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<td>9.30</td>
<td>9.45</td>
<td>12.45</td>
<td>13</td>
<td>18</td>
<td>20.30</td>
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<td>36</td>
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<td>11 L C/S</td>
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<td>7.24</td>
<td>8.48</td>
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<td>12</td>
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<table>
<thead>
<tr>
<th>Temp. ºC</th>
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<th>200</th>
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<th>400</th>
<th>600</th>
<th>600</th>
<th>800</th>
<th>800</th>
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<tbody>
<tr>
<td>Trial No.</td>
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<td></td>
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<tr>
<td>14 F C/S</td>
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<td>3.15</td>
<td>6.15</td>
<td>6.30</td>
<td>9.30</td>
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<td>18</td>
<td>20.30</td>
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<td>24.15</td>
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<td>37</td>
<td>37.15</td>
<td>40.15</td>
<td>40.30</td>
<td>45.30</td>
<td>48</td>
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<td>16.15</td>
<td>30.15</td>
<td>30.30</td>
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<td>37.15</td>
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<td>17 F C/S</td>
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<td>4.15</td>
<td>25.15</td>
<td>25.30</td>
<td>37</td>
<td>37.15</td>
<td>40.15</td>
<td>40.30</td>
<td>45.30</td>
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<tr>
<td>18 L C/S</td>
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<td>4.15</td>
<td>25.15</td>
<td>25.30</td>
<td>37</td>
<td>37.15</td>
<td>40.15</td>
<td>40.30</td>
<td>45.30</td>
<td>48</td>
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</tbody>
</table>
A summary observation during firing trials including different temperature levels and time used for every level are summarised in Table 5.3. Detail discussion regarding each trial is given in section 5.5.1.

The firing trials produced bricks with cracks, different colours and several other properties. The following abbreviations are used to describe the various conditions of bricks fired in the kiln for each trial.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>R</td>
<td>Red</td>
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<tr>
<td>B</td>
<td>Brown</td>
</tr>
<tr>
<td>Y</td>
<td>Yellow</td>
</tr>
<tr>
<td>O</td>
<td>Orange</td>
</tr>
<tr>
<td>BY</td>
<td>Brown yellow</td>
</tr>
<tr>
<td>DB</td>
<td>Dark brown</td>
</tr>
<tr>
<td>BF</td>
<td>Bloating and fissures</td>
</tr>
<tr>
<td>G</td>
<td>Good</td>
</tr>
<tr>
<td>BO</td>
<td>Brown orange</td>
</tr>
<tr>
<td>OY</td>
<td>Orange yellow</td>
</tr>
<tr>
<td>S</td>
<td>Shrinkage all faces</td>
</tr>
<tr>
<td>S1</td>
<td>Shrinkage one face</td>
</tr>
<tr>
<td>S2</td>
<td>Shrinkage two faces</td>
</tr>
<tr>
<td>S3</td>
<td>Shrinkage three faces</td>
</tr>
<tr>
<td>S4</td>
<td>Shrinkage four faces</td>
</tr>
</tbody>
</table>

5.5.1. “Biofly” Brick Trials

Trial 1

A preliminary firing curve was chosen as shown in Fig 5.8 which is based on the industrial firing curve and the firing curve developed for Biofly Stage I. The Biofly brick raw material consists of sludge, fly ash and clay/shale. The sewage sludge is in fact a potential energy source, and dry sewage sludge has a heat value of 10 MJ/kg (Sivakumar and Sidrak, 1992). Fly ash is a fused material having received considerable heat work in an electric utility boiler. When fly ash is formed into a brick or other structural shape, little additional heat work is required to form the ceramic bonds necessary to produce a superior quality brick. Firing cycles of 18 hours are common with fly ash brick (Slonaker, 1978).

Hence, utilisation of fly ash and sewage sludge for making biofly brick should significantly assist in reducing the total firing time. Modification from 60 hours for industrial firing curve to 20 hours for biofly brick curve were selected for the first trial. The soak time in hours at different temperature levels were chosen as {1, 1, 1, 1 h} at 200, 400, 600, 800 and 1100 °C respectively. The average rate of firing is 0.91°C/min.
with a total firing time of 20 hours. 24 bricks from Bellambi mix using one composition (20% sludge/40% fly ash/40% clay by weight and material was used "as is' condition) were fired. Only 5 fired bricks were found by visual inspection to be of good quality. Good bricks were located in the kiln in positions 4; 5; 11; 12 and 19 as shown in Table 5.4. It appears from Table 5.4, that there is no direct relationship between the flame impingement and location of good quality bricks in the kiln. All other bricks had significant cracks and excessive shrinkage on one face as shown in Fig. 5.9.

![Development of firing curve for Biofly Brick Trial 1](image)

**Figure 5.8. Development of firing curve for Biofly Brick Trial 1**

All bricks were dark brown in colour. One possible reason may due to the formation of different forms of iron oxides. The iron content as shown in Chapter 4 for these biofly brick samples was found to be 14% by weight. During the firing process, CO₂ is liberated from the sludge and this may cause a reducing atmosphere within the brick if fired rapidly. During rapid firing, the iron oxide (Fe₂O₃) is converted to wustite (FeO) or magnetite (Fe₃O₄), both of which are black in colour. Hence, it is felt that the cause of shrinkage, cracks and black colour may be due to the rapid rate of firing and in the next trial, the rate of firing was reduced by half at all levels.
Chapter 5: Development of Firing Curve

Table 5.4. Visual observation of biofly brick trial 1

<table>
<thead>
<tr>
<th></th>
<th>Upper level</th>
<th></th>
<th>Lower level</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>8 G. DB</td>
<td>12</td>
<td>16 S₂ DB</td>
</tr>
<tr>
<td>3</td>
<td>7 S₁ DB</td>
<td>11 G. DB</td>
<td>19 G. B</td>
</tr>
<tr>
<td>2</td>
<td>6 S₁ DB</td>
<td>10 S₂ B</td>
<td>18 S₂ DB</td>
</tr>
<tr>
<td>1</td>
<td>5 S₁ DB</td>
<td>9 S₂ DB</td>
<td>17 S₂ DB</td>
</tr>
</tbody>
</table>

Figure 5.9. Visual characteristic of biofly brick for trial 1

Trial 2

The firing curve selected for trial two is shown in Fig. 5.10. It was chosen based on the conclusion given in trial one that the shrinkage and cracks may be due to the rapid rate of firing at different levels (1.11, 1.11, 1.11, 1.11, 1.67)°C/min. The rate of firing is reduced by nearly half (0.56, 0.56, 0.56, 0.56, 0.56)°C/min. However, the soak time in hours at different temperature levels were exactly the same as curve one (1, 1, 1, 1, 1.67) hours.
h min) at 200, 400, 600, 800 and 1100 °C, respectively. The average rate of firing is 0.48°C/min with a total firing time of 38 hours.

24 bricks from Bellambi mix using one composition (25% sludge/30% fly ash/45% clay) were fired and only 2 fired bricks were found by visual inspection to be of good quality. The location of the good bricks are in position 19, 22 lower level as shown in Table 5.5. One possible reason may be that the lowest part of the kiln is the last to receive the benefit of heat from the burner, resulting in a lag behind the top in the early and middle part of the firing. All other bricks had significant bloating and fissures. The bricks were dark brown in colour with formation of black cores in the centre of the brick as shown in Fig 5.11.

![Figure 5.10. Development of firing curve for biofly brick Trial 2](image)

Hence, it is felt that the cause of bloating and fissures may be due to the long firing time of 38 hours. The heat work becomes very excessive, causing strain in the brick body and exceeding the range of firing time suitable for biofly brick material. In the next trial, the rate of firing was increased and soak time was decreased to prevent the bricks from over firing problems.
Table 5.5. Visual observation of biofly brick trial 2

<table>
<thead>
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<th>Upper level</th>
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<td>16 BF.DB</td>
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<tr>
<td>3 BF.DB</td>
<td>15 BF.DB</td>
</tr>
<tr>
<td>2 BF.DB</td>
<td>14 BF.DB</td>
</tr>
<tr>
<td>1 BF.DB</td>
<td>13 BF.DB</td>
</tr>
<tr>
<td>8 BF.DB</td>
<td>19 G.B</td>
</tr>
<tr>
<td>7 B. S1. DB</td>
<td>18 BF.DB</td>
</tr>
<tr>
<td>6 BF.DB</td>
<td>17 BF.DB</td>
</tr>
<tr>
<td>5 BF.DB</td>
<td>21 BF.DB</td>
</tr>
</tbody>
</table>

Figure 5.11. Visual characteristic of biofly brick for trial 2

Trial 3

The firing curve selected for trial three is shown in Fig. 5.12. It was chosen based on the conclusion given in trial two that the bloating and fissures may be the result of the long firing time of 38 hours. The rate of firing is increased by nearly half (1.11, 1.11, 1.11, 1.11, 1.67) °C/min. However, the soak time in hours at different temperature levels were considerably reduced (0.12, 0.12, 0.12, 0.12, 0.12 h.min) at 200, 400, 600, 800 and 1100 °C, respectively. The average rate of firing is 1.14 °C/min with a total firing time of 16 hours.
24 bricks from Bellambi mix using one composition (20% sludge/40% fly ash/40% clay) were fired and only 5 fired bricks were found by visual inspection to be of good quality. The composition of raw materials in the biofly mix was identical to trial 1. The good bricks were located in position 4, 5, 7, 8 and 12 upper level of the kiln as shown in Table 5.6. It appears from Table 5.6 that in this trial there is no direct relationship exist between the flame impingement and location of good quality bricks in the kiln. All other bricks had significant cracks and shrinkage on all four faces as shown in Fig 5.13.

Figure 5.12. Development of firing curve for biofly brick Trial 3

The good bricks were orange in colour. One possible explanation may due to the fact that in the highest oxidation state, hematite (Fe$_2$O$_3$) is produced, and its colour is temperature and heat work dependent. Hematite derives its colour from a defect crystal structure, and the number of defects per unit of volume increase with temperature and heat work. At this level of temperature and heat work, hematite (Fe$_2$O$_3$) exhibits an orange colour.

Hence, it is felt that the cause of the significant cracks and shrinkage may be due to the short firing time of 16 hours, and in the next trial the total firing time was increased.
Chapter 5: Development of Firing Curve

Table 5.6. Visual observation of biofly brick trial 3

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower level</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 S4.0</td>
<td>8 G. O</td>
</tr>
</tbody>
</table>

Figure 5.13. Visual characteristic of biofly brick for trial 3

Trial 4

The firing curve selected for trial four is shown in Fig. 5.14. It was chosen based on the conclusion given in trial three that, the cracks and shrinkage may be the result of the short firing time of 16 hours. The soak time in hours at different temperature levels were chosen as (0.15, 0.15, 0.15, 0.15, 0.25 h.min) at 200, 400, 600, 800 and 1100°C respectively. The average rate of firing is 1.0°C/min with a total firing time increased to 18.25 hours.
Chapter 5: Development of Firing Curve

24 bricks from Bellambi mix using one composition (20% sludge/ 50% fly ash/ 30% clay which is the highest percent waste replacement) were fired and all of them were found by visual inspection to be of good quality as illustrated in Fig 5.15.

The bricks were brown in colour. One possible reason may due to the formation of different forms of manganese compounds. The iron content as shown in Ch. 4 for these biofly brick samples was found to be high, and the mullite phase low due to using less clay (30% by weight). During the firing process, low mullite phase and high iron oxide content, the effect of manganese is likely to form more stable compounds composed of oxides which are brown in colour.

![Figure 5.14. Development of firing curve for biofly brick Trial 4](image)

**Figure 5.14. Development of firing curve for biofly brick Trial 4**

Hence, it is felt that the successful curve is a combination between suitable rate of firing at different temperature levels, suitable soak time and suitable total firing time. The fired biofly bricks from trial 4 were cut to examine the extent of vitrification within the body. As shown in Fig. 5.15, black cores is readily visible and this may be attributed to incomplete firing of carbon from the raw material. Hence in the next trial the soak time was increased at different temperature levels to eliminate black cores.
Table 5.7. Visual observation of biofly brick trial 4

<table>
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<tbody>
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</tr>
<tr>
<td>3 G.B 7</td>
<td>11 G.B</td>
</tr>
<tr>
<td>2 G.B 6</td>
<td>10 G.B</td>
</tr>
<tr>
<td>1 G.B 5</td>
<td>9 G.DB</td>
</tr>
</tbody>
</table>

Figure 5.15. Visual characteristic of biofly brick for trial 4

Trial 5

The firing curve selected for trial five is shown in Fig. 5.16. The total firing time was modified from 18.25 hours for the previous trial to 20.36 for firing trial No 5. The soak time in hours at different temperature levels were chosen as (0.24, 0.24, 0.24, 0.24, 2 h.min) at 200, 400, 600, 800 and 1100°C respectively. The average rate of firing was 0.90 °C/min. One of the reason for raising up the soak time at 1100°C from 0.25 to 2
hours during the vitrification stage is to increase the strength of the brick. Further discussion with reference to the brick strength is discussed in section 5.3.4.

24 biofly bricks from Bellambi mix using 5 different compositions previously shown in Table 5.1. were fired and all the bricks were found by visual inspection to be of good quality as illustrated in Table 5.8 and shown in Fig. 5.17. No black cores is visible outside or inside the brick and showing great improvement from Trial No.4.

The bricks were orange in colour. One possible reason may be due to the oxidation state, hematite (Fe2O3) is produced, and its colour is temperature and heat work dependent. At this level of heat work and temperature, the hematite compound exhibits an orange in colour.

This was considered a very successful trial, however it was decided to alter the soak time and evaluate the result in order to work towards the most optimum firing curve.

![Figure 5.16. Development of firing curve for biofly brick Trial 5](image)
Table 5.8. Visual observation of biofly brick trial 5

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Figure 5.17. Visual characteristic of biofly brick for trial 5

Trial 6

The firing curve selected for trial six is shown in Fig. 5.18. The soak time in hours at different temperature levels were chosen as \{0.15, 0.10, 0.40, 0.07, 2.18\ h.min\} at 200, 400, 600, 800 and 1100 °C respectively. It was chosen to determine if there was any
effect on the characteristic of the brick with changes in soak time. The average rate of firing was 0.90°C/min. The total firing time was 20.30 hours.

24 bricks from Bellambi mix using 5 different compositions were fired and all the bricks shown in Table 5.9 were found by visual inspection to be of good quality. It appears, that there is no direct relationship exist between the change in small amount of soak time and good quality bricks produced. One possible reason may be due to the fact that total firing time was kept approximately the same as in trial 5 as 20.30 hours.

The colour of the bricks as orange, as shown in Fig 5.19. The hematite (Fe₂O₃) effect exhibits an almost orange colour as explained in trial 5.

It is felt that this was another successful firing curve, however it was decided to alter the soak time to be uniform, keeping the same rate of firing at different temperature levels with total firing time of 20.30 hours, for the next two trials and evaluate the effect.

![Figure 5.18. Development of firing curve for biofly brick Trial 6](image)
Table 5.9. Visual observation of biofly brick trial 6

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Trial 7 and Trial 8

The firing curve selected for trial seven and eight is shown in Fig. 5.20. It was chosen with modification in the soak time at different temperature levels {0.15, 0.15, 0.15, 0.15, 2.30 h.min} at 200, 400, 600, 800 and 1100 °C respectively. The average rate of firing was 0.90 °C/min with total firing time of 20.30 hours.
Table 5.10 (a) and (b) summaries the findings of the visual quality of the 24 bricks from 4 different compositions in trial 7 and 3 different compositions in trial 8 respectively. All the bricks were found by visual inspection to be of good quality.

The colour of all the bricks are orange as clearly seen in Fig 5.21. There is no black core visible in the cut brick. It is felt that this is the common colour of the biofly bricks. One possible reason may due to the effect of adding the sludge and fly ash to the clay has made the biofly brick this colour.

The repeatability of the firing curve in trials seven and eight, for different composition suggests that this is one of the best firing curve for biofly brick making. The total firing time is 20.30 hours to make biofly brick in comparison to the order of 80 hours to make clay/shale factory brick. Hence, it is concluded that utilisation of fly ash, sewage sludge and a small amount of clay for making the biofly brick can significantly reduce the total firing time.

![Graph showing the development of firing curve for biofly brick Trial 7 and Trial 8](image)

**Figure 5.20 Development of firing curve for biofly brick Trial 7 and Trial 8**
Table 5.10.(a) Visual observation of biofly brick trial 7

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Figure 5.21. Visual characteristic of biofly brick for trial 7 and 8
Table 5.10.(b) Visual observation of biofly brick trial 8

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</table>

- The length of time spent in biofly brick firing, including any soak time, is of particular importance in achieving the correct heat work for maturation. Temperature alone is not enough. Heat work relates to time plus temperature, and to optimise the heat work, it is critical to optimise the heating rate.

- 24 bricks from 4 different compositions were fired in successful trial 7 and 3 different compositions in successful trial 8. All the bricks were found by visual inspection to be of good quality. Hence, it is felt that the amount of material replacement using different mix proportions does not alter the firing curve, showing the viability of the curve for different biofly brick mixes.

- The colour of all the successful bricks are orange. It is felt that this is the common colour of the biofly bricks. One possible reason may be due to the effect of adding the sludge and fly ash to the clay has made the biofly brick this colour.

- The total firing time is 20.30 hours to make biofly brick in comparison to the order of 80 hours to make clay/shale factory brick. Hence, it is concluded that utilisation of fly ash, sewage sludge and a small amount of clay for making the biofly brick can significantly reduce the total firing time.
5.5.2. Laboratory Clay/Shale Brick

Trial 9

In order to make a true comparison of various properties of biofly brick or clay/shale brick, it was felt that both bricks should be fired using the same firing curves. Hence trial 9 used the same firing curve as trial 7 and trial 8. Fig. 5.22 shows the firing curve for trial 9.

![Temperature vs Time for Clay/Shale Brick Trial 9](image)

Time hr

**Figure 5.22. Development of firing curve for clay/shale brick Trial 9**

24 bricks from Badgery’s Creek clay/shale were fired and only 5 fired bricks were found by visual inspection to be of good quality. The good bricks were located in positions 16, 17, 19, 21 and 22 as shown in Table 5.11. All other bricks had significant cracks and excessive shrinkage.

The colour of the bricks is red as shown in Fig. 5.23. This was due to the formation of iron oxide (Fe₂O₃). The cut bricks shows that the inner core has not been fired adequately due insufficient time of firing. Also, it is felt that the cause of the excessive shrinkage may be due to the rapid rate of firing and in the next trial, the soak time was increased significantly at all levels.
The firing curve selected for this trial used increased soak times as suggested by trial 9 and is shown in Fig. 5.24. The soak time in hours at different temperature levels were chosen as $\{3, 3, 3, 3, 7\}$ h at 200, 400, 600, 800 and 1100 °C respectively. The average rate of firing was 0.50 °C/min with a total firing time of 36 hours.

24 Laboratory clay bricks were fired and only 2 bricks were found by visual inspection to be of good quality. The good bricks were located in positions 13 and 23 as shown in Table 5.12. All other bricks had significant cracks and excessive shrinkage.
Chapter 5: Development of Firing Curve

The bricks were red in colour due to the formation of hematite (Fe₂O₃). Most of the bricks had shrinkage, cracks, bloating and black cores were visible in the cut bricks as shown in Fig. 5.25. Hence, it is felt that the cause of bloating and shrinkage may be due to the long soak time at different temperature levels and in the next trial, the soak time was reduced by about half at all levels.

![Graph showing temperature over time](image)

**Figure 5.24. **Development of firing curve for clay/shale brick Trial 10

**Table 5.12. Visual observation of clay/shale brick trial 10**

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</table>
Chapter 5: Development of Firing Curve

Figure 5.25. Visual characteristic of clay/shale brick for trial 10

Trial 11

The firing curve chosen for trial 11 is shown in Fig. 5.26. The soak time at different temperature levels were chosen as \{1.24, 1.24, 1.24, 1.24, 1.24\ h.min\} at 200, 400, 600, 800 and 1100 °C respectively. Soak temperatures were significantly altered to fall between trial 9 and trial 10 temperatures in order to understand the effect of soak time. The average rate of firing was 0.76 °C/min with a total firing time of 24 hours.

24 Laboratory clay bricks were fired and only 8 bricks were found by visual inspection to be of good quality. The good bricks were located in positions 13, 14, 16, 17, 19, 20, 21 and 22. This means, eight out of twelve bricks in the lower level were good. None were good from the upper level. Hence, it is clear that there is a direct relationship exist between the flame impingement and location of good quality bricks in the kiln. All the other bricks had significant cracks, bloating and excessive shrinkage.
The colour of the bricks is red as shown in Fig. 5.27. The poor quality bricks depicted bloating, fissures and shrinkage. Hence, it is felt that the cause of bloating may be due to vitrification before various gas-evolving reactions are completed, caused by gases being trapped in the vitreous body. Bloating is generally caused by too rapid firing cycle. In the next trial, the rate of firing was decreased by half at all levels.

Figure 5.26 Development of firing curve for clay/shale brick Trial 11

Table 5.13. Visual observation of clay/shale brick trial 11

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Chapter 5: Development of Firing Curve

Figure 5.27 Visual characteristic of clay/shale brick for trial 11

Trial 12

The firing curve selected for this trial is shown in Fig. 5.28. It was selected based on the recommendation given in trial 11 that the rate of firing be decreased by half at all levels as shown in Table 5.2. The soak time at different temperature levels were chosen as \{1.40, 1.40, 1.40, 1.40, 6.40 \text{ h.min}\} at 200, 400, 600, 800 and 1100 °C respectively. The average rate of firing significantly changed to be 0.36 °C/min with total firing time increased from 24 hours to 50 hours.

24 Laboratory clay bricks were fired and only 7 fired bricks were found by visual inspection to be of good quality. The positions of the good bricks were 2, 3, 4, 16, 17, 20 and 21. Unlike in trial 11, the good bricks were found randomly at both upper and lower levels of the kiln. Hence, there is no direct relationship exist between the flame impingement and location of good quality bricks in the kiln for this firing trial. All the other bricks had significant cracks and excessive shrinkage.
The colour of the bricks as red as shown in Fig. 5.29. Hence, it is felt that the cause of cracks and shrinkage may be due to the excessive heat work, and in the next trial the total firing time should be reduced but soak time was increased.

![Graph showing development of firing curve for clay/shale brick Trial 12](image)

**Figure 5.28. Development of firing curve for clay/shale brick Trial 12**

**Table 5.14. Visual observation of clay/shale brick trial 12**

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Chapter 5: Development of Firing Curve

Figure 5.29. Visual characteristic of clay/shale brick for trial 12

Trial 13

The firing curve selected for trial 13 is shown in Fig. 5.30. It was selected based on the conclusion from trial 12 that the total firing time is to be decreased but with increased soak time as shown in Table 5.1. Time was chosen to be between 36 hours (trial 10) and 50 hours (trial 12) so that the effect of the total firing time can be studied. The soak time at different temperature levels were chosen as \{3, 3, 3, 3, 3 h\} at 200, 400, 600, 800 and 1100 °C respectively. The average rate of firing was 0.57 °C/min with a total firing time of 32 hours.

24 Laboratory clay bricks were fired and only 4 bricks were found by visual inspection to be of good quality. Good bricks were located in positions 14, 20, 23 and 24 as shown in Table 5.15. All other bricks had significant cracks, bloating and excessive shrinkage.

The bricks were red in colour due to the formation of iron oxides and typical bricks are shown in Fig. 5.31. It is seen that due to rapid firing, the outside bricks were
vitrified leaving significant black cores inside. Hence, in the next trial, the rate of firing as well as the soak time need to be decreased.

However, it is felt that there is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at a suitable firing temperature to develop the desired properties. This maximum temperature was taken to be 1030°C for Sydney area Wianamatta Group of clays and shales, (Prokopovich, 1993b). Hence, in the next trial the maximum temperature of firing was decreased from 1100 to 1030°C.

![Figure 5.30 Development of firing curve for clay/shale brick Trial 13](image)

### Table 5.15. Visual observation of clay/shale brick trial 13

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Figure 5.31. Visual characteristic of clay/shale brick for trial 13

It is felt that there is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at a suitable firing temperature to develop the desired properties for a certain type of clay/shale. This maximum temperature was taken to be 1030°C for the Sydney area Wianamatta Group of clays and shales. Hence, in the next set of trials the maximum temperature of firing was taken as 1030°C.

5.5.3. Factory Clay/Shale Brick

The next four firing trials were conducted to obtain a suitable curve to fire the factory extruded brick in the laboratory kiln. The primary difference between the factory extruded bricks and laboratory bricks are that the former has 12 holes and they were extruded using a more powerful industrial extruder.
Trial 14

For the first trial, it was felt that a significantly lower firing time may be adequate due to the number of holes present. Hence a trial firing time of 20.30 hours was chosen together with a lower maximum temperature. The soak times at different temperature levels were chosen as {0.15, 0.15, 0.15, 0.15, 2.30 h.min} at 200, 400, 600, 800 and 1030 °C respectively. The average rate of firing was 0.84 °C/min.

24 Factory clay bricks were fired and only 4 bricks were found by visual inspection to be of good quality. Good bricks were located in positions 20, 21, 22 and 23 as shown in Table 5.16. All other bricks had significant cracks, bloating and excessive shrinkage.

The bricks were brown in colour and black cores were visible throughout the bricks as shown in Fig. 5.33. The black cores were associated with inadequate vitrification. This may be due to the rapid rate of firing and in the next trial, the rate of firing was reduced at all levels.

Figure 5.32 Development of firing curve for clay/shale brick Trial 14
Table 5.16. Visual observation of clay/shale brick trial 14

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<td>7 BF</td>
</tr>
<tr>
<td>2 BF</td>
<td>6 BF</td>
</tr>
<tr>
<td>1 BF</td>
<td>5 BF</td>
</tr>
</tbody>
</table>

Figure 5.33. Visual characteristic of clay/shale brick for trial 14

Trial 15

The firing curves selected for the next four successful trials 15, 16 and 17 (factory brick) are shown in Figs. 5.34, 5.35 and 5.36 respectively and for trial 18 (laboratory brick) in Fig. 5.36. It should be noticed that trial 17 and 18 has used the same firing curve despite the fact that trial 17 used the factory brick with holes, and trial 18 used the laboratory brick without the holes. The soak times at different temperature levels were chosen as \{0.15, 0.15, 0.15, 0.15, 2.30 \text{ h.min}\} at 200, 400, 600, 800 and 1030 °C
respectively for all the four trials. The soak time was exactly the same as the one used for the biofly brick optimum firing curve. However the total firing time was significantly different. The average rate of firing was 0.35 °C/min with a total firing time of 48 hours.

The trials 15, 16, 17 and 18 were conducted to assess whether the structural properties of the clay/shale be increased. Hence the vitrification portion of the firing was kept constant but the dehydration of the curve was significantly modified keeping the overall time for the above stages within 36 hours between 0-600°C. The firing curves for 15, 16 and 17/18 used the temperature levels of \{0.13, 0.37, 0.83, 1.11, 0.76\} \{0.20, 0.23, 0.47, 1.11, 0.76\} and \{0.83, 0.15, 0.27, 1.11, 0.76\} °C/min respectively.

24 Factory and laboratory clay bricks were fired and all the bricks were found by visual inspection to be of good quality. The colour of factory and laboratory bricks are brown as shown in Figs. 5.36 and 5.37, respectively. Hence, the successful time variability give strong evidence that the firing curve consists of two main groups, water evaporation which needs at least 36 hours and heat work also needs another 12 hours. During this trial temperature was raised to the maximum of 1030 °C as recommended for the Sydney area Wianamatta Group of clays and shales. Beyond this temperature, this group of clay/shale are unable to accept heat work.

![Figure 5.34 Development of firing curve for clay/shale brick Trial 15](image-url)
Table 5.17. Table 5.18 and Table 5.19 Visual observation of clay/shale brick trials 15, 16, 17 and 18

<table>
<thead>
<tr>
<th>Upper level</th>
<th>Lower level</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>G. B</td>
<td>G. B</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>G. B</td>
<td>G. B</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
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<td>G. B</td>
<td>G. B</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>G. B</td>
<td>G. B</td>
</tr>
</tbody>
</table>

Trial 16

![Temperature vs Time Graph](image)

Figure 5.35 Development of firing curve for clay/shale brick Trial 16
Chapter 5: Development of Firing Curve

**Trial 17 and 18**

![Graph of firing curve](image)

**Figure 5.36 Development of firing curve for clay/shale brick Trial 17 and 18**

![Visual characteristic of clay/shale brick](image)

**Figure 5.37. Visual characteristic of clay/shale brick for trial 15, 16 and 17**
• 24 Factory and laboratory clay bricks were fired and all the bricks were found by visual inspection to be of good quality. The common colour of factory and laboratory bricks are brown. Hence, it is felt that the laboratory clay bricks without holes does not alter the firing curve, showing the viability of using the same firing curve for different clay/shale brick types.

• The trials conducted with clay/shale bricks indicate that it is possible to obtain good quality bricks provided that the dehydration stage is completed within 36 hours and oxidation and vitrification time be kept 12 hours.

• It is clear that there is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at a suitable firing temperature to develop the desired properties. During these successful trials, the temperature was raised to the maximum of 1030 °C which is recommended for the Sydney area Wianamatta Group of clays and shales.
The total firing time is 20.30 hr to fire biofly brick in comparison to the order of 48 hours to fire clay/shale factory or laboratory brick. Hence, it is concluded that utilisation of fly ash, sewage sludge and a small amount of clay for making the biofly brick can significantly reduce the total firing time.

A considerable amount of time has taken to develop the eighteen firing curves for biofly and clay/shale bricks. It has taken nearly six months of equivalent full time work.

5.6. Colour development and control

Iron oxide is the most important and flexible colorant in all structural clay products. It is present in almost all clay raw materials in the range from 1% to 8%. In some cases extra iron oxide may be added to intensify its colouring effect. However, iron as Fe₂O₃ represented in biofly brick raw materials was high, ranging between 14 and 21 % due to the percentage of fly ash and sewage sludge. When reduced by carbon monoxide, the form of iron oxide can be either magnetite (Fe₃O₄) or wustite (FeO) both of which are black at all temperatures. In the highest oxidation state, hematite (Fe₂O₃) is produced, and its colour is temperature dependent. Hematite derives its colour from a defect crystal structure, and the number of defects per unit of volume increases with temperature. The development of defects is a reversible reaction, but the rate of removing defects is very much slower in air than the production of defects on heating, therefore, it is easy to cool a product locking in the defect structure obtained at the highest temperature. At very low temperatures, Fe₂O₃ is almost orange in colour, and as the temperature is increased darker reds are produced until the colour is almost black at 1316°C. This means that the development and control of colour is extremely dependent on the highest temperature the product reaches (Taylor, 1993).

When one thoroughly understands the behaviour of iron oxide in firing clay products, many kinds of manipulations can be employed to produce special effects. For example, a pink fireclay product can be made. Mullite phase of such products takes ferric iron into solid solution at high temperatures. By firing fireclay products under a slightly reducing atmosphere and maintaining the environment while cooling to 982°C, the iron oxide is prevented from going into solid solution with mullite. A highly oxidizing atmosphere is introduced at 982°C and the temperature held for a few hours in order to oxidize the iron oxide to the ferric state to produce a light red colour. Other manipulations of the valance state of iron oxide in biofly produce special effects (Taylor, 1993).
Body stains of various kinds are sometimes used for various colours and shades, and some of these are sensitive to atmospheric conditions. Manganese compounds are frequently added to produce gray fire clay products and black to brown illitic clay products. When the mullite phase in a product is low and the iron oxide content high, the effect of manganese is to produce brown colours (Taylor, 1993).

5.7. Kiln firing

A typical firing curve for structural clay products was shown in Fig. 5.3. The various rate periods have been plotted proportional to time, since the charging rate of a tunnel kiln determines the firing time. The actual times in the periods will vary from one material to another, but the curve presented here could be for a rather high-temperature, red-firing material or a low-temperature fireclay. The oxidation holds around 843°C for a period of about 6 hours, or in some cases it may require 12 to 24 hours in this period. However, this process took only 5 hours in biofly brick because of the volatile content of the sludge and the reduction in the amount of clay contained within the brick. The addition of sludge and fly ash accomplishes this by partially replacing the volume normally occupied by the clay. In the beginning, the temperature is brought up to the oxidation temperature at about 16.2 °C/hour for clay brick.

However, for biofly brick it was 66.6 °C/hour, which is four times the rate used for the clay brick. Not all materials require an oxidation delay, especially if plenty of excess air is used across the temperature range involved, consequently this part of the firing curve would be deleted and the final temperature can be achieved sooner.

After the oxidation has been completed, the temperature should be raised as rapidly as possible, without too much differential within the setting, to the maximum. A hold of at least 2 hours should be made at or close to the top temperature to allow for reaction rates to slow down which is the case of biofly brick. However, in the case of clay brick, the hold time was about 20 hours as shown in Figure 5.3. Ordinarily, not much phase development occurs after 2-hours except when high-lime bodies are being fired. Holding periods of between 8 to 48 hours are required for the desirable lime-silicate reactions to be completed. The exact time of hold for biofly brick would depend on the higher temperature reached, and soak times at different temperature levels. Natural cooling can be carried out slowly without causing damaging cracks.
5.8. Firing and cooling stresses

The ultimate strength and uniformity of strength values for structural clay products is dependent on the phases present and the cooling rate. The amount present at each phase contribute its own thermal expansion to the overall expansion of the product. It is the thermal expansion, or rather contraction, which on firing and cooling sets up stresses in the product and can lead to loss of strength through cracking. The faster firing and cooling rates promote greater temperature differentials within the products which, in turn, leads to greater stresses. The magnitude of the stress development at any particular temperature differential is determined by the thermal expansion.

The structural clay products are far from being homogeneous bodies. They may have from 4 to 8 individual phases of primary importance to final properties. Because the constitution of these clay products is complex, it may be that no two factories produce exactly the same product. It has been found that when two phases in a rather dense body have differences in the coefficients of linear thermal expansion of \(4\times10^{-7}\) cm/cm/°C or greater, the weaker phase will be fractured by cooling stresses. Since the particle sizes of the phases are small, the fractures are called microcracks. Two phases which were shown to be compatible had a difference in their coefficients of \(4\times10^{-7}\) cm/cm/°C (Hunter & Brownell, 1967). From this, one can begin to appreciate the importance of combining phases together which do not tear the microstructure apart.

Microcracking is the start of complete product failure. When microcracking occurs, the strength of the ware is lowered, and the strength values become erratic. Extensive microcracking occasionally leads to macrocracking when the whole piece is weakened by fortuitously located faults, and the situation is noticed by striking two articles together. A dunted product gives a dull thud instead of the ringing sound characteristic of good strength.

In order to predict phase compatibility as far as thermal expansion is concerned, the average coefficients of linear thermal expansions of various phases should be shown and they are presented in Table 5.20. From this data it is not difficult to see that the common mullite-quartz body is beset with microcracking difficulties if one tries to fire or cool it rapidly. On the other hand, a phase assemblage of pseudowollastonite, diopside, corundum, and hematite, which results from the use of dolomitic clays, could be fired or cooled much more rapidly without extensive damage.
Considering the realities of structural clay products with regard to phases, particle sizes, and porosities, the general shape of the firing and cooling curve can be determined to avoid catastrophic failure. The resistance to failure of the overall body can be expressed as

Table 5.20. Average coefficients of linear thermal expansion for phases commonly found in structural clay products

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Formula</th>
<th>Thermal expansion coefficient (cm/cm/°C) x 10^-7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum</td>
<td>a-Al_2O_3</td>
<td>88</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO_2</td>
<td>120</td>
</tr>
<tr>
<td>Mullite</td>
<td>Al_4O(Al_2Si_2O_12)</td>
<td>53</td>
</tr>
<tr>
<td>Pseudowollastonite</td>
<td>CaSiO_3</td>
<td>96</td>
</tr>
<tr>
<td>Anorthite</td>
<td>Ca(Al_2Si_2O_8)</td>
<td>43</td>
</tr>
<tr>
<td>Forsterite</td>
<td>Mg_2SiO_4</td>
<td>98</td>
</tr>
<tr>
<td>Clinoenstatite</td>
<td>MgSiO_3</td>
<td>82</td>
</tr>
<tr>
<td>Diopside</td>
<td>CaMg(Si_2O_6)</td>
<td>68</td>
</tr>
<tr>
<td>Cordierite</td>
<td>Mg_2Al_3(AlSi_5O_18)</td>
<td>11</td>
</tr>
<tr>
<td>Albite(feldspar)</td>
<td>Na(AlSi_3O_3)</td>
<td>90</td>
</tr>
<tr>
<td>Hematite</td>
<td>Fe_2O_3</td>
<td>94</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe_3O_4</td>
<td>87</td>
</tr>
<tr>
<td>Glass</td>
<td>Na_2O-CaO-SiO_2</td>
<td>90</td>
</tr>
<tr>
<td>Fused silica</td>
<td>SiO_2</td>
<td>5</td>
</tr>
</tbody>
</table>

\[ R = \frac{M_a}{E_e} \]  \hspace{1cm} (5.1)

where \( M_a \) is the modulus of rupture, \( a \) the thermal diffusivity, \( E_e \) the modulus of elasticity, and \( e \) the coefficient of linear thermal expansion. Using this relation the maximum rate of firing and cooling without complete thermal failure can be formulated as:

\[ \frac{dT}{dt} = - K \cdot \frac{M_a}{E_e} \]  \hspace{1cm} (5.2)

where \( T \) is temperature, \( t \) represents time, and \( K \) is a size-shape factor, constant for a given system. The integral form of Eq. (5.2) may be written as

\[ t_2 - t_1 = - \left( \frac{1}{K} \right) \int_{t_1}^{t_2} \left( \frac{E_e}{M_a} \right) dT \]  \hspace{1cm} (5.3)
Since the variables associated with $Ee / Ma$ are all functions of temperature, they should be determined experimentally, then the integral can be graphically evaluated by plotting $Ee / Ma$ as a function of temperature. From this type of solution, a safe relative firing and cooling schedule can be plotted. The actual times are then found for a particular product by trial-and-error.

Attention should be given to controlling the microcrack structure in order to prevent complete failure of the products. Hasselman (1971) has given much attention to crack propagation through ceramic bodies. He has found that weaker materials with relatively high densities of long microcracks can be subjected to considerably more severe temperature differentials before complete failure occurs than can stronger materials with short microcracks. This describes fairly well the state of affairs in structural clay products where long microcracks, a wide particle-size distribution, and pores all act to limit crack propagation.

5.9. Summary

• It has been shown that development of a suitable firing curve is a crucial step for any high temperature solidification process. Improvement in reducing firing schedules can also result in substantial cost savings in fuel.

• The firing schedule of a brick body may be divided into three parts, representing structural changes that occur with temperature, and which determine the body’s ability to absorb elastic strain energy:

1. During heating, the green body is a rather fragile, brittle compact.
2. Above 900 °C, a glass phase begins to develop and increase in volume while decreasing in viscosity to the final maturation temperature.
3. The third division is the final portion of the cooling curve below the glass transition temperature, where the body is a relatively strong, elastic, and brittle ceramic.

• The changes that take place in the brick during heating are of vital importance to a thorough understanding of the firing operation. The principal chemical and physical changes which occur during firing are:
Chapter 5: Development of Firing Curve

1. The removal of residual moisture in the ware.
2. Decomposition of the ware minerals with evolution of steam.
3. Oxidation and decomposition reactions.
4. Vitrification or sintering.
5. Polymorphic transformations.

The sequence of events that occur during the firing of the brick have been presented and discussed.

• The aim of the work was to develop two firing curves, one for biofly brick and the other one for clay/shale brick using a trial and error method. Based on the industrial firing curve the time at different stages were modified by considering, the sequence of events during firing, water smoking, dehydration, oxidation, and vitrification.

• The length of time spent in biofly or clay/shale brick firing, including any soak time, is of particular importance in achieving the correct heat work for maturation. Temperature alone is not enough. Heat work relates to time plus temperature, and to optimise the heat work will certainly need to optimise the heating rate.

• A total 18 firing trials were conducted using over 500 bricks over a period of six months. It took 8 such trials to establish a suitable firing curve for the biofly brick. However it took ten trials to develop the firing curve the clay/shale brick. During the firing of biofly bricks several composition of waste material have been used with a maximum replacement of 70%. It is concluded that the change of composition did not affect the optimum firing curve.

• The colour of all the successful biofly bricks were orange. It is felt that this is the common colour of the biofly bricks. One possible reason may due to the effect of adding the sludge and fly ash to the clay which has made the biofly brick this colour. However, the fired clay/shale bricks were found to be brown in colour. This colour was consistent for bricks with and without holes.

• The trials with clay/shale indicates that good quality bricks can be obtained by keeping the dehydration stage for 36 hours and vitrification for 12 hours.
• It is clear that there is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at a suitable firing temperature to develop the desired properties. During this successful trials temperature was raised to the maximum of 1030 °C as recommended for the Sydney area Wianamatta Group of clays and shales.

• The total firing time is 20.30 hr to fire biofly brick in comparison to the order of 48 hr to fire clay/shale factory or laboratory brick. Hence, it is concluded that utilisation of fly ash, sewage sludge and a small amount of clay for making the biofly brick can significantly reduce the total firing time.

• Finally it is concluded that the most suitable firing curve for biofly process is firing curve no 7 and 8. For clay/shale the most suitable curve has been found to be 17 for factory and 18 for laboratory.
Chapter Six

Structural and Related Properties of “Biofly” and Clay/Shale Brick

6.1. Introduction

The biofly and clay/shale bricks were tested for 12 properties in accordance with Australian and overseas standards. Detailed description of the experimental methods were presented in Chapter 4. The raw material for the biofly bricks came from different sources. The sewage sludge was collected from Shellharbour, Port Kembla, Bellambi and Wollongong sewage treatment plants, the fly ash from Eraring Power station and the clay/shale from Badgery’s Creek. The sewage sludge and fly ash varied between 50% to 70% of the raw feed for the biofly bricks.

Utilization of alternate sludge sources provided a variation in the percent solids content, percent volatile content, treatment and dewatering processes. In addition, the effect of using these sludges, on the physical properties of the biofly bricks was determined. Biofly bricks produced with dewatered sludge from the various sources typically contained between 15 and 25 percent sludge by weight.

6.2 Material proportions and coding system

A coding system was developed for specimen identification because of the large number of proportions investigated. The identification code contained two digits followed by one alphabetic symbol. The different proportions of materials used are presented in Table 6.1 and expressed as percentage of total weight “as is” and “dry” conditions.

For example, the symbol 70 S represents the proportion 20 SS/50 FA/30 C/S which is a mixture of 20 percent Shellharbour sludge (SS) and 50 percent Eraring fly ash (FA) with 30 percent Badgery’s Creek clay/shale (C/S). The percentage are by weight of the respective materials in “as received” conditions. In terms of dry weight, the proportion would be 5.1:62.2:32.7
Chapter 6: Structural and Related Properties of “Biofly” and clay/shale Brick

70 P represents the proportion 20 PS/50 FA/30 C/S which is a mixture of 20 percent Port Kembla sludge (PS) and 50 percent Eraring fly ash (FA) with 30 percent Badgery’s Creek clay/shale (C/S). The percentage are by weight of the respective materials in “as received” conditions. In terms of dry weight, the proportion would be 5.2:62.7:32.1

70 B represents the proportion 20 BS/50 FA/30 C/S which is a mixture of 20 percent Bellambi sludge (BS) and 50 percent Eraring fly ash (FA) with 30 percent Badgery’s Creek clay/shale (C/S). The percentage are by weight of the respective materials in “as received” conditions. In terms of dry weight, the proportion would be 5.6:61.9:32.5

70 W represents the proportion 20 WS/50 FA/30 C/S which is a mixture of 20 percent Wollongong sludge (WS) and 50 percent Eraring fly ash (FA) with 30 percent Badgery’s Creek clay/shale (C/S). The percentage are by weight of the respective materials in “as received” conditions. In terms of dry weight, the proportion would be 4.9:62.9:32.2

<table>
<thead>
<tr>
<th>Table 6.1 Proportion of materials and coding system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material Proportions % “as is”</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>20 SS/50 FA/30 C/S</td>
</tr>
<tr>
<td>15 SS/50 FA/35 C/S</td>
</tr>
<tr>
<td>20 SS/40 FA/40 C/S</td>
</tr>
<tr>
<td>25 SS/30 FA/45 C/S</td>
</tr>
<tr>
<td>20 SS/30 FA/50 C/S</td>
</tr>
<tr>
<td>20 PS/50 FA/30 C/S</td>
</tr>
<tr>
<td>15 PS/50 FA/35 C/S</td>
</tr>
<tr>
<td>20 PS/40 FA/40 C/S</td>
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<tr>
<td>25 PS/30 FA/45 C/S</td>
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<tr>
<td>20 PS/30 FA/50 C/S</td>
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<tr>
<td>20 BS/50 FA/30 C/S</td>
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<td>15 BS/50 FA/35 C/S</td>
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<td>20 BS/40 FA/40 C/S</td>
</tr>
<tr>
<td>25 BS/30 FA/45 C/S</td>
</tr>
<tr>
<td>20 BS/30 FA/50 C/S</td>
</tr>
<tr>
<td>20 WS/50 FA/30 C/S</td>
</tr>
<tr>
<td>15 WS/50 FA/35 C/S</td>
</tr>
<tr>
<td>20 WS/40 FA/40 C/S</td>
</tr>
<tr>
<td>25 WS/30 FA/45 C/S</td>
</tr>
<tr>
<td>20 WS/30 FA/50 C/S</td>
</tr>
<tr>
<td>Clay/Shale Laboratory Brick</td>
</tr>
<tr>
<td>Clay/Shale Factory Brick</td>
</tr>
</tbody>
</table>

In the following sections, the results of the structural and related properties of the bricks are described. A concise summary is given at the conclusion of the Chapter. The
detailed results of each of the experiment are given in Volume 2 Appendix 1 (Tables 1.1-1.206).

6.3 Water content

The water contents of the three materials used to make biofly bricks vary widely. These water contents were determined in accordance with Australian Standard 1289. As indicated in Chapter 4, the total solids content of the four types of sewage sludge ranged between (18-22%), moisture content ranged between (345-437%) and the water content ranged between (78-82 %). The clay/shale was of fine granular nature and the water content ranged between 14-18%. Dry fly ash was used which had water content less than 2-4%.

<table>
<thead>
<tr>
<th>Mix Identification Symbol</th>
<th>Specimen Water Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>28.5</td>
</tr>
<tr>
<td>65 S</td>
<td>29.7</td>
</tr>
<tr>
<td>60 S</td>
<td>26.6</td>
</tr>
<tr>
<td>55 S</td>
<td>33.5</td>
</tr>
<tr>
<td>50 S</td>
<td>31.3</td>
</tr>
<tr>
<td>Average S</td>
<td>29.9</td>
</tr>
<tr>
<td>70 P</td>
<td>26.5</td>
</tr>
<tr>
<td>65 P</td>
<td>26.7</td>
</tr>
<tr>
<td>60 P</td>
<td>26.1</td>
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<tr>
<td>55 P</td>
<td>24.8</td>
</tr>
<tr>
<td>50 P</td>
<td>31.3</td>
</tr>
<tr>
<td>Average P</td>
<td>27.0</td>
</tr>
<tr>
<td>70 B</td>
<td>24.5</td>
</tr>
<tr>
<td>65 B</td>
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<td>60 B</td>
<td>24.5</td>
</tr>
<tr>
<td>55 B</td>
<td>25.3</td>
</tr>
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<td>50 B</td>
<td>26.7</td>
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<tr>
<td>Average B</td>
<td>25.1</td>
</tr>
<tr>
<td>70 W</td>
<td>24.5</td>
</tr>
<tr>
<td>65 W</td>
<td>23.6</td>
</tr>
<tr>
<td>60 W</td>
<td>25.6</td>
</tr>
<tr>
<td>55 W</td>
<td>27.0</td>
</tr>
<tr>
<td>50 W</td>
<td>24.5</td>
</tr>
<tr>
<td>Average W</td>
<td>25.0</td>
</tr>
<tr>
<td>Total Average</td>
<td>26.7</td>
</tr>
<tr>
<td>LB</td>
<td>21.6</td>
</tr>
<tr>
<td>FB</td>
<td>16.5</td>
</tr>
</tbody>
</table>
Chapter 6: Structural and Related Properties of "Biofly" and clay/shale Brick

The optimum water contents for workability of the various mixtures ranged between 24-33%, primarily due to the nature of the raw materials used. The different proportions given in Table 6.2 have been used to determine the effects of various proportions of sludge and fly ash on the structural properties of the brick.

Figure 6.1 shows the various optimum water contents with percent of material replacement on the green bricks. For comparison, the water content of 100% clay/shale bricks are also shown in Figure 6.1. It is clear that the addition of sludge and fly ash alter the water content of the green bricks. The variation of optimum water content for each sludge type indicates that each sludge has different moisture retention capacity. The effect of percent material replacement on the water content is not clear but increasing trend of Bellambi and Shellharbour mixes is visible.

![Figure 6.1. Average Water Content of Green Bricks](image)

All of the biofly brick types exhibited water content higher than the two reference samples made from clay/shale. However it can be seen from this figure that the water content of the factory brick sample was lower than that of the laboratory brick sample. This may be related to the forming procedure. The laboratory brick was formed using a soft mud process, and the water content ranged between 16% to 23%, whereas, the
factory brick was formed using a stiff extrusion process, and water contents ranged between 13% to 18%. It is expected, based on the forming procedure in the factory that the biofly brick will have a lower optimum water content than that has been actually measured in these trials.

6.4. Dimensions and tolerances

Table 6.3. Results of Dimensions compared to the standard

<table>
<thead>
<tr>
<th>Mix</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>238.8</td>
<td>113.9</td>
<td>79.4</td>
</tr>
<tr>
<td>65 S</td>
<td>237</td>
<td>111.5</td>
<td>78</td>
</tr>
<tr>
<td>60 S</td>
<td>235.5</td>
<td>110</td>
<td>76.5</td>
</tr>
<tr>
<td>55 S</td>
<td>236.5</td>
<td>111.5</td>
<td>76.5</td>
</tr>
<tr>
<td>50 S</td>
<td>233</td>
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</tr>
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</tr>
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<td>111.5</td>
<td>78.5</td>
</tr>
<tr>
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<td>112.7</td>
<td>79.2</td>
</tr>
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<tr>
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<td>232</td>
<td>110.5</td>
<td>79</td>
</tr>
<tr>
<td>Average B</td>
<td>232</td>
<td>110.6</td>
<td>79</td>
</tr>
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</tr>
<tr>
<td>65 W</td>
<td>235</td>
<td>112.5</td>
<td>79</td>
</tr>
<tr>
<td>60 W</td>
<td>236.8</td>
<td>113</td>
<td>78.8</td>
</tr>
<tr>
<td>55 W</td>
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<td>110</td>
<td>80</td>
</tr>
<tr>
<td>50 W</td>
<td>232.5</td>
<td>110</td>
<td>76.5</td>
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<tr>
<td>Average W</td>
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<td>112.1</td>
<td>78.8</td>
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<td>111.6</td>
<td>78.6</td>
</tr>
<tr>
<td>C/S LB</td>
<td>234</td>
<td>109</td>
<td>76.5</td>
</tr>
<tr>
<td>C/S FB</td>
<td>227.5</td>
<td>108.5</td>
<td>76.5</td>
</tr>
<tr>
<td>Specification AS</td>
<td>225.5</td>
<td>107.5</td>
<td>73.5</td>
</tr>
<tr>
<td>1226-84</td>
<td>234.5</td>
<td>112.5</td>
<td>78.5</td>
</tr>
<tr>
<td>Average</td>
<td>230</td>
<td>110</td>
<td>76</td>
</tr>
<tr>
<td>Standard tolerance</td>
<td>±1.91%</td>
<td>± 2.22%</td>
<td>± 3.18%</td>
</tr>
<tr>
<td>Biofly brick laboratory specification</td>
<td>231.2</td>
<td>109.1</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>240.4</td>
<td>114.1</td>
<td>81.2</td>
</tr>
</tbody>
</table>
Twenty bricks from each batch were selected and tested in accordance with Australian Standard 1226.2. Any blisters or other small projections, together with any loose particles which might have adhered to the surfaces of the bricks, were removed and the bricks assembled in a straight line on a smooth concrete surface.

The dimensions of the fired brick depends on the size of the mould as well as the amount of shrinkage which occurs during drying and firing. The laboratory mould was fabricated to provide a finished brick of dimensions similar to a conventional clay/shale brick. In the laboratory, the bricks were cut by hand as such it is expected that the final dimensions of the bricks made in the laboratory may not be identical to a conventional brick. However, it is felt that the various dimensions of the biofly brick should fall within the dimensional tolerances specified by the Australian Standard.

The Australian Standard specifies a size-checking method which involves taking of the overall dimension (length, width and height) of 20 bricks placed in contact in a straight line and sets limits, based on standard tolerances (±1.91% in length, ± 2.22% in width and ± 3.18% in depth) as indicated in Table 6.3. Based on that tolerance and the total average dimensions of the biofly bricks shown in Table 6.3, the appropriate range of dimensions for the biofly bricks were calculated. This ranged between 231.2 to 240.4 mm for length, 109.1 to 114.1 mm for width, and 76 to 81.2 mm for depth.

It can be seen from Table 6.3 that only a few specimens exceed the specification range and this may be attributed to the following causes.

• The higher tolerances observed in length is most probably associated with the normal method of cutting using a hand saw. In a factory, this can be readily overcome using an automatic cutting device.
• Possible variations in expansion of the extruded materials after the extrusion process due to the different moisture and material contents of the sewage sludge, the fly ash and the clay/shale in the mix proportions.
• Variation in expansion and contraction of the brick during the firing and cooling process.

However most of the biofly brick samples satisfied the specific dimensional tolerances shown in Table 6.3 and the results are illustrated in Figures 6.2 to 6.4
Chapter 6: Structural and Related Properties of “Biofly” and clay/shale Brick

Figure 6.2. Overall Length of 20 Biofly Bricks

Figure 6.3. Overall Width of 20 Biofly Bricks
6.5. Transverse strength

Table 6.4 shows the characteristic transverse strength values for biofly and clay/shale bricks made in the laboratory. It is clear from Table 6.4 that all the biofly brick samples have characteristic transverse strength in excess of the standard value of 1 MPa and it exceeds the values for clay/shale bricks. However, it has been noted that characteristic transverse strength of factory clay/shale bricks are also below the standard and this can be attributed to the effects of perforations present.

The effect of percentage material replacement to clay on the characteristic transverse strength is illustrated in Fig 6.5. The values of transverse strength vary with the type of sludge present in the biofly bricks. There appear to be a general increase in transverse strength with the addition of waste materials between 50%-65% and most mixes show a drop in strength after 65%. It can be observed from Table 6.4 that Shellharbour mix produced the highest average transverse strength.
It can be concluded that the addition of waste materials as well as the type of sludge affects the characteristic transverse strength. The general trend is not clear, however the overall average values for biofly bricks are higher than the clay/shale bricks.

An estimate of standard deviation of characteristic transverse strengths was made to establish confidence in the measured values. However findings in Table 6.4 showed that average standard deviation of biofly bricks is generally high compared with the clay/shale bricks.

### Table 6.4. Results of characteristic transverse strength

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average Transverse Strength (MPa)</th>
<th>Average Characteristic Transverse Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>8.88</td>
<td>6.5</td>
<td>1.3</td>
</tr>
<tr>
<td>65 S</td>
<td>10.3</td>
<td>8.7</td>
<td>0.9</td>
</tr>
<tr>
<td>60 S</td>
<td>8.46</td>
<td>6.6</td>
<td>1.0</td>
</tr>
<tr>
<td>55 S</td>
<td>7.50</td>
<td>5.3</td>
<td>1.2</td>
</tr>
<tr>
<td>50 S</td>
<td>4.50</td>
<td>3.2</td>
<td>0.7</td>
</tr>
<tr>
<td>Average S</td>
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<td>6.06</td>
<td>1.02</td>
</tr>
<tr>
<td>70 P</td>
<td>7.16</td>
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<tr>
<td>55 P</td>
<td>8.29</td>
<td>5.3</td>
<td>1.7</td>
</tr>
<tr>
<td>50 P</td>
<td>6.50</td>
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<td>1.4</td>
</tr>
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<td>Average P</td>
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<td>4.8</td>
<td>1.76</td>
</tr>
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<td>1.9</td>
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<td>1.81</td>
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<td>LB</td>
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</tr>
</tbody>
</table>
Chapter 6: Structural and Related Properties of "Biofly" and clay/shale Brick

Figure 6.5 Overall Average Characteristic Transverse Strength of Biofly Bricks

This can be attributed to the variability in the different properties of raw materials. Shellharbour mix exhibited the least variation calculated, followed by Port Kembla mix, Wollongong mix and then Bellambi mix.

6.6. Compressive strength

Compressive strength of the conventional clay bricks will be affected by the addition of sludge and fly ash. The addition of sludge into the brick will reduce the quantity of material able to vitrify during firing. The voids and gas bubbles formed by oxidation of the sludge, will tend to produce a slightly less solid brick. Therefore, the strength of the brick is expected to vary inversely with the quantity of sludge added.

Fly ash is comprised of very fine particles, the majority of which are glassy spheres, scoria and some crystalline matter and carbon. The addition of fly ash into the brick will increase the quantity of material able to vitrify during firing. During this stage the clay and fly ash particles begin to flow, either partially or completely filling the voids and gas bubbles left by the oxidation of the sludge. Hence the addition of fly ash will tend to increase the strength of the brick.
Table 6.5 shows the characteristic compressive strength values for biofly and clay/shale bricks made in the laboratory. An overall average value of 24.95 MPa for biofly bricks indicates that it is higher than laboratory and factory clay/shale brick values by 10.22% and 6.61% respectively. It can be observed from Table 6.5 that Shellharbour and Wollongong mixes produced the highest average compressive strength, 24.47% and 25.08% respectively, more than laboratory clay/shale brick.

Table 6.5. Results of characteristic compressive strength

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average Compressive Strength (MPa)</th>
<th>Characteristic Compressive Strength (MPa)</th>
<th>Assessed Compressive Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
</tr>
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<tbody>
<tr>
<td>70 S</td>
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<td>29.5</td>
<td>31.9</td>
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</tr>
<tr>
<td>65 S</td>
<td>46.6</td>
<td>38.5</td>
<td>41.9</td>
<td>4.9</td>
</tr>
<tr>
<td>60 S</td>
<td>47.3</td>
<td>33.6</td>
<td>38.9</td>
<td>8.2</td>
</tr>
<tr>
<td>55 S</td>
<td>33.8</td>
<td>21.5</td>
<td>26.6</td>
<td>7.4</td>
</tr>
<tr>
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<td>39.2</td>
<td>25.2</td>
<td>30.6</td>
<td>8.5</td>
</tr>
<tr>
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<td>33.98</td>
<td>6.52</td>
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<td>22.9</td>
<td>4.1</td>
</tr>
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<td>16.2</td>
<td>19.7</td>
<td>5.7</td>
</tr>
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<td>18.1</td>
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</tr>
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<td>23.1</td>
<td>4.0</td>
</tr>
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<td>24.3</td>
<td>29.3</td>
<td>4.5</td>
</tr>
<tr>
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<td>17.8</td>
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<td>10.3</td>
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<tr>
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<td>25.1</td>
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<td>6.96</td>
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<td>FB</td>
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<td></td>
<td></td>
</tr>
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</table>

The characteristic compressive strength values of biofly bricks appear to vary with the type of sludge added. The effect of percentage material replacement on the characteristic compressive strength is illustrated in Fig 6.6. The Shellharbour and Wollongong mixes
generally show an increasing trend in characteristic compressive strength values. The Port Kembla and Bellambi mixes show a generally decreasing trend and this is primarily attributed to the type of sludge used.

It can be concluded that the addition of waste materials as well as the type of sludge effects the characteristic compressive strength. The general trend is not clear, except for Port Kembla sludge, for all other sludges an increasing trend is observed. However the absolute values of biofly bricks are higher than the recommended standard value of 7 MPa. In general, the differences in characteristic compressive strength show in the results is likely to be related to the method of extruding the bricks.

Standard Deviation was performed. An estimate of standard deviation was made on the characteristic compressive strength data to establish confidence in the measured values. Findings illustrated in Table 6.5 show that average standard deviation in most of the mixes is generally less compared with the clay/shale brick but similar to bricks made in the factory.

Port Kembla mix exhibited the least variation calculated, followed by Shellharbour mix, Bellambi mix and then Wollongong mix. There appears to be a general trend which shows that the higher the compressive strength the corresponding standard deviation is also high.

Table 6.6 provides a summary of the characteristic compressive strengths of Australian bricks made by extrusion published in the Masonry Code of Practice (1984). Attention to the number of tests conducted in each state are different, but there is clear evidence to illustrate a general trend. On average these results indicate that the Australian bricks made in the factory in general exhibit compressive strengths substantially larger than the Australian standard of 7 MPa. In particular, the Victorian and South Australian extruded bricks show higher values than the bricks from other states. This is primarily attributed to the type of shale used.

The characteristic compressive strengths of the Australian bricks shown in Table 6.6 are substantially higher than the biofly and clay/shale bricks shown in Table 6.5. This may be attributed to type of clay, firing characteristics and type of extrusion used in the laboratory and in a conventional manufacturing process. However comparison should be strictly made only from data from the same type of process.
### Table 6.6. Compressive strength of Australian clay bricks (MPa) (Masonry Code of Practice, 1984)

<table>
<thead>
<tr>
<th>Place &amp; method of manufacture</th>
<th>No. of sets tested</th>
<th>Average $\bar{C}$</th>
<th>Average $C_c$</th>
<th>Extremes of $C_c$</th>
</tr>
</thead>
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<tr>
<td>NSW Extruded</td>
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<td>46.5</td>
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<td>18.5-84.0</td>
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<tr>
<td>QLD Extruded</td>
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<td>35.5</td>
<td>14.5-56.0</td>
</tr>
<tr>
<td>SA Extruded</td>
<td>47</td>
<td>59.0</td>
<td>52.0</td>
<td>31.0-85.5</td>
</tr>
<tr>
<td>TAS. Extruded</td>
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<td>48.5</td>
<td>42.5</td>
<td>14.0-85.0</td>
</tr>
<tr>
<td>VIC. Extruded</td>
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<td>71.0</td>
<td>63.0</td>
<td>20.5-102.5</td>
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<td>24</td>
<td>38.5</td>
<td>34.5</td>
<td>22.5-75.5</td>
</tr>
<tr>
<td>Total Average</td>
<td>36</td>
<td>42.6</td>
<td>44.6</td>
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</tr>
</tbody>
</table>

$\bar{C}$: Average compressive strength  
$C_c$: Characteristic compressive strength

---

**Figure 6.6. Overall Average Characteristic Compressive Strength of Biofly Bricks**
6.7. Characteristic expansion

Masonry units change in dimensions due to variations in temperature, wetting and drying, and long-term chemical changes associated with moisture (Schellbach and Schmidt, 1980).

• Thermal Change: The thermal expansion of masonry units varies slightly depending upon their colour and the method of manufacture, but the actual value is likely to be in the range of 0.008 to 0.01 mm/m/°C.

• Wetting and Drying Change: All masonry units expand on wetting and contract on drying, but in no case is the change sufficient to require consideration in practical masonry.

• Long-Term Permanent Change: The long-term permanent change in dimensions of masonry units depends upon the material from which they are made. For clay masonry a long-term expansion occurs between low and high category. Long term expansion for biofly bricks likely to be between the medium and high category.

In discussing the phenomenon of the moisture related expansion of fired clay bricks, it seems necessary first to emphasise the great variation in the magnitudes of expansions that occur in bricks made in different parts of the world and the rates at which those expansions take place. In some parts of the world, the magnitudes of brick growth is of only negligible importance, but such is not the case in Australia. Although the situation is now much better than it was fifteen years ago, a common reaction among local architects, builders and structural engineers is still one of resentment and anger at the phenomenon that has caused them great trouble.

For bricks made in Germany, the magnitude of ultimate expansion is shown to vary from 0.05 mm/m up to a maximum of 0.62 mm/m. By comparison, the Australian bricks have ultimate expansions varying from 0.6 mm/m to at least 2.2 mm/m. Although it is now known that less than 0.6 mm/m is close to the minimum Australian average, it has to be acknowledged that there is a substantial difference in the magnitudes of growth that must be accommodated in these two countries. However, more important is the rate at which the expansion takes place. For the majority of German bricks, Schellbach and Schmidt (1980) show that growth close to the ultimate is usually achieved in five to ten
days from the kiln fresh state, although there are some cases where up to 90 days must elapse before this occurs. By contrast, it takes at least 5 years before most Australian bricks approach their ultimate growth.

All Australian expansion measurements are taken on the length of the brick specimens. Those of Schellbach and Schmidt (1980) were taken on the height of their extruded specimens because they believed that growth in the height of a brick should be greater than in its length as a result of the method of manufacture. On the site where construction is taking place or in the drawing office where construction is being planned, differences between the magnitudes and rates at which expansion takes place would cause operatives in the two countries to doubt if they were dealing with the same phenomenon. Schellbach and Schmidt (1980) correctly described moisture related brick expansion as being of little or no importance in most of the types of bricks used in Germany. Such is not the case in Australia even though the situation has improved considerably from that represented by the growth patterns of the 15 year old bricks quoted by Goldfinch (1985).

It seems reasonable to assume that the German and Australian moisture related expansion values represent something close to the extremes of world patterns of this property. Some evidence favouring this conclusion is given by Hosking, White and Parham (1966) who examined the moisture related expansion of bricks and laboratory specimens in Illinois, USA. The expansion magnitudes they reported were slightly higher than those given for Germany, but the rate of growth is much closer to the slower change found to apply to Australian bricks.

Cole (1983), has identified that Australian brick making clays are high in K₂O + Na₂O and low in CaO + MgO, and consequently have high expansions. British and American brick clays are in the reverse. Differences of this sort between the mineralogical and chemical compositions of different clays are shown by Cole to account for differences in expansion magnitudes. A number of Australian manufacturers have used this information and added lime or crushed basalt to their clay mixes as part of the procedures employed to bring about substantial reductions in the total growth of their products. Still to be explained is the high early growth rates of some bricks and the lower early growth rates of others, particularly those made in Australia. If all bricks could be induced to substantially complete their expansion in five to ten days, problems associated with moist expansion could simply be eliminated by ensuring that all bricks are at least ten days out of the kiln before shipment.
In Britain, there are some clays that follow the very fast early growth of German bricks and some that follow the much slower early growth of Australian and some USA bricks. Thomas (1971), for example, examined two UK brick types, both made by extrusion. The first type was made from a blue boulder clay fired at 980°C and the second from carboniferous shale fired at 1050°C. The clay brick grew a total of 0.72 mm/m in 517 days, but managed 32% of that total in the first two days. By contrast, the shale brick grew 0.27 mm/m in the same period but only 3.5% occurred in the first two days. These results serve to show that variations within brick type can be considerable and possibly account for different past perceptions of the need to take the phenomenon seriously.

A view seems to be developing that bricks should be separated into groups with low, medium and high characteristic expansions or expansion indices. Foster and Johnson (1982) have made a suggestion for grouping UK bricks, and a similar Australian proposal has been developed by the Association of Consulting Structural Engineers of New South Wales and published in the Masonry Code of Practice (1984). It also appears in the Australian Building Specification (1982) where it is accompanied by a requirement that a certificate be obtained prior to the delivery of bricks to a building site stating the characteristic expansion of the bricks. The certificate must not be more than six months old and must have been produced by a laboratory registered with the National Association of Testing Authorities to carry out the standard accelerated test.

Both the UK and the Australian proposals set out as part of the information are given below.

<table>
<thead>
<tr>
<th>Category</th>
<th>(UK and Aust)</th>
<th>(UK)</th>
<th>(Aust)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>less than 0.6</td>
<td>0.6 - 1.0</td>
<td>0.6 - 1.2</td>
</tr>
<tr>
<td>Medium</td>
<td></td>
<td>0.6 - 1.2</td>
<td>0.6 - 1.2</td>
</tr>
<tr>
<td>High</td>
<td></td>
<td>1.0 - 1.8</td>
<td>1.2 - 2.4</td>
</tr>
</tbody>
</table>

As might be expected, the Australian categorisation covers bricks with higher expansion values than those proposed by Foster and Johnson (1982). Since many Australian brick manufacturers have successfully reduced the expansion of their products, it seems possible that the UK values and categories may come to be suitable for Australian bricks. On the other hand, the measurement of expansion values of bricks made in many parts of the world other than Australia has not been particularly extensive or systematic and a complete survey of the property may disclose that, in many places, there are some
products that can have characteristic expansions as high as 2.4 mm/m. Table 6.7 gives information about the characteristic expansion of the Australian bricks published in the Masonry Code of Practice (1984).

Table 6.7 provides a summary of the characteristic expansion of Australian bricks made by extrusion methods. Considering that the number of tests conducted in each state are different, there is no clear evidence to illustrate any general trend. On the averages these results indicate that the Australian bricks made in the factory in general exhibit a characteristic expansion in the medium category. In particular, the Tasmanian extruded bricks are in the high category and the bricks from other states are within the low to medium category of characteristic expansion.

Table 6.8 and Fig. 6.7 show the average characteristic expansion of biofly and clay/shale bricks. The overall average characteristic expansion of each type of the biofly mixes range between 0.62 to 1.74 mm/m which falls into the medium to high category. The biofly bricks made from Bellambi sludge exhibited expansion values in the medium category primarily due to the high silica, alumina and iron content. The Shellharbour, Wollongong and Port Kembla mixes show expansions in the high category.

The results obtained in this study is shown in Fig. 6.7. The average characteristic expansion for each mix varies widely. This may be associated with the type and nature of brick making in the laboratory using a custom built extruder. However, it is clear from Fig. 6.7 that the biofly bricks in general have lower characteristic expansions compared with clay/shale bricks fired in the laboratory. The absolute values for the clay/shale bricks fired in the laboratory are higher than the thermal expansion values observed in the factory bricks as shown in Table 6.7. This may be attributed to the different firing characteristics and type of extrusion used in the laboratory. Hence, it is concluded that in general the addition of fly ash and sewage sludge tend to decrease the characteristic expansion.
### Table 6.7 Characteristic expansion of Australian bricks (mm/m) (Masonry Code of Practice, 1984)

<table>
<thead>
<tr>
<th>Place &amp; Method of manufacture</th>
<th>No. of sets tested</th>
<th>Average</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSW Extruded</td>
<td>18</td>
<td>0.74</td>
<td>0.15-1.63</td>
</tr>
<tr>
<td>QLD Extruded</td>
<td>16</td>
<td>0.40</td>
<td>0.07-0.64</td>
</tr>
<tr>
<td>SA Extruded</td>
<td>28</td>
<td>0.92</td>
<td>0.24-2.03</td>
</tr>
<tr>
<td>TAS. Extruded</td>
<td>9</td>
<td>1.11</td>
<td>0.24-2.41</td>
</tr>
<tr>
<td>VIC. Extruded</td>
<td>52</td>
<td>0.60</td>
<td>0.16-1.02</td>
</tr>
<tr>
<td>WA Extruded</td>
<td>24</td>
<td>0.54</td>
<td>0.18-1.05</td>
</tr>
<tr>
<td><strong>Total Average</strong></td>
<td><strong>24.5</strong></td>
<td><strong>0.71</strong></td>
<td></td>
</tr>
</tbody>
</table>

### Table 6.8 Characteristic expansion of biofly bricks (mm/m)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average Characteristic Expansion (mm/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>1.67</td>
</tr>
<tr>
<td>65 S</td>
<td>1.83</td>
</tr>
<tr>
<td>60 S</td>
<td>0.26</td>
</tr>
<tr>
<td>55 S</td>
<td>1.79</td>
</tr>
<tr>
<td>50 S</td>
<td>1.86</td>
</tr>
<tr>
<td><strong>Average S</strong></td>
<td><strong>1.48</strong></td>
</tr>
<tr>
<td>70 P</td>
<td>1.84</td>
</tr>
<tr>
<td>65 P</td>
<td>1.42</td>
</tr>
<tr>
<td>60 P</td>
<td>1.86</td>
</tr>
<tr>
<td>55 P</td>
<td>1.79</td>
</tr>
<tr>
<td>50 P</td>
<td>1.82</td>
</tr>
<tr>
<td><strong>Average P</strong></td>
<td><strong>1.74</strong></td>
</tr>
<tr>
<td>70 B</td>
<td>1.07</td>
</tr>
<tr>
<td>65 B</td>
<td>0.75</td>
</tr>
<tr>
<td>60 B</td>
<td>0.15</td>
</tr>
<tr>
<td>55 B</td>
<td>0.46</td>
</tr>
<tr>
<td>50 B</td>
<td>0.71</td>
</tr>
<tr>
<td><strong>Average B</strong></td>
<td><strong>0.62</strong></td>
</tr>
<tr>
<td>70 W</td>
<td>0.58</td>
</tr>
<tr>
<td>65 W</td>
<td>1.57</td>
</tr>
<tr>
<td>60 W</td>
<td>1.48</td>
</tr>
<tr>
<td>55 W</td>
<td>1.16</td>
</tr>
<tr>
<td>50 W</td>
<td>1.77</td>
</tr>
<tr>
<td><strong>Average W</strong></td>
<td><strong>1.31</strong></td>
</tr>
<tr>
<td><strong>Total average</strong></td>
<td><strong>1.28</strong></td>
</tr>
<tr>
<td>LB</td>
<td>1.70</td>
</tr>
<tr>
<td>FB</td>
<td>1.86</td>
</tr>
</tbody>
</table>
Chapter 6: Structural and Related Properties of “Biofly” and clay/shale Brick

6.8. Efflorescence and pitting due to lime particles

Efflorescence

Extensive Australian testing published by the Brick Development Research Institute (1983) has shown that efflorescence resulting from the presence of salt in the bricks is very uncommon. It does not appear that efflorescence from this cause is even more than a slight problem in this country.

More often efflorescence originates from salts in the mortar materials or in adjacent soil. The generally low level of efflorescent salts in Australian bricks suggest that the provisions in AS 1225 covering permissible salt content will seldom be invoked.

Some of the lighter-coloured clay bricks occasionally contain soluble salts of vanadium that can cause staining as they come to the surface. By contrast with efflorescing salts, vanadium stains do not cause damage. They will often be washed away by rain or can be removed by fairly simple methods. Soluble salts can cause fretting of
brick surfaces especially those in contact with ground water and below the damp course in building structures.

The way in which soluble salts disrupt porous materials is basically simple. As the material dries, the concentration of salts in solution gradually increases until crystallization begins, when the volume of water remaining can no longer dissolve all the salts present. During crystallization, considerable pressure is applied to the walls of the pores. When this process takes place near the surface of the material, the pressure applied on the pore walls may exceed the tensile strength of the material and fretting will take place which is called "salt attack".

The efflorescence observed in each batch of biofly bricks is summarised in Table 6.9. The efflorescence was described in terms of liability of efflorescence, represented by the worst specimen inspected in each batch. Table 6.9 shows that where the effect of efflorescence was designated as "slight" it occurred only on the corners of the surface of three types of samples containing 65%, 60% and 50% replacement of material with Bellambi mix and no efflorescence was detected for any other mix. Salt deposits were very light, and in most cases, could only be detected as a very slight staining or colour change on the surface of the brick. Salt deposits on the bricks assessed as slight, consisted of an extremely thin deposit. The salts could not be removed from the surface due to the thinness of the layer.

Most of the samples were indicated as "Nil" efflorescence, thus most of the samples were able to meet the specification. During the assessment of efflorescence, the following criteria from AS 1226.6 were used:

- **Nil**: no observable efflorescence
- **Slight**: not more than 10% of any surface of the specimen covered by a thin deposit of salt
- **Moderate**: more than 10% of one surface but not more than 50% of the total specimen surface covered by a thin deposit of salt
- **Heavy**: a deposit of salts covering more than 50% of the total brick surface
- **Serious**: any efflorescence that is accompanied by powdering and/or flaking of the surface of the specimen
Pitting due to lime particles

If the clay used for brickmaking contains particles of limestone, these will be converted to quicklime when the bricks are fired. Subsequent exposure of the bricks to moisture, either as vapour in the air or as liquid water, will slake the quicklime and cause it to expand. If the lime particles are large, their expansion can cause flakes or chips to be forced off the surfaces of the bricks. Pitting due to lime is a rare occurrence. The biofly bricks had clay/shale contents ranging between 30 to 50%, which means less limestone particles compared to 100% clay/shale bricks. The results for pitting were indicated “Nil” for all mixes as given in Table 6.9. This means that there is no pitting observed due to lime particles in both biofly bricks and clay/shale bricks. The following specification was used.

<table>
<thead>
<tr>
<th>Nil</th>
<th>No pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>Not more than five small pits, none exceeding 3 mm in diameter</td>
</tr>
<tr>
<td>Appreciable</td>
<td>More than five small lime pits, none exceeding 3 mm in diameter, or one or more pits exceeding 3 mm in diameter</td>
</tr>
</tbody>
</table>

Table 6.9. Liability to efflorescence and pitting due to lime particles

<table>
<thead>
<tr>
<th>Mix</th>
<th>Liability to efflorescence</th>
<th>% of surface area</th>
<th>Amount of pitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>65 S</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>60 S</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>55 S</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>50 S</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>70 P</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>65 P</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>60 P</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>55 P</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>50 P</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>70 B</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>65 B</td>
<td>Slight</td>
<td>2% of three surfaces</td>
<td>Nil</td>
</tr>
<tr>
<td>60 B</td>
<td>Slight</td>
<td>2% of one surface</td>
<td>Nil</td>
</tr>
<tr>
<td>55 B</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>50 B</td>
<td>Slight</td>
<td>2% of two surfaces</td>
<td>Nil</td>
</tr>
<tr>
<td>70 W</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>65 W</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>60 W</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>55 W</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>50 W</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>LB</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
<tr>
<td>FB</td>
<td>Nil</td>
<td></td>
<td>Nil</td>
</tr>
</tbody>
</table>
6.9. Initial rate of absorption (suction)

The Brick Development Research Institute (1980) describes the bond between brick and mortar as largely influenced by the “tug-of-war” between the brick’s capacity to absorb water and the mortar’s ability to retain it for proper hydration of cement at the interface.

If the brick wins this tug-of-war, the brick has too high a suction for the mortar, the mortar strung out for the bed joint stiffens so rapidly that the bricks in the next course cannot be properly bedded. If the mortar has too high a water retention for the brick, the bricks tend to float on the mortar bed, making it difficult to lay up plumb walls at a reasonable rate. In both cases bonding is not properly established.

The power of the brick in this tug-of-war is measured in terms of the Initial Rate of Absorption (IRA or suction). If the brick manufacturer was able to vary the IRA values of his bricks by simple changes to his manufacturing process, there would be considerable attraction in working towards a situation in which all bricks would have optimum IRA properties. This is not possible and IRA values are therefore used in determining which of several available techniques should be used to ensure reasonable compatibility between the bricks chosen for a particular project and the mortar with which they are laid.

The provision of a complete set of answers to the problem of ensuring brick and mortar compatibility is still the subject of research, but some guidelines can be given. The Masonry Code of Practice (1984) recommends optimum values in the range 0.5-1.5 kg/m²/min. Compared with these values low suction bricks (IRA <0.5 kg/m²/min) can be used without a harsher mortar which is obtained by increasing the proportion of washed sand in the mix to give a good bond. With high suction bricks (IRA >1.5 kg/m²/min), the appropriate techniques include ensuring very high retentivity in the mortar, shortening the length of the bed joint strung out by the bricklayer and wetting the bricks to reduce their suction.

Table 6.10 gives information about the IRA properties of Australian bricks published in Masonry Code of Practice (1984). This information can be readily used to determine whether or not bricks should be wetted before laying. It is clear from the Table 6.10 that few bricks require it, and they are likely to be WA extruded bricks, however the rest of the bricks retained between the optimum values of 0.5 and 1.5 kg/m²/min. It is also quite
clear from Table 6.10 that those building specifications in Masonry Code of Practice (1984) still containing the 18th or 19th century requirement that all bricks be wetted before laying are long overdue for revision.

Table 6.10. Initial rate of absorption (IRA) of Australian bricks (kg/m²/min)
(Masonry Code of Practice, 1984)

<table>
<thead>
<tr>
<th>Place &amp; Method of manufacture</th>
<th>No. of sets tested</th>
<th>Average</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSW Extruded</td>
<td>23</td>
<td>1.08</td>
<td>0.34-2.05</td>
</tr>
<tr>
<td>QLD Extruded</td>
<td>24</td>
<td>1.23</td>
<td>0.05-2.36</td>
</tr>
<tr>
<td>SA Extruded</td>
<td>47</td>
<td>0.90</td>
<td>0.14-1.58</td>
</tr>
<tr>
<td>TAS. Extruded</td>
<td>35</td>
<td>1.69</td>
<td>0.31-6.56</td>
</tr>
<tr>
<td>VIC. Extruded</td>
<td>56</td>
<td>0.47</td>
<td>0.12-2.17</td>
</tr>
<tr>
<td>WA Extruded</td>
<td>24</td>
<td>2.12</td>
<td>0.95-3.78</td>
</tr>
<tr>
<td>Average</td>
<td>38.8</td>
<td>1.24</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.11 Initial rate of absorption of biofly bricks (kg/m²/min)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average Initial rate of absorption (kg/m²/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>0.70</td>
</tr>
<tr>
<td>65 S</td>
<td>0.52</td>
</tr>
<tr>
<td>60 S</td>
<td>0.60</td>
</tr>
<tr>
<td>55 S</td>
<td>0.75</td>
</tr>
<tr>
<td>50 S</td>
<td>0.74</td>
</tr>
<tr>
<td>Average S</td>
<td>0.66</td>
</tr>
<tr>
<td>70 P</td>
<td>0.90</td>
</tr>
<tr>
<td>65 P</td>
<td>0.81</td>
</tr>
<tr>
<td>60 P</td>
<td>0.84</td>
</tr>
<tr>
<td>55 P</td>
<td>0.75</td>
</tr>
<tr>
<td>50 P</td>
<td>0.76</td>
</tr>
<tr>
<td>Average P</td>
<td>0.81</td>
</tr>
<tr>
<td>70 B</td>
<td>0.50</td>
</tr>
<tr>
<td>65 B</td>
<td>0.64</td>
</tr>
<tr>
<td>60 B</td>
<td>0.31</td>
</tr>
<tr>
<td>55 B</td>
<td>0.17</td>
</tr>
<tr>
<td>50 B</td>
<td>0.26</td>
</tr>
<tr>
<td>Average B</td>
<td>0.37</td>
</tr>
<tr>
<td>70 W</td>
<td>0.67</td>
</tr>
<tr>
<td>65 W</td>
<td>0.62</td>
</tr>
<tr>
<td>60 W</td>
<td>0.70</td>
</tr>
<tr>
<td>55 W</td>
<td>0.74</td>
</tr>
<tr>
<td>50 W</td>
<td>0.87</td>
</tr>
<tr>
<td>Average W</td>
<td>0.72</td>
</tr>
<tr>
<td>Total average</td>
<td>0.64</td>
</tr>
<tr>
<td>LB</td>
<td>0.50</td>
</tr>
<tr>
<td>FB</td>
<td>0.44</td>
</tr>
</tbody>
</table>
Table 6.11 shows the IRA values for biofly and clay/shale bricks made in the laboratory. An overall average value of IRA 0.64 kg/m²/min for biofly bricks indicated that it is within the recommended optimum values. The IRA values of biofly bricks and clay/shale bricks are very similar. In general the average values obtained in the laboratory are approximately half of the average values of Australian extruded bricks.

The IRA values vary with the type of sludge addition in the biofly bricks. The Bellambi mix shows an average value of 0.37 kg/m²/min which may be due to the high percentage of silica, alumina and iron percent in the Bellambi sludge.

The effect of IRA on the percentage material replacement in a clay/shale brick is illustrated in Fig. 6.8. The Wollongong and Shellharbour sludge mixes generally show a decreasing trend in IRA values when material addition increase from 50% to 70%. The Port Kembla and Bellambi sludge mixes shows a generally increasing trend.

It can be concluded that the addition of waste materials as well as the type of sludge affects the IRA. The absolute values of biofly bricks are within the recommended optimum values.

![Figure 6.8. Average Initial Rate of Absorption of Biofly Bricks](image-url)
6.10. Water absorption properties

The average absorption values for the ten bricks of each batch tested under both hot and cold water conditions are given in Table 6.12.

The overall average of hot water absorption values for the biofly bricks is substantially larger than for the clay/shale bricks. This is primarily attributable to the addition of waste materials and in particular to the addition of sewage sludge. It is expected that the volatile matter in the sludge will disappear in the flue gas during firing and pores get created. Although the pores can be filled by fly ash, the net effect is that the increase in the number of pores corresponds to 100% clay/shale bricks.

Table 6.12 Summary of water absorption properties for biofly bricks (%)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Average cold water absorption</th>
<th>Average boiling water absorption</th>
<th>Average saturation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>20.0</td>
<td>20.2</td>
<td>0.98</td>
</tr>
<tr>
<td>65 S</td>
<td>15.3</td>
<td>14.0</td>
<td>1.09</td>
</tr>
<tr>
<td>60 S</td>
<td>12.6</td>
<td>12.2</td>
<td>1.04</td>
</tr>
<tr>
<td>55 S</td>
<td>18.6</td>
<td>17.5</td>
<td>1.06</td>
</tr>
<tr>
<td>50 S</td>
<td>10.4</td>
<td>9.63</td>
<td>1.08</td>
</tr>
<tr>
<td>Average S</td>
<td>15.38</td>
<td>14.70</td>
<td>1.05</td>
</tr>
<tr>
<td>70 P</td>
<td>21.6</td>
<td>21.9</td>
<td>0.98</td>
</tr>
<tr>
<td>65 P</td>
<td>19.2</td>
<td>18.8</td>
<td>1.01</td>
</tr>
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<tr>
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<td>Total average</td>
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<td>0.96</td>
</tr>
<tr>
<td>LB</td>
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<td>4.93</td>
<td>0.97</td>
</tr>
<tr>
<td>FB</td>
<td>7.52</td>
<td>6.64</td>
<td>1.13</td>
</tr>
</tbody>
</table>
Except for Bellambi mix, no significant difference in hot and cold water absorption values is observed for the Shellharbour, Wollongong and Port Kembla mixes. The Bellambi mix shows cold and hot water absorption values similar to those for clay/shale bricks and this is primarily attributable to the high alumina and silica contents of sludge from the Bellambi drying beds.

Although the hot and cold water absorption values of biofly bricks are higher than clay/shale bricks, they are in fact comparable to average values obtained from other waste bricks (Slim and Wakefield, 1991). In addition, higher water absorption may be a useful feature especially if the bricks are to be used as pavers. Some stormwater will be absorbed and retained in the bricks which will have an overall effect on flow reduction downstream.

The saturation coefficient is a parameter which represents a ratio between 24 hour cold water absorption and the 5 hour hot water absorption. The saturation coefficient values for biofly bricks are found to be similar to clay/shale brick values.

The effect of percentage waste material replacement on the cold water absorption, hot water absorption and the saturation coefficient of biofly and clay/shale bricks is shown in Figures 6.9, 6.10 and 6.11 respectively. It appears that there is no effect on the absorption values of cold or hot water absorption of biofly bricks when the waste material percentage is varied from 50% to 70% except for Bellambi mix. For all other mixes, the average cold water absorption is high when % material replacement is high. The saturation coefficient shows a generally decreasing trend with the addition of waste materials.

Discussion

The ability of the bricks to absorb water that falls on them is one of their most useful properties. The amount of water that the bricks can absorb is indicated by the water absorption test. Attempts made during the last hundred years to relate water absorption to watertightness of walls, to the durability of bricks themselves, or to the adequacy of the firing treatment in manufacture, have all failed to establish any useful correlations. Clause 6.5 of AS A21-1964 implies that water-absorption results and the saturation coefficient calculated from them can be used as a measure of the durability of the bricks.
Figure 6.9. Average Cold Water Absorption of Biofly Bricks

Figure 6.10. Average Boiling Water Absorption of Biofly Bricks
Figure 6.11. Average Saturation Coefficient of Biofly Bricks

in conditions of severe frost. Butterworth and Baldwin (1964) clearly showed that no such relationship exists, and that the concept should not be accepted.

Blachere and Young (1974) pointed out that the freezing of water in a clay body has been observed to occur in two stages, and introduced the role of capillary shaped pores. Important observations made by Blachere and Young follow: First: water freezes in large pores at about 0°C. Second: water freezes in the capillaries when the temperature is between about -2°C and -8°C. Freezing occurs gradually in finer and finer capillaries as the temperature is lowered. Generally, more expansion takes place during capillary water freezing than by the freezing of water in the large pores. They concluded that higher resistance brick has a lower pore volume, a narrower pore size distribution, large average pore diameter, and a saturation coefficient equal to 0.72, which is below the value of 0.80 specified in ASTM (1993).

Grim and Houston (1975) concluded that, “There is evidence that waivers of water absorption requirements permitted by ASTM specification for bricks provide a high
probability of weathering failure” and Grim and Houston (1975) confirmed that “Although these requirements of compressive strength equal to or higher than 48.26 MPa, water absorption below 8.0 percent, meeting the freeze/thaw specification, usually ensures satisfactory performance, quite frequently bricks conforming to these specifications fail in service for no apparent reason”. Litvan proposed the performance of a new freeze/thaw test procedure to prove brick durability and pointed out significant differences in brick microstructure and pore system caused by 50°C difference in firing temperature.

Brownell (1976) indicated that frost resistant bricks have an average pore diameter of 1.6 mm, whereas the low frost resistant brick have an average pore diameter of 0.24 mm. Results of the measurement of 900 tiles and further studies Brownell (1976) showed a negative influence of fine pores on the frost resistance of fired clay products.

Eklind (1983) emphasized the importance of the irregularity of pore shape. Robinson (1984) concluded that bricks with poor durability had pores of <1 mm and durable brick had pores of >2 mm. Information on the critical pore radius for frost damage in the range of 100 to 400 mm was reported by Robinson (1984).

Raths (1975) declared that “possibly because of other unknown physical behaviour, bricks can satisfy ASTM requirements and have successfully passed ASTM C 67-87 freeze/thaw tests but fail in service by freezing and thawing. Another factor believed to be important to a brick’s durability is the size and distribution of the brick’s internal pores”. The importance of brick microstructure and related pore systems, which are created by firing and cooling procedures, on brick durability was discussed by Marusin (1983, 1985).

The prediction of brick durability using a measurement of pore size distribution was published by Winslow et. al. (1988). These authors used pore size distribution to calculate a durability factor which “is more accurate and faster for selecting potentially durable bricks than the current use of absorption measurements”.

As shown in this brief literature review, a number of researchers have tried to find and understand causes for the relationship between the pore size and brick durability as a means of predicting the brick durability. As some researchers have pointed out, the
ASTM C 216 - 88A waiver requirement and C 67-87 freeze/thaw testing criteria could be successfully met, however, still not provide a durable brick in service. The traditional reliance on the physical properties of the brick to predict durability is not sufficient. New satisfactory ASTM standards for durability need to be developed.

6.11. Resistance to salt attack

6.11.1. Introduction

In the selection of any fired clay product for a particular project, one of the main considerations must be the ability of the materials to withstand the damaging affects of the exposure conditions to which they are likely to be subjected during the life expectancy of the structure in which they are to be used. In Australia, where apart from a small number of ski resorts where frost resistance is also an important consideration, the ability to resist the action of salt attack by these products is the main concern. Frost and salt attack resistance of fired clay bodies are however not directly measurable properties, as they are dependent not only on material properties, but also on the exposure conditions. Therefore, the prediction of their performance under all exposure conditions is difficult, if not impossible.

An approach to the solution of this problem is to examine their performance under controlled conditions and hope that the observed behaviour of these materials under test can be related to that displayed under different conditions of exposure. To evaluate the salt attack resistance of fired clay bodies under controlled conditions salt cycling is an obvious technique to consider. Its drawback is the length of time required for the completion of the test. The experimental aim therefore was an attempt to relate the number of cycles leading to failure to more rapidly assessable physical properties.

6.11.2. Results and discussion

At the end of each cycle of soaking in sodium sulphate, the test specimens were inspected and loose particles (if any) were identified by rubbing between thumb and forefinger, and specimens were re-measured. In addition, any particle loss was recorded.
The drying and soaking cycles were repeated until either forty cycles had been completed without particle losses by any specimen in three consecutive cycles or a loss of particles was observed in any specimen at the end of each of three consecutive cycles.

A specimen was deemed to have failed during the first of the three consecutive cycles after each of which losses of particles were observed. The failure of the first specimen of each batch was deemed the failure of the batch.

Fig 6.12, 6.13 and 6.14 shows the results of resistance to salt attack for selected biofly and clay/shale bricks. Detailed results of resistance to salt attack can be found in Tables 170, 175 and 176 in Volume 2. Figure 6.16 (also see Table 170, V2) and Figure 6.17 (Table 175,V2) show that all specimens have survived the 40 cycle test for biofly (70 W) and clay bricks (laboratory) respectively. Hence it can be concluded that biofly brick quite successfully passes the test for resistance to salt attack.

The results shown in Fig 6.18 for the factory brick indicates that these bricks have survived 14 cycles of the test and hence it is considered a failure. It is felt that the cause of failure may be due to the effect of holes in the brick because the clay/shale bricks made in the laboratory without holes have passed the test successfully.

Zsembery and Phillips (1983) have shown that the clay brick with the highest water absorption have the lowest resistance to salt attack, but other tests (Murray et al 1981) indicate that extruded bricks fired with saw dust additives are highly resistance to salt attack inspite of them having higher water absorption. The biofly bricks show higher water absorption values but also show high resistance to salt attack which is in agreement with the views of Murray et al (1981) concerning the effects of water absorption.

The durability of clay bodies against salt attack clearly results from the balance between the disruptive forces exerted in the walls of open pores and the strength of the body. The fewer the open pores the less effective is the force exerted per unit volume, hence the lower the porosity the greater the durability. The same volume porosity would represent many more small pores than pores of intermediate or large diameter, so elimination of fine pores in the course of firing would have a reinforcing effect on improving durability to salt crystallisation.
Strengthening, which increases progressively with increase in firing temperature is due to recrystallisation and cross bonding by the glassy phase which plays a very significant if not preponderant role in resisting salt attack.

Tests of strength and porosity can be carried out much more rapidly than salt cycling to failure. By using correlations of these properties with durability for a wide spectrum of biofly brick types, reliable estimates of durability can be offered to brick users without the need for protracted salt cycling or exposure testing.

Study of the pore size distribution of the bricks with the aid of a mercury porosimeter and porosity evaluation by optical or electron microscope is needed to help gain an understanding of the role pore sizes play in fixing the salt attack resistance of fired products.

---

**Figure 6.12. Resistance to Salt Attack of Biofly Brick (70 W Mix)**

No of Cycles

<table>
<thead>
<tr>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
</tr>
<tr>
<td>150</td>
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<td>110</td>
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</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>40</td>
</tr>
</tbody>
</table>

--

S1  S2  S3  S4  S5  S6  S7  S8  S9  S10
Figure 6.13. Resistance to Salt Attack of Clay/Shale Laboratory Bricks

Figure 6.14. Resistance to Salt Attack of Clay/Shale Factory Bricks
6.12. Shrinkage

Shrinkage of the brick occurs during air and oven drying stages as well as during the firing stage.

Shrinkage occurs during drying due to the particles being physically drawn together after the evaporation of entrapped water. Firing shrinkage occurs when particles fuse together, thereby shrinking the voids left by the expelled water and volatiles.

The sludge tends to increase the chemically bound water contained within the brick. During the dehydration stage of firing chemically bound water is released causing the first stage of firing shrinkage to occur.

Shrinkage also occurs during the vitrification stage. During this stage the clay/shale and fly ash particles begin to flow, partially or completely filling the voids and gas bubbles left by the oxidation of the sludge. This causes the second stage of firing shrinkage.

Average values of linear shrinkage for the ten bricks of each batch under “Dry” and “Fired” conditions are given in Table 6.13.

The overall average linear shrinkage of the “Dry” biofly bricks is substantially lower than for the clay/shale bricks. This is primarily attributed to the addition of waste materials and in particular to the addition of fly ash. The composition of the spherical portion of the fly ash is somewhat immune to dissolution due to its glassy structure. The nature of the particles is quite similar to glass in elemental composition, and as such is relatively inert. Therefore during drying or firing the fly ash undergoes negligible shrinkage.

The overall average linear shrinkage of the “Fired” biofly bricks is slightly higher than for the clay/shale bricks. It is expected that the volatile matter of the sludge will disappear in the flue gas during firing, creating pores, although the particles then fuse together, shrinking the voids left by the expelled water and volatiles.
The mean linear shrinkage values for biofly bricks are found to be lesser than clay/shale brick values. This may be attributed to the effect of the fly ash during drying and firing.

The effect of percentage waste material replacement on the linear shrinkages of “Dry” and “Fired” biofly and clay/shale bricks is shown in Figures 6.15 and 6.16 respectively. It appears that there is a generally decreasing trend in the linear shrinkage values of the biofly bricks when the waste material percentage varies from 50% to 70%.

Table 6.13. Summary of linear shrinkage of biofly brick (%)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Linear shrinkage of “Dry” brick</th>
<th>Linear shrinkage of “Fired” brick</th>
<th>Total linear shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 S</td>
<td>3.58</td>
<td>3.42</td>
<td>7.00</td>
</tr>
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<td>65 S</td>
<td>2.93</td>
<td>3.80</td>
<td>6.73</td>
</tr>
<tr>
<td>60 S</td>
<td>3.86</td>
<td>4.35</td>
<td>8.21</td>
</tr>
<tr>
<td>55 S</td>
<td>5.20</td>
<td>6.03</td>
<td>11.23</td>
</tr>
<tr>
<td>50 S</td>
<td>3.96</td>
<td>6.01</td>
<td>9.97</td>
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<td>3.52</td>
<td>7.38</td>
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<tr>
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<td>4.17</td>
<td>12.49</td>
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</table>
Chapter 6: Structural and Related Properties of "Biofly" and clay/shale Brick

Figure 6.15. Average Linear Shrinkage of "Dry" Biofly Bricks

Figure 6.16. Average Linear Shrinkage of "Fired" Biofly Bricks
Figure 6.17. Total Linear Shrinkage of Biofly Bricks

It is clear from Fig 6.17 that the biofly bricks in general have less linear shrinkage compared with clay/shale bricks fired at the laboratory. Hence, it is concluded that the addition of fly ash and sewage sludge has the beneficial effect of decreasing the linear shrinkage.

6.13. Weight loss

The weight loss is directly related to water content, chemically bound water quantities and volatile content. During the drying process water is evaporated accounting for the first weight loss. Chemically bound water and volatiles are released during firing accounting for the second weight loss.

Average values of weight loss for the ten bricks of each batch under “Dry” and “Fired” conditions are given in Table 6.14.

The overall average dry weight loss for the biofly bricks is substantially higher than for the clay/shale bricks. This is primarily attributed to the addition of waste materials and in particular the addition of sewage sludge with higher percentage of moisture.
content. During drying, water is expelled rapidly from the brick accounting for the highest weight loss.

Table 6.14. Summary of weight loss of biofly bricks (%)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Dry weight loss</th>
<th>Firing weight loss</th>
<th>Total weight loss</th>
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<td>22.99</td>
</tr>
<tr>
<td>65 P</td>
<td>20.6</td>
<td>6.73</td>
<td>27.33</td>
</tr>
<tr>
<td>60 P</td>
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<td>31.03</td>
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<tr>
<td>50 P</td>
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<td>27.83</td>
</tr>
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<td>28.03</td>
</tr>
<tr>
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<tr>
<td>50 W</td>
<td>22.2</td>
<td>6.20</td>
<td>28.40</td>
</tr>
<tr>
<td>Average W</td>
<td>22.48</td>
<td>6.78</td>
<td>29.26</td>
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<tr>
<td>Total average</td>
<td>21.97</td>
<td>6.55</td>
<td>28.52</td>
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<tr>
<td>LB</td>
<td>13.1</td>
<td>6.93</td>
<td>20.03</td>
</tr>
<tr>
<td>FB</td>
<td>2.96</td>
<td>9.74</td>
<td>12.70</td>
</tr>
</tbody>
</table>

The overall average of weight loss during firing of biofly bricks are similar to clay/shale brick. Hence it appears that although volatile waste materials such as sludge is substituted, no overall effect can be noticed due to the combined presence of fly ash and sludge.

The effect of amount waste material replacement on the dry and fired weight losses of biofly and clay/shale bricks is shown in Figures 6.18 and 6.19 respectively. It appears that there is generally decreasing trend on the weight loss values of biofly bricks when the waste material percentage change from 50% to 70%.
Chapter 6: Structural and Related Properties of “Biofly” and clay/shale Brick

Figure 6.18. Average Dry Weight Loss of Biofly Bricks

Figure 6.19. Average Firing Weight Loss of Biofly Bricks
Chapter 6: Structural and Related Properties of “Biofly” and clay/shale Brick

Figure 6.20. Total Weight Loss of Biofly Bricks

It is clear from Fig 6.20 that the biofly bricks in general have higher weight loss compared to clay/shale bricks fired at the laboratory. Hence, it is concluded that the addition of fly ash and sewage sludge increases the weight loss.

6.14. Bulk density

Bulk density of the biofly bricks is expected to be lower than the clay bricks due to the presence of voids and gas bubbles from the volatile solids formed during the oxidation stage of the brick firing. Bubbles of gaseous water and carbon dioxide are formed from the oxidation of the organics contained within the sludge. However, during the firing process it is likely that the fly ash will occupy these voids thereby hardening the brick.

Assuming that the external parameters such as extrusion pressure are similar for all the extruded samples, then only variations in the relative amounts of water content, sludge and fly ash additions will affect the sample density. Sludge addition will increase both the quantities of chemically bound and volatile constituents contained within the sample. During drying and firing, the chemically bound water and volatile constituents are expelled from the sample in a gaseous form. This gas release leaves voids within the brick.
and thereby decreases density, but the addition of fly ash will increase the overall density again during firing due to the silica+alumina+iron content in the fly ash.

Table 6.15 provides the bulk densities biofly bricks. The average bulk densities of Shellharbour, Port Kembla, Bellambi and Wollongong mixes, were found to be 1644, 1578, 1724 and 1570 kg/m^3 respectively. The change in bulk density of each mix appears to vary with the quantity of silica+alumina+iron content in the sludge. The overall average bulk density of biofly brick is 1629 kg/m^3 which is 25% lighter than clay/shale brick, due to the volatile content of the sludge.

Table 6.15. Bulk density of biofly bricks (kg/m^3)

<table>
<thead>
<tr>
<th>Mix</th>
<th>Bulk density (kg/m^3)</th>
<th>Silica+Alumina+Iron (%)</th>
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<td>55 S</td>
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<tr>
<td>50 S</td>
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<tr>
<td>Average S</td>
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<td>26</td>
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<td>70 P</td>
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Figure 6.21 shows a comparison of bulk densities for clay/shale and biofly bricks, and from this plot it is clear that the addition of waste material has decreased the bulk density of the biofly bricks. However, when the percentage waste material content is increased, no significant change in bulk density occurs in any of the mixes.

A summary of results for all bricks produced is presented in Table 6.16. The Table shows the effect of sewage sludge and fly ash additions to clay/shale by testing a series of samples with sludge and fly ash compositions ranging from fifty to seventy percent by weight.

6.15. Summary

A coding system was developed for the identification of various mix. The waste materials sewage sludge and fly ash was mixed with clay/shale, in different proportions by weight in “as received” condition. The amount of water added to get the desired optimum mix varied from 24 to 33%. It has been found that the amount of water added for the mix varied with the sludge type primarily due to the difference in moisture content of the source of various sludges.
Visual inspection of the biofly bricks made from all sludge types indicated that the Wollongong mix was light orange in colour whereas Bellambi mix indicated a dark brown colour. The dimensional calculation performed in accordance with Australian Standards indicate that biofly bricks fall within specification range.

It has been found that the biofly brick samples have characteristic transverse strength in excess of the standard value of 1 MPa and exceed the value for clay/shale bricks. However it was observed that the characteristic transverse strength of factory clay/shale bricks fell below the standard and this can be attributed to the effects of perforations present. The transverse strength values of the biofly bricks vary with the type of mix and the type of sludge added. The mixes show both increasing and decreasing trends in the characteristic transverse strength when material additions vary between 50% and 70%.

The overall average characteristic compressive strength value of 24.95 MPa for biofly bricks indicates that it is significantly higher than the minimum standard value of 7 MPa for clay/shale brick, when the biofly strength is compared to clay/shale made with the same extruder, approximately an average increase in strength of 10% is observed. The characteristic compressive strength values of biofly bricks varied with the type of sludge addition. The Shellharbour and Wollongong mixes produce the highest compressive strength and that were respectively 24.5% and 25% higher than clay/shale brick. In general, the differences in the values of characteristic compressive strengths are likely to be related to the method of forming the bricks.

The overall average characteristic expansion of the biofly mixes ranged between 0.62 to 1.74 mm/m which falls into the medium to high category. The biofly bricks in general have less characteristic expansion compared with clay/shale bricks fired in the laboratory. However the absolute values for thermal expansion clay/shale bricks fired in the laboratory are higher than those observed in the factory bricks. This may be attributed to the different firing characteristics and type of extrusion used in the laboratory.

Efflorescence tests indicated some efflorescence present in bricks made from the Bellambi mix, whereas no efflorescence was detected for any other mix. Salt deposits were very light, and in most cases could only be detected as a very slight staining or colour change on the surface of the brick. No pitting due to lime particles was detected in bricks made from any mix.
An overall average value of initial rate of absorption 0.64 kg/m²/min for biofly bricks indicated that it is within the recommended optimum values. The initial rate of absorption values of biofly bricks and clay/shale bricks are very similar. In general, the average values obtained in the laboratory are approximately half of the average values of Australian extruded bricks. It was found that the addition of waste materials as well as the type of sludge affect the initial rate of absorption.

The hot and cold water absorption values of biofly bricks are much higher than for clay/shale bricks. Although, they are comparable to average values for other similar waste bricks produced in South Africa the absolute values are considered to be higher. However, the higher water absorption property may be a useful feature especially if the bricks are used as pavers. Further, higher water absorption also have better adhesion.

Resistance to salt attack was similar for all of the biofly and laboratory clay/shale bricks, all of which exceeded the recommended 40 cycles, including the clay/shale laboratory bricks. However the least resistance was observed in factory clay/shale brick which failed after 14 cycles. The porous nature of the surface of the factory brick caused particle loss due to salt attack resulting in failure. The biofly bricks passed the test without particle loss.

The biofly bricks in general have less linear shrinkage compared with clay/shale bricks fired in the laboratory. The biofly bricks have higher weight loss compared with clay/shale bricks fired in the laboratory. Hence, it is concluded that the addition of fly ash and sewage sludge tends to decrease the linear shrinkage and increase the weight loss of the bricks.

It is clear that the addition of waste material decreases the bulk density of biofly bricks. The change in bulk density of biofly bricks from each mix appears to vary with the quantity of silica+alumina+iron presents in the sludge. The overall average bulk density of the biofly bricks is 1629 kg/m³ which is 25% lighter than clay/shale brick. This is indeed one of the main advantages of biofly bricks.

The analysis of structural and related properties of full size biofly bricks and its comparison with clay/shale bricks made under similar condition indicate that:
• The biofly bricks can be made 10-25% stronger than clay/shale bricks which indicate that the addition of two waste materials does not affect but increases the compressive strength of bricks.

• The biofly bricks are 25% lighter than clay/shale bricks. This is a significant advantage for storage, transport and handling. It may also give superior thermal properties.

• The durability of the biofly brick is shown to be better than clay/shale brick.

• The type of sludge affect the colour, the strength and other properties. An industrial type sludge such as for Port Kembla may produce unusual structural characteristic which need further investigation.

• The optimum waste mix brick is likely to be 15% sludge, 50% fly ash and 35% clay/shale.
Chapter 6:

Structural and Related Properties of "Biofly" and clay/shale Brick

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Chapter Seven

Theoretical Considerations of the Firing Process

7.1 Introduction

The object of firing a clay product is to convert a fairly loosely compacted blend of various minerals into a strong, hard, and stable product. To achieve this conversion many chemical and physical processes come into play. The properties of the final product such as strength, porosity, stability against the action of moisture and chemicals, thermal expansion, thermal conductivity, and hardness are determined by the kind and amounts of the various phases resulting from the firing process.

It is important to review the reactions that take place on heating some of the important disilicate minerals. The raw materials for structural clay products contain between 40% to 80% of disilicate minerals, therefore, they are bound to have important influences on the final product and on the way that the final phases are achieved. It has been found that a single disilicate mineral may break down on heating to provide as many as four new compounds, to serve as reactants with each other and other minerals present. In many cases, one or more of these decomposition products remains in the final product and exerts its influence on the properties. This is likely to be the case in biofly bricks.

7.2 Identification of disilicate minerals

The most common tool used in observing high temperature reactions is Differential Thermal Analysis (DTA). It measures the exothermic and endothermic effects that occur on heating a sample at a constant rate, usually around 10°C per minute. These heat effects are noticeable on DTA when reactions take place fairly rapidly. Sluggish reactions are not visible, since the temperature differentials caused by them are too small and extend over time periods that are too long. DTA tells us the temperature ranges in which changes are taking place, and from its thermal effects, we can infer the type of reactions occurring (Smothers and Chiang, 1966). For example, decompositions and
transitions are endothermic, but oxidations and reactions to form new phases are exothermic.

More detailed study into the identity of the phase changes indicated by DTA are made by Thermal Gravimetric Analysis (TGA) and X-ray diffraction (XRD). TGA also is a dynamic process achieved by heating the sample at a constant rate. It gives weight changes that supplement the information gained from DTA. If an endothermic peak on DTA is accompanied by a weight loss as shown by TGA, the reaction is unquestionably a decomposition evolving a gaseous phase. If the reactants and products involved with DTA peaks are crystalline, direct identification of them are possible by X-ray powder diffraction methods (Wendlandt, 1964). Samples for X-ray examination can be obtained by quenching from a DTA furnace both below and above the temperature of visible peaks, or other samples can be heated to equilibrium at appropriate temperatures. The actual reaction temperatures are not often easy to determine from the DTA because they are the points where the peaks start. The temperatures of the maxima and minima on the DTA peaks have no physical meaning because of the dynamic nature of the heat treatment. They are simply reasonably reproducible points on the temperature scale. In some cases, but not all, the tops of the peaks may express the end of the reaction, then the rest of the peak is a cooling or heating curve bringing the sample back to the furnace temperature.

More detailed study into the identity of the crystal structures indicated by polarized light microscopy are made by thin sections. This tool is used to observe how these minerals are combined with one another (Van Der Marel and Beutelspacher, 1968). For this purpose a piece of the substance to be investigated is cut off with a diamond saw. A surface is ground, polished and cemented on to a microscope slide. This layer reduced to a thickness of about 30 mm by grinding and polishing, and finally covered with a coverglass.

Classification of clay minerals

The clay minerals have a number of characteristics in common. Important differences among them, however, lead to their subdivision into main groups. Simplified classification of the clay minerals is given below.
Group 1: Kaolinite group
Group 2: Illite group
Group 3: Montmorillonite group
Group 4: Chlorite group

7.3 High-temperature reactions in disilicate minerals

7.3.1 Kaolinite group

Since kaolinite is the purest and has the simplest crystal structure of all clay minerals, its thermal reactions have received considerable attention. A typical DTA curve for a purified, highly crystalline kaolinite is plotted in Fig. 7.1 (Brindley & Nakahira, 1957). Temperature of the furnace is plotted against the millivolts produced by the differential thermocouple. Quite arbitrarily, the plus sign indicates heat evolved from the sample, an exothermic reaction, and the minus sign denotes the absorption of heat by the sample as in endothermic reactions. The significant thermal effects for kaolinite up to 1000°C are an endothermic reaction near 600°C and a sharp exothermic peak around 970°C.

Figure 7.1 A typical differential thermal analysis of well crystallized kaolinite (Brindley and Nakahira, 1957)

On heating kaolinite, no change occurs until about 470°C where the OH⁻ ions of the crystal lattice are expelled in the form of water vapour. The actual temperature of this decomposition and the rate of evolution of moisture is dependent on the vapour pressure of water in the atmosphere surrounding the sample (Brindley & Nakahira, 1957). As the lattice water is driven off, the crystallinity disappears, but a considerable order remains
in the a and b crystallographic directions which has been reported by Brindley & Nakahira (1959a). The hexagonal form of the kaolinite crystals persists through this loss of crystalinity, and can be seen by electron microscopy even after heating to very high temperatures.

Metakaolin is the name given to the amorphous, metastable phase of kaolinite after dehydroxylation, and it has several interesting characteristics. MacKenzie, (1969), has described these characteristics as: the specific surface area increases dramatically, surface free energy for adsorption and catalytic activity increases, and it is highly reactive with other oxides in this form. When metakaolin is formed, the kaolinite layers collapse in the c direction from 7.14 to about 6.3 Å, some of the Al$^{3+}$ ions go into tetrahedral coordination with oxygen, and the tetrahedral silica sheet becomes quite distorted, however, the aluminium and silicon ions do not migrate very far from their original positions in the kaolinite structure.

On continued heating, the coordinated Al$^{3+}$ and Si$^{4+}$ ions gain increasing mobility, so that by 855°C a simple rotational movement produces the start of development of a cubic, spinel-like crystalline phase. At this low temperature, the crystallites are visible only by electron diffraction, but the cubic phase is well enough developed at 925°C or a little higher, to be detected by X-ray diffraction as reported by Roy and Francis (1955). The alumina-silica spinel, previously mistaken for gamma alumina, has an approximate composition of 2Al$_2$O$_3$.3SiO$_2$ which is called Mullite, and the rest of the silica not included in this rearrangement remains amorphous (Brindley & Nakahira, 1959b). This is the structural state up to the sharp exothermic reaction at about 970°C.

The exothermic peak seen in Fig 7.1 is the nucleation of mullite from the spinel phase. Such a sudden release of energy must be due to a simple transition of a metastable state of kaolinite to a stable one (Roy and Francis, 1955). Any reaction or transition requiring extensive rearrangement of ions is characteristically sluggish and such an exothermic effect would not be visible by DTA. If one builds a model of kaolinite, then makes a correction for the removal of hydroxyl ions by allowing some Al$^{3+}$ ions to go into 4-fold coordination, and distorts and breaks up the silica sheet, mullite is formed by simple, rotational movements of the coordinated aluminium and silicon ions. As mullite forms, some silicon ions diffuse to grain boundaries. The initial mullite crystals probably have a composition close to Al$_2$O$_3$.SiO$_2$, but as heating continues up to about 1300°C,
mullite continues to exsolve silica until it finally approaches a stable $3\text{Al}_2\text{O}_3.2\text{SiO}_2$ composition (Roy et al., 1955).

To make a model of mullite from kaolinite, as described above, it will be found that three kaolinite layers are required for each mullite unit cell. A view down the c-axis of a mullite unit cell is shown in Fig. 7.2A. We are looking down at the ends of five chains of aluminum octahedra, each sharing an edge with its two neighbours. The dashed lines represent edge boundaries of the three layers of kaolinite. The mullite crystal is completed by joining the alumina chains with alternating silica and alumina tetrahedra. Actually, the crystal described is sillimanite, and mullite is the result of silica vacancies along the chains (Mackenzie, 1972).

![Figure 7.2. Relation between mullite development and the structure of the original kaolinite (MacKenzie, 1972)](image)

The c-axis of elongated mullite crystals grow perpendicular to the original c-axis of the kaolinite crystal, and this picture is presented in a plane view in Fig. 7.2B. The hexagonal outline is that of a kaolinite crystal which has been converted to mullite. Elongated mullite crystals are shown as they grow inside the kaolinite crystal preferentially oriented to the sides of the kaolinite hexagon. The three c directions illustrated are those preferred by the mullite crystals growing in the ab plane of well crystallized kaolinite.

The superfluous silica and that expelled during the development of mullite finally crystallise as cristobalite around 1250°C, and the crystallisation is visible as a small exothermic peak on high-temperature DTA curves (Glass, 1954). The first cristobalite detected by X-ray diffraction at this temperature is not well crystallised, but the pattern
becomes clearer on heating to 1425°C as reported by Brindley & Nakahira (1959). The slow development of well-crystallised cristobalite from amorphous silica was observed by Verduch (1958), and Verduch has found that cristobalite crystals formed at temperatures below 1425°C were quite defective.

The overall chemical equation for the stable phases involved in the heating of kaolinite is

\[ 3[\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4] \rightarrow 3\text{Al}_2\text{O}_3.2\text{Si}_2\text{O}_5 + 4\text{Si}_2\text{O}_2 + 6\text{H}_2\text{O} \]  

\[ \text{kaolinite} \rightarrow \text{mullite+ cristobalite+ water} \]  

When kaolinitic clays are used for structural clay products, the presence of mullite in the product denotes a well-fired body. Mullite is a hard, chemical resistant phase in clay products, and its elongated crystal structure provides great strength. An underfired product with metakaolin or even poorly crystallised mullite would be totally unserviceable. As we shall see later, cristobalite is seldom observed as a phase in structural clay products, and mullite is not always a part of products prepared from clays containing kaolinite.

During the biofly brick process, it is likely that the transformation of Quartz to cristobalite is slow and dependant on the biofly brick temperature, time of firing, and on the presence of mineralizers which promote the change. The amount of cristobalite formed in biofly brick for a particular firing temperature depends largely on the size of the particles of Quartz present. The change takes place from the outer surface of each particle and then progresses inwards, hence the greater the surface exposed, the more finely ground the material, the greater the degree of conversion. The volume changes, even if it is large, does not occur suddenly and does not disrupt a body.

### 7.3.2 Illite group

The chemical composition of Illite is given by (Prokopovich, 1993b) as,

\[ \text{K}_{0.6}(\text{Mg}_{0.2}\text{Fe}_{0.3}^{2+}\text{Al}_{1.5})(\text{Al}_{0.6}\text{Si}_{3.4}\text{O}_{10})(\text{OH})_{2} \]

As might be expected from examination of the formula for illite, the paths of reactions are quite different from those of kaolinite, and different phases are formed on
the way towards a stable product. Surprisingly, in the end the only crystalline phase is still mullite. In this respect, the final phases resemble those of kaolinite, but in other ways they are not the same at all.

Since illite has a somewhat variable composition due to substitutions of one ion for another, the best we can do is to describe the course of events that take place on heating a particular illite. This approach will not lead us far astray, because the compositional range of illites is small enough so that deviations in phase development on heating are negligible. Great care was exercised in purifying an illitic clay before studying its thermal behaviour. Other minerals and carbonaceous matter were removed from the natural sample, and the formula for the pure illite is given by Prokopovich (1993b) as,

\[
\text{K}_{0.94}\text{Na}_{0.05}\text{(Mg}_{0.54}\text{Fe}^{2+}_{0.67}\text{Al}_{3.04})(\text{Al}_{1.28}\text{Si}_{6.72}\text{O}_{20})(\text{OH})_{4}
\]

The DTA for this illite clay mineral is shown in Fig. 7.3, and thermal reactions shown indicate the approximate temperatures where these reactions occur. Equilibrium heating studies (Prokopovich, 1993b) tell us only physically adsorbed water molecules are driven off up to 400°C, and this is the cause of the endothermic peak near 130°C. Between 400 and 550°C most of the lattice water is expelled, which accounts for the endothermic peak around 540°C, but TGA shows that water is continually driven off very gradually until melting starts. Unlike kaolinite, the X-ray crystallinity of Illite is not lost as a result of the dehydroxylation, but there is an increase in specific surface area. The only change in the X-ray pattern from 550 to 850°C is a drift of the 060 line from 1.50 to 1.53 Å. Between 800 and 850°C a rapid consolidation of the illite structure occurs and is noticed by a drastic loss in surface area. This is probably a collapse of the lattice with some distortion, but the crystalline arrangement of the ions still persists. The consolidation process may cause the endothermic effect near 900°C.

![Figure 7.3. Differential thermal analysis of a pure illite sample (Brownell, 1963)](image-url)
Above 850°C several reactions take place, most of which relate to the octahedral sheets in the illite layers. The exothermic peak a little above 900°C is caused by the formation of spinel (MgAl_2O_4), and it is observed on X-ray patterns of samples heated to approximately 850°C. When spinel of the illite pattern disappears except the basal spacing 001, but these also vanish at 900°C when hematite (Fe_2O_3) forms along with spinel. Some place along the line, the ferrous ions of the original illite structure are oxidized to the ferric state. Further heating to about 950°C causes corundum (α-Al_2O_3) to crystallise, then we have three crystalline phases, spinel, hematite, and corundum, present—but no silicates.

The first trace of melting on heating this illite occurs around 1050°C and the amount of liquid formed gradually increases until no crystals are left at about 1450°C (Prokopovich, 1993b). As soon as melting starts, the initial three crystalline phases dissolve in the fusion and react with silica to form mullite. The amount of mullite increases as the sample is heated to 1200°C, then it begins to dissolve in the liquid.

The beginning of melting around 1050°C and the appearance of mullite explains why many structural clay products made from predominantly illitic clays are fired from 1038°C to 1082°C. The glassy phase resulting from the fusion promotes a strong body with a reduction in porosity, and mullite gives it strength and durability. Products showing the spinel phase are underfired as far as a good, stable product is concerned.

During the vitrification stage, the biofly brick start melting between 1050°C and 1100°C. The appearance of mullite as a glassy phase resulting during vitrification promotes a hard, chemical resistant biofly brick as noticed earlier in section 6.11 of chapter 6. The elongated crystal structure of mullite is also likely to provide great strength.

7.3.3 Montmorillonite group

The high-temperature reactions of montmorillonite are similar to those of illite except that the DTA records show a larger and sometimes double endothermic peak in the temperature range of 150°C to 260°C. This heat effect is attributed to the evolution of interlayer water and the water associated with the hydration of the interlayer exchangeable cations. Even though the lattice water is driven off around 500°C, the X-ray crystallinity remains to about 800°C when spinel and hematite forms. As with illite,
when melting starts around 1050°C, spinel and hematite quickly dissolves and mullite crystals emerge, so that by 1300°C, the only two phases present are mullite and a silicate liquid as observed by Brindley (1951).

### 7.3.4 Chlorite group

The most important nonclay disilicate mineral affecting the properties of fired structural clay products is chlorite. It is commonly found in illitic shales and clay deposits derived from them. Because of the alternate stacking of trioctahedral mica and brucite layers, the different structural relations between magnesia and silica produce unique phases on firing.

One of the common chlorite minerals, prochlorite, has been examined carefully on heating to 1000°C. Its structural formula is given by Prokopovich (1993b) as,

\[
(Mg_{4.2}Fe^{2+0.78}Al_{1.03})(Al_{1.16}Si_{2.84}O_{10})(OH)_8
\]

and an interesting thing to note here is the absence of alkali ions. The DTA curve for this mineral is found in Fig. 7.4. No reactions occur up to 500°C, but the peak at 550°C is actually an exothermic reaction and only appears as a return to base line because of a base-line drift during the heating of this material. The heat evolved is caused by the oxidation of ferrous ions in the lattice to the ferric state, and hematite appears on the X-ray patterns on heating the sample to 550°C. Between 550 and 720°C, the water is expelled from the brucite layers causing the endothermic effect around 700°C. During this period, the crystallinity of the prochlorite weakens. At 780°C the removal of the lattice water from the biotite-like layers is responsible for the endothermic effect on the DTA at about 860°C. Immediately following this dehydroxylation, the chlorite crystallinity disappears, and an olivine crystalline phase, like forsterite \((Mg_2SiO_4)\), appears along with \((MgAl_2O_4)\) spinel. The reactions to form these compounds are visible on the DTA curve as a small exothermic peak at 920°C.

Apparently, the magnesium ions which belonged to the brucite layers react with the silica sheets of the adjoining biotite layers, the first 3-layer mineral develops a silicate compound before nullitization. As prochlorite is heated above 920°C, further magnesia-silica reactions take place and clinoenstatite \((MgSiO_3)\) appears. At 1000°C, the crystalline phases present are forsterite, spinel, and clinoenstatite. Possibly these crystals
have taken iron into solid solution, because hematite is not present above 780°C (Prokopovich, 1993b).

![Figure 7.4. Differential thermal analysis of prochlorite (Brownell, 1963)](image)

Melting occurs in chlorites somewhat above 1000°C, perhaps at a higher temperature than with the 3-layer clay minerals due to the lack of interlayer alkali ions, however, one can expect from the crystalline phases developed that very fluid melts are going to appear when melting occurs. In practice this is noticed with clay raw materials containing chlorite as narrow temperature ranges for the development of suitable properties in the products (Prokopovich, 1993b).

One might expect that cordierite, \((\text{Mg}_2\text{Al}_3)(\text{AlSi}_5\text{O}_{18})\), would be developed on heating chlorite, but in the structural clay products industry, the firing temperatures are not high enough when materials are used that contain chlorite naturally. Segnit & Holland (1971) have used chlorites to produce a cordierite body by fortifying the composition with kaolinite and firing to a relatively high temperature. This idea may be of some interest to those structural clay products plants having access to fireclays. Cordierite products have a good resistance to thermal shock and are often classed as a low temperature refractory.

Pyrophyllite is a micaceous mineral which can be used in ceramic bodies to provide alumina and silica without increasing plasticity and shrinkage as would be the case with kaolin. It may occur as a minor constituent in some illitic shales, but it is added directly
to floor and wall tile bodies. Tauber & Pepplinkhouse (1972) has reported that on heating, pyrophyllite loses its lattice water around 600°C, and the dehydroxylation is followed by an abrupt expansion close to 800°C. The crystallinity is lost by the time the mineral reaches 1000°C, but mullite does not develop until 1400°C. Pyrophyllite is thus a very refractory ingredient which can be added to ceramic bodies.

Due to less clay being used during the biofly brick process, no effect is indicated from the Chlorite group.

7.4 Reaction in typical clay bodies

Non-refractory clays and shales are used in the manufacture of structural clay products. In general, these materials are siliceous and contain a relatively large amount of fluxes. Although no specifications are applied to brickmaking clays, the particular properties of any given mix must be suited to the manufacturing process involved. Important properties include plasticity, drying and firing shrinkage, fired strength, soluble salts content, and fired colour.

Some typical mineralogical composition of buff to white firing clays and shales are shown in Table 7.1A. The buff to white firing clays materials show three ways by which light colours are produced. Fireclay fires to buff shades because kaolinite is the principal clay mineral and the total iron oxide content is relatively low, perhaps 3 to 4 percent. The gray shale and the blue clay are buff firing because of the presence of the relatively large amounts of calcite (CaCO₃). The white clay is a typical residual kaolin, and it fires white because of the absence of colouring oxides.

The red firing materials are shown in Table 7.1B. The colour is caused by the presence of free iron oxide, or by iron ions in the crystal structure of illite and other minerals.

The biofly brick raw materials used consist largely of quartz, kaolinite, and montmorillonite and non-clay minerals, gypsum and talc as minor components as shown in Table 7.1C.
7.4.1 Brickmaking clays

Structural clay products are not made from clay minerals alone as seen in Table 7.1A, B and C. Plastic clays require fillers which are sometimes inert in the firing process while others must be classified as reactive. To make a dense, strong body, fluxes are also required. The 3-layer clay and micaceous minerals are, in themselves, fluxes, but kaolinitic clays require additional minerals that will produce some melting at the firing temperatures, however, the amount of liquid phase developed in structural clay products must remain small, probably around 2% or less. Excessive fluxing allows for plastic flow and serious distortion of the ware under load. On the other hand, extensive fluxing is not required to produce optimum properties in structural clay products. On firing, the silicate melts are viscous, and they produce glassy phases on cooling.

In the classical clay body, reaction occurs between the clay minerals, fluxing minerals, and minerals that can be called reactive fillers. In order to understand and be able to predict the final properties of a clay product, it is necessary to examine all of the high-temperature reactions that take place, since the phases formed determine the properties to a large extent. The paths of these reactions are determined primarily by the assemblage of minerals in the raw materials, therefore, it is absolutely necessary to know what the starting minerals are and what happens to them on firing.

Table 7.1. Typical mineral compositions for structural clay products (percent)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Fireclay</th>
<th>Gray Shale</th>
<th>White Clay</th>
<th>Blue clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>49</td>
<td>52</td>
<td>40</td>
<td>38</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>35</td>
<td>-</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>Illite</td>
<td>10</td>
<td>30</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Chlorite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Muscovite</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Microcline</td>
<td>2</td>
<td>-</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Calcite</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pyrite</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Rutile</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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B. Red-firing clays and shales (Prokopovich, 1993b)

<table>
<thead>
<tr>
<th></th>
<th>Hard, Blue Shale</th>
<th>Brown Clay</th>
<th>Red Shale</th>
<th>Black Clay</th>
<th>Soft, Gray Clay</th>
<th>Blue Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>40</td>
<td>49</td>
<td>46</td>
<td>39</td>
<td>45</td>
<td>48</td>
</tr>
<tr>
<td>Illite</td>
<td>30</td>
<td>40</td>
<td>37</td>
<td>29</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chlorite</td>
<td>14</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Sericite</td>
<td>6</td>
<td>5</td>
<td>-</td>
<td>5</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Microcline</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>8</td>
<td>1.0</td>
</tr>
<tr>
<td>Oligoclase</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Calcite</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Gypsum</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Pyrite</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Rutile</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Limonite</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

C. Biofly brick raw materials

<table>
<thead>
<tr>
<th>Eraring fly ash</th>
<th>Shellharbour sewage sludge</th>
<th>Badgery's Creek clay/shale</th>
<th>&quot;Dry&quot; biofly brick (15 S/50 FA/35 C/S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mullite Quartz</td>
<td>Gypsum Quartz Talc</td>
<td>Quartz Muscovite Montmorillonite Albite Kaolinite</td>
<td>Quartz Mullite Kaolinite Gypsum</td>
</tr>
</tbody>
</table>

A basic principle in the theory of firing of structural clay products is that the final development of an acceptable product is a dynamic process as observed by Hedges (1961). That is, the reactions, both physical and chemical, proceed towards some theoretical equilibrium but never attain it. These reactions are allowed to proceed until the product has developed the phases necessary to give the desired product, then they are arrested by cooling. The idea of a dynamic process presents the feeling of motion, and the rate of this movement becomes important to us if we are to stop it at precisely the right time. If we know where the reactions are going and how fast they are getting there, then, we can tell when the firing process gives an optimum product. The processes occurring in clay products are solid-state reactions, solid-liquid reactions, solid-gas reactions, and sintering which results in larger particles by grain growth.

The raw materials of structural clay products are complex mixtures of natural and some times synthetic minerals. Because of this complexity, the overall chemical analysis does not tell very much about what is going to happen on firing. A mineralogical analysis is a great deal more valuable. In spite of this apparent complexity, we are
fortunate that nature loves simplicity. Pauling (1968) stated that the number of essentially different kinds of constituents in a crystal tends to be small which means that even though we have a very complex chemical system, the phases that develop on heating will tend to be simple. For example, a mixture of CaO, MgO, SiO₂, Al₂O₃, and Fe₂O₃ can produce the following simple phases: CaSiO₃, Al₆Si₂O₁₃, Mg₂SiO₄, and Fe₂O₃. Because of this tendency towards simplicity, two- and three- component phase diagrams are invaluable sources of information, even though they are derived from equilibrium conditions. Phase diagrams are useful to predict the phases that will be developed because they give the ultimate goals of the reactions that are being promoted by firing. These goals may not be achieved during firing of clay products, but we will know where the reactions are going. In other words, the very complex system can be broken down into three or four simpler systems in our high-temperature reaction studies.

### 7.4.2 Sydney clays and shales

The Wianamatta Group is the main source of raw materials for the manufacture of bricks the Sydney region. It consists of the Bringelly Shale and Ashfield Shale. The reminder of the materials come from Londonderry and Hawkesbury Sandstone. There is also a small clay deposit at the Roberts Creek. Some of the characteristic properties are given below.

- **Pleistocene clay**: Pale firing and red firing, moderate to high plasticity clay.
- **Tertiary clay**: Red firing and rarely white firing, high plasticity clay.
- **Bringelly Shale**: Red firing and cream firing, low to moderate plasticity clay/shale, red and cream firing, medium to high plasticity clay (weathered shale).
- **Ashfield Shale**: Red firing, low plasticity shale and low to medium plasticity red firing clay (weathered shale).
- **Hawkesbury Sandstone**: Red firing, low plasticity shale and white firing moderate to high plasticity weathered shale from lenses in the Hawkesbury Sandstone.

For the biofly brick project, Bringelly Shale from Wianamatta Group located in Badgery's Creek area was used.
7.4.3 Reaction in buff to white-firing clays and shales

Because fireclays, like the one listed in Table 7.1A, occur naturally as well-balanced clay bodies, they are often used directly for structural clay products. This particular fireclay contains 45% clay minerals, 52% inert filler, 1% reactive filler, and 2% carbon burnout. The clay content is composed of 35% kaolinite and 10% illite, and such a combination puts it into the class of low-grade fireclay. Fireclays become higher in grade as the amount of illite decreases, and those with no illite are classed as high-grade and are used primarily for refractories.

The differential thermal analysis curve shown in Fig. 7.5 indicates the reactions taking place on firing fireclays like the low grade one described above. As the temperature is increased the curve shows carbon burnout at a, pyrite oxidation at b, dehydroxylation of clay minerals at c, and mullite nucleation at d. The mullite exothermic peak is greatly subdued over the one shown on Fig. 7.1, and this is caused by the lower degree of crystallinity of the fireclay type of kaolinite and the dilution by other minerals present.

![Differential thermal analysis curve](image_url)

Figure 7.5. Differential thermal analysis of a low grade fireclay (Brownell, 1950)

On firing a clay body of this type, properties, such as water absorption on submersion and linear shrinkage, change as shown in Fig. 7.6. Open porosity as measured by
absorption gradually decreases as firing temperature is increased while shrinkage increases due to consolidation, reactions, and melting. The decrease in shrinkage above 1177°C indicate overfiring through the formation of closed-pore bubbles in the body. Such behaviour is called bloating and is usually noticed first by a reversal of shrinkage, even though distortion of the ware may not yet be visible. Soon after shrinkage reverses, absorption increases, bloating becomes visible, and the amount of liquid phase allows plastic flow of the ware under load. Of course, structural clay products cannot be fired into the temperature range where bloating occurs. The best raw material compositions produce rather flat shrinkage and absorption curves over a range of temperatures where the values of these properties are satisfactory and the desired colour is obtained. For practical considerations it is important to have this temperature range as long as possible, since there is always a temperature differential in ceramic kilns, and it is necessary to have all the ware fired to acceptable properties regardless of temperature differences. To this end, the vertical dashed lines on Fig. 7.6 indicate the firing or maturing range for this particular fireclay. In commercial practice, the temperature differential within the kiln will be much less than the 37°C range suggested here. Small temperature differentials are all to the good as far as general uniformity of products is concerned.

Figure 7.6. Variation of fired properties produced by a fireclay typical of those used for structural clay products (Brownell, 1950)
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The X-Ray diffraction results obtained for Shellharbour biofly mix dry “Green” brick sample (15 S/50 FA/35 C/S) are presented in Table 7.1C. The minerals mainly identified are Quartz, Mullite, Kaolinite and Gypsum. This particular biofly brick material contain a high proportion of clay minerals (Quartz, Mullite, Kaolinite) and Gypsum as reactive filler. Such a combination puts it into the class of high-grade brick material.

Colour

The fired colour of fireclays is buff, even with an iron oxide Fe₂O₃ content as high a 5%. Of course this is a somewhat lower iron content than is usually encountered with red-firing, illitic clay bodies, but the quantity still does not explain the light buff colour of fireclay products because, by judicious manipulation of the firing atmosphere, fireclay products can be made in pink and light red colours. The buff colour can be explained on the basis of the ability of Fe³⁺ ions to enter the mullite crystals by substitutional solid solution. Fe³⁺ ions plays the role of Al³⁺ ions in mullite to a limited extent. When iron enters mullite, the white colour of mullite is changed to light yellow. At 1100°C, mullite can take 1.2% by weight of Fe₂O₃ into a solid solution, 3.8% at 1200°C, and 7.6% at 1300°C. This solid-solution reaction between mullite and Fe₂O₃ removes the red hematite phase from the body when enough mullite has been developed to accommodate all the iron oxide present thereby eliminating its characteristic red colour (Brownell, 1958).

The orange colour of biofly brick can be explained based on the iron and mullite content. When iron substitutes mullite, the colour changed to light yellow. At 1100°C, mullite is likely to take 1.2% by weight of Fe₂O₃ into a solid solution. This solid-solution reaction between mullite and iron removes the red phase from the body based on the quantity of mullite. Hence, the orange colour of the biofly brick.

7.4.4 Reaction in red-firing clays and shales

Illitic clay and shale compositions can be expected to mature at lower temperature than fireclays. Fig. 7.7 shows the changes in shrinkage and absorption with temperature for the hard, blue shale that was listed in Table 7.1B. The maximum firing range for good quality products including colour is from 1036°C to 1092°C. Note that this material overfires at 1121°C, and the characteristic increase in absorption after over firing. The rapid increase in shrinkage, and decrease in absorption followed by bloating...
above 1092°C, is characteristic of illitic clay bodies containing chlorite. The fired colour of illite mixtures is always red on oxidation because they do not develop a sufficiently large mullite phase to accommodate all the ferric iron in solid solution, and since Fe₂O₃ is unreactive at these temperatures, it remains, giving its red colour to the products. The phases present in this shale in the suggested firing range are mullite, quartz, hematite, and a trace of glass. Over the maturing range mullite increases while quartz decreases, and the amount of glass increases slightly.

Figure 7.7. Variation of fired properties produced by an illitic shale typical of those used for structural clay products (Brownell, 1950)

7.4.5 Effect of magnesium and calcium

Some raw clay materials have carbonates of magnesium and calcium present in the form of magnesite, calcite, or dolomite, and these minerals tend to change the course of the high-temperature reactions to the extent that quite different products are produced. In spite of certain misgivings in the industry that have directed it away from the use of calcareous clays, these materials can produce unusually good products when treated properly. On heating up to 900°C, the carbonates decompose with the evolution of carbon dioxide and leave very reactive oxides in the body. Solid-state reactions, occur between the magnesium and calcium oxides and fine quartz particles and the aluminosilicates of the clays, which are, in themselves, very reactive at this temperature.
In solid-state reactions, two reactant particles must be in contact when enough energy in the form of heat is applied to make the reaction go. This is the activation energy. If a particle of CaO touches a particle of SiO₂ in this energetic state, the first product to be formed from the reaction is Ca₂SiO₄. As the reaction progresses, the product layer separates the reacting particles by an ever-increasing distance until one of the reactant particles is consumed. The reaction continues by the diffusion of cations through the reaction product layer, and since the diffusion path becomes longer with time, the reaction rate slows down exponentially. The process is expressed theoretically by the parabolic diffusion equation (Jander, 1927).

\[
\frac{dy}{dt} = \frac{k}{y}
\]  

(7.2)

where \( y \) is the thickness of the product layer, \( t \) is time, and \( k \) is a reaction-rate constant. The equation shows that the rate of growth of the product layer is inversely proportional to its thickness. The integrated form of Eq. (7.2) becomes

\[
y^2 = 2kt
\]  

(7.3)

Attempts have been made by several scientists to set up reaction-rate equations for powders by introducing various boundary parameters that seemed realistic, but none of them fit the situations found in clay products or, in fact, in most ceramic products (Carter, 1961). The actual reaction rates in practical ceramics are always much slower at any given temperature than predicted by the rate equations developed so far. The reasons for this discrepancy are due to our inability to put in quantitative terms the probability of particle contact, grain-size distribution, particle shapes, and the extent and influence of surface diffusion.

The rate of high-temperature reactions is of great practical concern in the brick industry in order to assure completion of certain reactions in the least possible time. Probably the most important general principal of reaction rates to be appreciated by ceramists is the effect of temperature on the rate of all chemical reactions. The increase in rates with temperature is expressed by an exponential function which we call the Arrhenius equation. This equation is

\[
d \ln k/dt = \frac{E_a}{RT^2}
\]  

(7.4)
where $k$ is the reaction-rate constant as used in Eq. (7.2) and (7.3), $T$ represents absolute temperature, $E_a$ the activation energy, and $R$ gas constant. Integration of this equation gives

$$k = A \exp(-E_a/RT)$$

(7.5)

where $A$ is the integration constant. From this equation it can be inferred that the extent of reaction per mole in a unit of time is inversely proportional to the exponential value of the activation energy and directly proportional to the exponential of temperature, therefore, we must keep in mind that a slight increase in temperature causes a large increase in the rate of reaction.

The relations expressed in Eq. (7.3) and (7.5) become extremely important in the solid-state reactions involving CaO, MgO, and silicates. We shall also use the rate temperature relation expressed in Eq. (7.5) in the consideration of the proper temperature for oxidation reactions.

Calcium carbonate reacts with silica in a series of consecutive steps when excess silica is present, as is the case in structural clay products. The reaction starts as soon as the carbonate is decomposed, and certainly it will go to completion in time at 1000°C if the particle size of the reactants are small (around 20 mesh or 0.85 mm in dia.). There are three consecutive reactions in reaching the final stable phase, pseudowollastonite (CaSiO$_3$). In order of occurrence, these are

$$2\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4$$

(7.6)

$$3\text{Ca}_2\text{SiO}_4 + \text{SiO}_2 \rightarrow 2\text{Ca}_3\text{Si}_2\text{O}_7$$

(7.7)

$$\text{Ca}_3\text{Si}_2\text{O}_7 + \text{SiO}_2 \rightarrow 3\text{CaSiO}_3$$

(7.8)

The initial reaction shown in Eq. (7.6), regardless of the amount of CaO present, represents a fast reaction, but the reaction of Ca$_2$SiO$_4$ with silica is slow. The third step, presented as Eq. (7.8), is a fast reaction, therefore, the amount of Ca$_3$Si$_2$O$_7$ present at any time is small, and in properly constituted clay bodies its concentration is always negligible (Jander & Hoffmann, 1934).

This sequence of events is illustrated as Fig. 7.8 where the amounts of the various phases are given with respect to time at some constant temperature. Calcium oxide (a)
disappears rapidly as a reactant while Ca$_2$SiO$_4$ (b) quickly becomes the major phase. Since the reaction to form Ca$_3$Si$_2$O$_7$ (c) is slow and its subsequent reaction with silica to form the metasilicate is fast, calcium pyrosilicate turns out to be a transient phase, coming and going without ever building up a substantial concentration. The final phase, CaSiO$_3$ (d), start to form early in the sequence, and its concentration increases rapidly as the orthosilicate begins to disappear with time.

![Figure 7.8. Phases developed in the reactions between CaO and excess silica, curves for (a) CaO, (b) Ca$_2$SiO$_4$, (c) Ca$_3$Si$_2$O$_7$, and (d) CaSiO$_3$ (Brownell, 1963)](image)

Calcium oxide also reacts simultaneously with aluminosilicates in clay products. In addition to the above consecutive reactions with silica, gehlenite, Ca$_2$Al(AlSiO$_7$), and anorthite, Ca(Al$_2$Si$_2$O$_8$), are the products of lime reaction with dehydroxylated clay minerals. When the amount of CaO in the mixture is small (up to about 10%), anorthite is the phase produced with regard to the constitution of dryer scum, however, if the amount of CaO is 20% or more, gehlenite is produced as soon as the carbonate is decomposed. From the start of the reaction, the concentration of gehlenite increases to a maximum around 1100°C. During this period gehlenite begins to react with silica from the clay and quartz at about 1000°C to form CaSiO$_3$, and the alumina from gehlenite is released to crystallise as corundum, consequently, a well-fired, high-lime body has quartz, gehlenite, pseudowollastonite, corundum, and hematite as final phases. Practically no fusion occur up to 1100°C, so there is no glassy phase in this type of product (Brownell, 1950).

When magnesium oxide (MgO) is present in clay products as might be derived from magnesite, chlorite, or talc, the first reaction product is forsterite, Mg$_2$SiO$_4$, and it appears at about 900°C. As heating proceeds, forsterite reacts with silica to form...
enstatite, MgSiO₃, directly. Structural clay products containing magnesia are not usually fired high enough to form the magnesium aluminosilicate, cordierite.

Dolomite is a double carbonate of calcium and magnesium, and when it is the source of CaO and MgO, diopside, CaMg(Si₂O₆), is a reaction product, although, some anorthite may also be produced. These reactions take place on heating immediately after the release of the oxides from the carbonates, and free MgO is never found in clay bodies. This may be due to the fact that the double carbonate decomposes separately, and the MgO is released first to react with the dehydroxylated clay minerals.

The biofly brick raw materials presented in Table 7.1C have carbonates of magnesium and calcium present in the form of Talc (Mg₃Si₄O₁₀(OH)₂) and Gypsum (CaSO₄.2H₂O), and these minerals tend to change the course of the high temperature reactions to the extent that quite different products are produced. On heating up to 900°C, the carbonates decompose with the evolution of carbon dioxide and leave very reactive oxides in the body. Solid-state reactions, occur between the magnesium and calcium oxides and fine quartz particles and the aluminosilicates of the clay in the form of Akermanite (Ca₂MgSi₂O₇). These alkaline-earth carbonates produce excellent face biofly brick when treated properly. The actions of the calcium, magnesium and aluminosilicates in biofly brick are likely to maintain good resistance to the action of salt attack.

Lime popping

In practical structural clay bodies such as those employed for structural clay products, the total amounts of calcium and magnesium oxides, as determined by chemical analysis, rarely exceeds 15%, however, the bodies can contain twice this amount before running into the danger of having excess free lime or magnesia in the product. The presence of these oxides in the fired product causes disastrous effects because both will hydrate on exposure to atmospheric moisture and convert back to the carbonate form by reaction with carbon dioxide in the air. This hydration and carbonation results in expansions of these phases within the product and complete disintegration will occur in a few days. For this reason the clay raw materials which happen to be interbedded with limestone or dolomite must be ground to 20 mesh or finer in order to prevent lime popping. In discussion of the rates of solid-state reactions, particle size was described as a controlling factor. Larger particles of the carbonates in the raw materials cannot
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completely react after decomposition because the product layer becomes too thick, and for all practical purposes the reaction stops before all the CaO has reacted. Such particles will soon cause localized expansions which fracture the body, and when they are located near the surface, spalling occurs and a circular section of the surface of the product break off. This is known as lime popping.

The fired colour of high lime and magnesia products is buff, even though the basic clay mineral may be illite. From time to time the light colours have been attributed to the "bleaching action" of lime, however, this idea leads in an erroneous direction. CaO, MgO, or their silicates have no power to alter the red colour of hematite. As a matter of fact, calcium and magnesium silicates are white in colour and have no affinity for Fe₂O₃. As they become major phases in the product and the silicate crystals grow by continued reaction and sintering, they expel ferric ion oxide into grain boundaries. An examination of the microstructure will show points of hematite concentration where three silicate crystals join. This isolation of hematite into little pockets within the body causes the macroscopic visible appearance to be pink, buff, or yellow depending on the relative concentrations of the alkaline-earth silicates and hematite and on the extent of grain growth.

An example of the development of fired properties with an illitic clay containing dolomite and quartz is given in Fig. 7.9. This particular mixture contains 7.5% CaO and 6.6% MgO. The unusual characteristics shown are the maintenance of high absorption and low shrinkage until a temperature of 1147°C is reached, when melting occurs abruptly. Upon comparing the curves of Fig. 7.9. to those of Fig. 7.7, the action of the alkaline earth oxides becomes strikingly apparent. The product appears to be more refractory at low temperatures and certainly more porous when calcium and magnesium silicates are present. Note also the narrower firing range for the production of satisfactory quality products.

The action of alkaline-earth oxides to reduce the amount of liquid phase produced below 1092°C can be used to good advantage in some cases. Illitic clays and shales that contain chlorite and sericite may develop a liquid phase at temperatures below the point where stable crystalline phases are produced. In such cases the shrinkage and absorption values are within acceptable limits, but the product will not withstand moisture and chemical attack as it should. Further firing of such products produces too much liquid phase, and severe slumping and distortion occurs.
The addition of just 3% CaO as CaCO₃ to this type of raw material extends the firing range by at least 37°C. MgO or SrO can be used for the same purpose, and from the stand-point of quality, SrO is probably the best. The influence of 3% CaO to a low temperature clay body is shown in Fig. 7.10. The curves in this figure were derived by heating a specimen under a load of 172 kPa and measuring the change in height parallel to the applied load. Up to 871 °C, the expansion of the clay body without CaCO₃, represented by a dashed line, is due to thermal expansion, but the rapid subsidence thereafter is caused by a loss of strength as a liquid phase develops. This low temperature melting and the resultant distortion under load was corrected by the CaO addition and is represented by the solid line.

Figure 7.9. Variations of fired properties produced by an illitic clay containing dolomite (Brownell, 1963)

Figure 7.10. The effect of CaO addition to a clay body on the high temperature slumping behavior. Solid line represents the addition and the dashed line without (Brownell, 1963)
Now, the same clay products can be fired to 1038°C with equivalent absorptions and shrinkages without slumping under load. The higher temperature product will be more stable against various service conditions, and all of this is accomplished with 3% addition of calcium oxide.

A caution is introduced here for those unaccustomed to dealing with calcium carbonate in the clay raw materials. This addition will immediately create dryer scum if the dryer is contaminated with sulphurous gases. Such a situation must be cleared up before pulverized limestone can be used as an additive to increase firing range and temperature. The substitution of strontium carbonate in this situation would alleviate this difficulty, but it may be more costly.

The biofly brick results for pitting due to lime particles have indicated "Nil" for all the mixes as given in section 6.8 chapter 6. Hence, the amount of alkaline-earth oxides in biofly bricks is likely to be less than 30%.

**7.4.6 Effect of calcium sulphate**

The reaction between calcium sulphate and the quartz-clay mixture should be of some concern to the structural clay products industry because it is related to the efflorescence problem and the contamination of dryer air with sulphurous gases. Calcium sulphate occurs in many clay and shale deposits in the form of gypsum, and it can be created in the body during the drying operation. Incidentally, magnesium sulphate is of little concern in these matters, since it will completely decompose in one hour at a temperature as low as 971°C, then MgO is free to react with the silicates as usual. On the other hand, calcium sulphate does not decompose by itself in the temperature ranges of most structural clay products. Calcium sulphate requires about two-and-a half hours to completely decompose at 1316°C, and the extent of decomposition in any reasonable length of time at 1204°C is negligible (Brownell, 1963).

Calcium sulphate will react with silica and aluminosilicates and liberate sulphurous gases at considerably lower temperatures than those required for simple decomposition. An example of this type of reaction is expressed in the following equation.

$$2\text{CaSO}_4 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\text{SO}_3$$  \hspace{1cm} (7.9)
Some particular cases of reactions between calcium sulfate and silicate and an aluminosilicate are illustrated on Fig. 7.11. The solid lines show the extent of the reaction between calcium sulfate and cristobalite during the first hour at two temperatures of interest to us. It can be seen that the reaction is very slow at 1055 °C, but it goes nearly to completion in one hour at 1117 °C. The dashed lines indicate that the activation energy for the reaction of calcium sulfate with mullite is lower than that for cristobalite. The CaSO₄ mullite mixture reacts appreciably at 1022°C and goes practically to completion in 30 minutes at 1097°C. These reactions were carried out on uncompacted powders with a large excess of cristobalite and mullite to increase the probability of reactant particles in surface contact (Brownell, 1963).

An examination of the results of the experiments described by Fig. 7.11 shows that there is a good possibility that some calcium sulphate will remain unreacted in some structural clay products where the maximum firing temperatures are from 1010°C to 1066°C. These are typical firing temperatures for illitic clay products. Even if a trace of the sulphate remains, it will cause efflorescence when the product is exposed to moisture due to the solubility of this salt. In addition, these reactions are going on with the evolution of sulphurous gases in the furnace zone of tunnel kilns, therefore, great care should be taken to prevent these gases from entering the waste-heat air for drying purposes. Since these reactions are slow around 1038°C, there is a good possibility that they will continue to evolve sulphurous gases in the top of the cooling zone where the temperature is still high enough for the reactions. When this happens it would be impossible to keep sulphur contamination out of the dryer atmosphere if cooling air is used.

![Figure 7.11. CaSO₄-cristobalite and CaSO₄-mullite reactions at various temperatures. Solid lines are for the cristobalite reactions, and dashed lines represent reactions with mullite (Brownell, 1963)](image-url)
In the biofly brick process, the presence of calcium sulphate (CaSO4) derived from Gypsum (CaSO4.2H2O) as shown in Table 7.1C is likely to react with Cristobalite (SiO2) between 1055°C and 1100°C. However, the reaction with Mullite (Al6Si2O13) likely to be between 1022°C and 1097°C during the vitrification stage of biofly brick process. Hence, the advantage to have a body of high durability and strength.

When one learns how to handle clay raw materials containing alkaline-earth carbonates, excellent face bricks, structural tile, and quarry tile can be made. The actions of the calcium, magnesium, and strontium silicates and aluminosilicates in clay products are to increase the coefficient of linear thermal expansion, reduce secondary moisture expansion to negligible values, maintain good resistance to the action of frost in spite of the increased absorption, and provide for narrower dimensional tolerances. The increased thermal expansion coefficient is of primary concern to those applying glazes to these products. It is a distinct advantage to have a body of higher thermal expansion if low-temperature glazes are to be applied. The reduction in long range moisture expansion is due to the lower amount of glassy phase in these products.

7.5. Thin sectioning microscope analysis

Identification of clay minerals often requires the application of a number of auxiliary techniques, such as chemical, differential thermal analysis, and others. A chemical analysis gives only the amount of chemical elements that are present, it does not give information about how these elements are combined with one another. Thin sectioning using polarized light microscopy gives principal crystallographic pattern, and hence, gives the actual minerals that are presented in a mixture and how they are combined together.

Kiln dry and fired samples were cut from selected bricks from two batches, namely 15% S/50% FA/35% C/S Shellharbour biofly brick and 100% clay/shale brick for thin sectioning microscope analysis. Specimens from each of the two types of bricks were prepared for thin sectioning analysis at the Department of Geology of the University of Wollongong. Two 10 mm thick slabs were sliced, from each brick. Slices were taken at a position approximately midway along the longitudinal face. The “open” porosity cut face of each slice was impregnated with a low viscosity, blue coloured epoxy resin. Approximately 2 mm from the face of each sample was ground off using coarse carborundum powders. A slice, measuring approximately 50 mm by 25 mm, was cut
from each slab, glued to a glass slide and ground down to a thickness of 30 mm (0.030 mm). A coverglass was attached to the thin section with Canadian balsam. For observation and analysis, the thin section was mounted in a Leitz orthoplan microscope and observed in transmitted light at a nominal microscope magnification of 1 x = 9.31 mm, 2.5 x = 3.95 mm and 10 x = 1.11 mm. The results of the thin section are illustrated by photographs in Figures 7.12 through 7.34.

**Key**

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>White particles</td>
</tr>
<tr>
<td>Sludge</td>
<td>Black spots</td>
</tr>
<tr>
<td>Clay</td>
<td>Dark brown particles</td>
</tr>
<tr>
<td>Shale</td>
<td>Brown particles</td>
</tr>
<tr>
<td>FeOx</td>
<td>Orange particles</td>
</tr>
<tr>
<td>Quartz</td>
<td>Black particles</td>
</tr>
<tr>
<td>Felspar</td>
<td>White-brown-yellow particles</td>
</tr>
</tbody>
</table>

**Biofly Dry Brick**

Thin sections of Figures 7.12-7.17 illustrates the typical features and characteristics of biofly dry brick 65S mix.

Figure 7.12 illustrates matrix of fly ash in white circles with FeOx in orange lower right hand side of the picture and Quartz in black spots can be observed, micro cracks can be detected by the blue resin.

Figure 7.13 illustrates matrix of fly ash, FeOx, Quartz and silicon bonding together can be detected with very few spots of micro cracks detected by blue resin, a spot of sludge can be observed on the upper centre of the picture.
Figure 7.12. Thin section of Biofly dry brick sample-Field of view 1.11 mm.

Figure 7.13. Thin section of Biofly dry brick sample-Field of view 1.11 mm.
Figure 7.14 illustrates adequate bonding between fly ash, quartz, felspar and silicon can be observed. However from the texture it can be observed micro cracks length (4.2 mm) primarily connected with the drying stage of the brick.

Figures 7.15. and 7.16 illustrates poor bonding between fly ash and fine clay with large particles of shale stone (2.7 mm) can be observed by a resin ring completely encircling the particle. Cracks are observed in the early stage with drying. However compaction of the matrix looks satisfactory.

Figure 7.17 illustrates an adequate bonded matrix. However micro cracks connected with drying, can be observed in the lower right hand side of the picture. Shale stone particles can be detected and a spot of sludge can be observed on the left hand corner of the picture.
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Figure 7.15. Thin section of Biofly dry brick sample-Field of view 3.95 mm.

Figure 7.16. Thin section of Biofly dry brick sample-Field of view 9.31 mm.
Clay/Shale Dry brick

Figures 7.18-7.22 illustrates the thin section feature and characteristics of 100% clay/shale dry brick.

Figure 7.18 shows the presence of a felspar particle which is adjacent to very large pores. The pores being quite irregular in cross section, and of maximum dimension approaching 3.16 mm. The large pores were dispersed throughout the full area of the sample. The parallel cracking, which was observed in the biofly dry brick, was not observed in the clay brick. A number of coarse grain particles were detected whose sizes are approximately 1.9 mm and it is compacted through the fine grain particles.

Figure 7.19 illustrates felspar in coarse grain matrix observed with poor bonding recognised by a resin ring completely encircling the shale particle in light brown. Internal porosity exhibited with blue resin. Quartz and FeOx also detected.
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Figure 7.18. Thin section of Clay/Shale dry brick sample-Field of view 3.95 mm.

Figure 7.19. Thin section of Clay/Shale dry brick sample-Field of view 1.11 mm.
Figure 7.20. Thin section of Clay/Shale dry brick sample-Field of view 9.31 mm.

Figure 7.21. Thin section of Clay/Shale dry brick sample-Field of view 3.95 mm.
Figure 7.20 illustrates FeOx compacted in the matrix with fine and coarse grains was observed, felspar in the upper centre and lower corner of the picture. Spots of resin detected through out the matrix.

Figure 7.21 illustrates very porous type of material surrounded by coarse grains, considerable porosity exists with poor bonding of particles.

Figure 7.22 illustrates very high porosity in mixed grains, with shale particles been observed in light brown which reflect poor bonding in the matrix. Irregular shape of cracking were detected with particles of felspar, FeOx and Quartz.

Figure 7.22. Thin section of Clay/Shale dry brick sample-Field of view 9.31 mm.

- Thin section analysis for dry bricks illustrated that there were no similarities between the two types of bricks regarding pores phenomena. Biofly bricks contained micropores and enechelon type of cracking in the matrix however clay/shale bricks contained larger pores and large cracking in the matrix as indicated in the figures.
• In addition, some poorly bonded inclusions especially around shale stones were observed in both types of bricks illustrating the similarities between the two types regarding inclusion phenomena.

• Generally the matrix for both bricks exhibited different types of fractured surface topography. In comparison, clay/shale brick exhibited rough fracture surface texture with large pores being evident however biofly brick exhibited powdery fracture surface texture with micropores being evident.

• In general, the biofly brick matrix exhibited good compaction of materials, which is related to the fine particles of fly ash however in the clay/shale matrix there is less fine particles producing a matrix in which individual shale particles were weakly bonded.

**Biofly Fired Brick**

Thin sections of Figures 7.23-7.28 illustrates the features and characteristics of Biofly Fired Brick (65 S mix).

![Figure 7.23. Thin section of Biofly fired brick sample-Field of view 3.95 mm.](image-url)
Figure 7.23 illustrates felspar mineral originally from clay on the right hand side of the picture in white yellow brown colour, fly ash cenospheres, spots of FeOx and quartz in black colour. The enechelon cracks length roughly (1.2 and 1.5 mm) in blue colour showing the porosity.

Figure 7.24 illustrates poor bonding between FeOx, Quartz and the matrix shown by the blue colour around the Quartz. In general, relatively large discrete pores (diameter 1.0 mm) were observed, these pores considered to be the result of the shrinkage.

![Quartz](image)

**Figure 7.24. Thin section of Biofly fired brick sample-Field of view 3.95 mm.**

Figure 7.25 illustrates several relatively large enechelon in the sample. These regularly shaped enechelon having a length roughly between 0.9 and 0.8 mm extended through the length of the thin section, fine grained fly ash can be observed, spots of black Quartz and red FeOx can be detected.

Figure 7.26 illustrates very fine porosity can be detected by many blue resin particles, which reflect poor bonding between the fly ash matrix, the spots of Quartz and FeOx. Cracks cannot be observed in this picture.
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Figure 7.25. Thin section of Biofly fired brick sample-Field of view 1.11 mm.

Figure 7.26. Thin section of Biofly fired brick sample-Field of view 9.31 mm.
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Figure 7.27. Thin section of Biofly fired brick sample-Field of view 3.95 mm.

Figure 7.28. Thin section of Biofly fired brick sample-Field of view 9.31 mm.
Figure 7.27 illustrates significantly large cracks showing a large amount of shrinkage. The presence of felspar is seen in white and black colour and Quartz originally from clay observed in the upper left hand side of the picture.

Figure 7.28 illustrates very high porosity by the cracks, felspar particles in brown colour can be detected between (2.4 and 1.1 mm), with fragmentation of black FeOx, and poorly bonded fly ash particles.

**Clay/Shale Fired brick**

Thin sections of Figures 7.29-7.34 illustrates the features and characteristics of 100% Clay/Shale Fired brick.

Figure 7.29 illustrates high porosity with different shape and texture of cracks, like fragmented irregular cracks in cross section. The parallel cracking, which was observed in biofly brick was not observed here. Felspar was detected on the upper right hand side of the picture plus spots of FeOx.

![Figure 7.29. Thin section of Clay/Shale fired brick sample-Field of view 3.95 mm.](image)
Figure 7.30 illustrates considerable porosity fragmented by blue resin, however resin impregnation was not as complete. Felspar and Quartz was detected on the top left hand corner. Shale stone particle can be recognised in the upper right hand exhibiting internal porosity.

Figure 7.30. Thin section of Clay/Shale fired brick sample-Field of view 3.95 mm.

Figure 7.31 illustrates micro porosity observed with fewer large pores. Individual particles are generally poorly bonded. Felspar, Quartz and FeOx fragmented through the matrix were also observed.

Figure 7.32 illustrates closed fine porosity indicated with good compaction and fine texture. A considerable amount of FeOx is observed and are black in colour. Although the light coloured particles appear bonded with the matrix.

Figure 7.33 illustrates very fine texture with closed porosity, the pores being quite irregular in cross section. Felspar and FeOx were detected in the lower middle of the picture with two large particles of shale stone with brown colour exhibiting fine internal porosity.
Figure 7.31. Thin section of Clay/Shale fired brick sample-Field of view 3.95 mm.

Figure 7.32. Thin section of Clay/Shale fired brick sample-Field of view 3.95 mm.
Figure 7.33. Thin section of Clay/Shale fired brick sample-Field of view 3.95 mm.

Figure 7.34. Thin section of Clay/Shale fired brick sample-Field of view 9.31 mm.
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Figure 7.34 illustrates considerably high porosity with irregular pores shown throughout the matrix. Shale stones in light brown colour is recognised with fine internal porosity with spots of FeOx also detected.

- Thin sectioning for fired bricks confirmed the porosity as determined by water absorption testing indicated in Chapter 6. Absolute values of porosity, using thin section and point counting techniques, were not estimated due to lack of equipment such as an automatic point counter.

- The irregular shapes of the pores can be easily observed in clay/shale brick however enechelon types of pores can be easily detected in biofly brick, confirming that the normal assumptions of cylindrical pores does not hold true for the two types of bricks.

- The ill-defined pore structure for clay/shale brick was highlighted and its coarse, large-pored nature was obvious. Poor bonding of much of the shale was evident for the two types of bricks.

7.6. X-Ray diffractometry

It is important to review the reactions that takes place on heating some of the important disilicate minerals. The raw materials for the biofly brick will likely to contain these minerals, therefore, they are bound to have important influences on the final product and on the way that the final phases are achieved. It has been found that a single disilicate mineral may break down on heating to provide as many as four new compounds, to serve as reactants with each other and other minerals present. In many cases, one or more of these decomposition products remains in the final product and exerts its influence on the properties. This is likely to be the case in biofly bricks. Hence X-Ray diffraction technique are used to evaluate the phase changes during firing of the biofly brick.

7.6.1. Raw materials

X-Ray diffraction patterns were made for the biofly raw materials namely the Shellharbour sludge, Eraring fly ash and Badgery's creek clay/shale to determine and compare the mineralogical characteristics of the raw materials of the biofly brick. Each material was pulverised with a mortar and pestle to produce a powder <75 μm suitable
for placing in aluminium mounts. The pulverised material was lightly compacted in the mount ready for powder X-Ray diffractometry.

Absolute X-Ray wavelengths were measured at the Department of Geology by means of diffraction by ruled gratings. With this technique, the wavelength $\lambda$ is given by the relation

$$n \lambda = a \{ \cos \phi - \cos (\phi + \alpha) \}$$

where $n$ is of the order of the diffraction spectrum, $a$ is the spacing of the grating, $\phi$ is the glancing angle of incidence, and $(\phi + \alpha)$ the glancing angle of diffraction. The values of $a$, $\phi$, and $\alpha$ are capable of being measured with great accuracy, and the ruled-grating method yields the best absolute wavelength values.

Key

<table>
<thead>
<tr>
<th>Letter</th>
<th>Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>Quartz</td>
</tr>
<tr>
<td>G</td>
<td>Gypsum</td>
</tr>
<tr>
<td>T</td>
<td>Talc</td>
</tr>
<tr>
<td>M</td>
<td>Mullite</td>
</tr>
<tr>
<td>K</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>MO</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>A</td>
<td>Albite</td>
</tr>
<tr>
<td>C</td>
<td>Cristobalite</td>
</tr>
<tr>
<td>MA</td>
<td>Margarite</td>
</tr>
<tr>
<td>A*</td>
<td>Akermanite</td>
</tr>
</tbody>
</table>

Figure 7.35 shows the X-Ray diffraction patterns determined for raw Shellharbour sludge fraction. The material was tested in the “as-received” condition. The XRD technique revealed that the sludge essentially consists of the minerals Gypsum, Quartz and Talc.

Figure 7.36 shows the X-Ray diffraction patterns determined for raw Eraring fly ash fraction in the as-received condition. This sample consisted mainly of Mullite and Quartz.
Figure 7.37 shows the X-Ray diffraction patterns determined for raw Badgery’s Creek clay/shale fraction in the as received condition. The material mainly consisted of Quartz, Muscovite, Montmorillonite, Albite and Kaolinite.

### 7.6.2. Brick material

**Biofly dry brick**

Samples for X-Ray diffraction were taken from dry and fired brick of Shellharbour mix (65S) consisting of 15% S + 50% FA + 35% C/S. The samples were pulverised with mortar and pestle to produce a powdered material <75 µm suitable for placing in aluminium mounts. The pulverised material was lightly compacted to mount ready for powder X-Ray diffractometry.

The X-Ray diffraction patterns obtained for Shellharbour mix dry brick sample are presented in Figure 7.38. The minerals mainly identified here were Quartz, Mullite, Kaolinite and Gypsum. However the raw materials used for the biofly brick consisted mainly of Quartz, Kaolinite, Mullite, Gypsum, Muscovite, Montmorillonite, Albite and Talc. Hence it can be seen that, after compaction that Montmorillonite, Muscovite, Albite and Talc are not recognised by the XRD patterns because make up only a small proportion of the raw material.

**Biofly fired brick**

The X-Ray diffraction patterns obtained for Shellharbour mix fired brick sample are presented in Figure 7.39. The minerals mainly identified were Quartz, Mullite, Cristobalite, Akermanite and Margarite. It can be seen that, after firing, the Kaolinite has transposed to Mullite + Cristobalite with some enhancement of Akermanite and Margarite. The recrystalisation of the minerals to Mullite was common in fired brick and Cristobalite is occasionally detected in hard fired brick. Mullite is a hard, chemical resistant phase in fired brick, and its elongated crystal structure provides great strength. The glassy phase resulting from the fusion promotes a strong body and both Mullite and Cristobalite give the brick strength and durability. The overall chemical equation for the stable phases involved in the heating of kaolinite was indicated earlier in equation 7.1.
Clay/Shale fired brick

The X-Ray diffraction patterns obtained for clay/shale fired brick sample are presented in Figure 7.40. The minerals identified were Quartz and Mullite. Hence, the presence of very small quantity of Muscovite, Montmorillonite and Albite is not indicated by X-Ray diffraction. However the Kaolinite from clay/shale dry brick sample as indicated above in Fig 7.37 is most likely to be transposed to Mullite. The recrystalisation of the minerals to Mullite was common in both biofly brick and clay/shale brick. However, it has been found that the minerals in raw fly ash and fired clay/shale were namely Mullite and Quartz, this type of similarity shows that fly ash can be used very easily to replace the clay/shale in biofly brick.

7.6.3 Development of Mullite and Cristobalite

One of the most important and common examples of a material exhibiting polymorphism in the ceramic industry is silica SiO$_2$. Silica exhibits both types of transformations. Reconstructive transformation involves the three forms of silica: quartz, cristobalite and tridymite, but it must be emphasized that only the quartz is commonly found in fired bricks. Cristobalite is occasionally detected in hard fired bricks. However, it is exhibited in biofly bricks.

The transformation of quartz to cristobalite is slow and dependant on the biofly brick temperature, and time of firing, also on the presence of mineralizers which promote the change. The amount of cristobalite formed in biofly brick for a particular firing temperature depends largely on the size of the particles of quartz present. The change takes place from the outer surface of each particle and then progresses inwards, hence the greater the surface exposed, the more finely ground the material, the greater the degree of conversion. The volume changes, even if large, do not occur suddenly and do not disrupt a body.

Displacive transformation is exhibited by each of the three forms of silica. The change between the two forms of quartz occurs rapidly as the temperature changes around 573 °C.
Figure 7.35 X-Ray diffraction for Shellharbour sludge
Figure 7.36 X-Ray diffraction for Eraring fly ash
Figure 7.38. X-Ray diffraction for Shellharbour dry brick sample
Figure 7.40. X-Ray diffraction for Clay/Shale fired brick sample
The sudden expansion or contraction of about 2% by volume which accompanies the transformation can result in cracking during heating or cooling of the brick in the kiln. Cooling cracks, or dunts are more common due to the fact that as the brick cools and contracts in the normal way, the outside is cooler than the interior and is thus shrinking in advance of the inside. This means that the outside is in tension and the sudden increase in the tensile stresses, in the outer layers, as the \( \beta \rightarrow \alpha \) transformation occurs, may be sufficient to exceed the strength of the material so that it fractures. During heating, the converse applies and the stresses in the outer layer are compressive. Since the compressive strength of most ceramic products is usually more than ten times greater than the tensile strength, the risk of cracking is correspondingly lower (Prokopovich, 1993a).

Cristobalite also exists in \( \alpha \) and \( \beta \) modifications, the displacive change in this case occurring around 220\(^\circ\)C and the accompanying volume change is about 5%. Cristobalite, however, as indicated above is not usually found in the clay fired brick.

The practical significance of the presence of materials exhibiting displacive transformation is that the heating and/or cooling cycles must be such that the temperature change over a particular inversion point is very gradual, otherwise failure of the brick may occur.

7.7. Summary

The theoretical aspects of the firing process of clay products as well as the thin sectioning and XRD analysis of the biofly bricks and clay/shale bricks were described in this chapter. The important conclusions are:

- The object of firing a clay product is to convert a fairly loosely compacted blend of various minerals into a strong, hard, and stable product. In the path of achieving this conversion, many chemical and physical processes come into play.

- The properties of the final product such as strength, porosity, stability against the action of moisture and chemicals, thermal expansion, thermal conductivity, and hardness are determined by the kind and amounts of the various phases resulting from the firing process.
• The raw materials of structural clay products are complex mixtures of natural and some times synthetic minerals. Because of this complexity, the overall chemical analysis does not tell very much about what is going to happen on firing. A mineralogical analysis is a great deal more valuable.

• Phase diagrams are useful to predict the phases that will be developed because they give the ultimate goals of the reactions that are being promoted by firing. These goals may not be achieved during firing, but we will know where the reactions are going. In other words, the very complex system can be broken down into three or four simpler systems in our high-temperature reaction studies.

• The clay minerals have a number of characteristics in common. Important differences among them, however, lead to their subdivision into main groups. Simplified classification of the clay minerals is given below.

Group 1: Kaolinite group
Group 2: Illite group
Group 3: Montmorillonite group
Group 4: Chlorite group

• When kaolinitic clays are fired, the presence of mullite in the product denotes a well-fired body. Mullite is a hard, chemical resistant phase in clay products, whose elongated crystal structure provides great strength.

• Illitic clays are fired from 1038°C to 1082°C. The glassy phase of mullite resulting from the fusion promotes a strong body with a reduction in porosity, and mullite gives it strength and durability.

• As with illite, montmorillonite melting starts around 1050°C, spinel and hematite quickly dissolve and mullite crystals emerge, resulting in the only two phases present being mullite and a silicate liquid, tending to give a strong body.

• The most important nonclay disilicate mineral affecting the properties of fired structural clay products is chlorite. It is commonly found in illitic shales and clay deposits derived from them. Because of the alternate stacking of trioctahedral mica and brucite layers, the different structural relations between magnesia and silica produce unique phases on firing.
Biofly brick raw materials likely to be classified as clay minerals, contain predominantly kaolinite group plus a small amount of illite group. This is classed as a high-grade type of clay.

The most common tool used in observing high temperature reactions is X-ray diffraction. It tells us the temperature ranges at which changes occurred, and from these thermal effects, we can infer the type of reactions occurring. This technique had been used to identify Biofly brick raw materials as well as green and fired bricks.

A more detailed study into the identity of the crystal structures were indicated using polarized light microscopy using thin sections. An understanding of how these minerals combined with one another was gained by this method.

It has been found that after firing, the Kaolinite has transposed to Mullite + Cristobalite. The recrystalisation of the minerals to Mullite was common in fired brick.

It was shown that mineralogical analysis of raw fly ash and fired clay/shale were namely Mullite and Quartz, this type of similarity shows that fly ash can be used to replace the clay/shale in biofly brick.

Thin sectioning of fired bricks confirmed the irregular shapes of the pores which can be easily observed in clay/shale brick however enechelon types of pores can be easily detected in biofly brick. The ill-defined pore structure for clay/shale brick was highlighted and its coarse large-pored nature was obvious.

Thin section analysis for dry bricks illustrated that there were no similarities between the two types of bricks regarding pores phenomena. Biofly bricks contained micropores and enechelon type of cracking in the matrix however clay/shale bricks contained larger pores and large cracking in the matrix as indicated in the figures.

In addition, some poorly bonded inclusions especially around shale stones were observed in both types of bricks illustrating the similarities between the two types regarding inclusion phenomena.
• Generally the matrix for both bricks exhibited different types of fractured surface topography. In comparison, clay/shale brick exhibited rough fracture surface texture with large pores being evident however biofly brick exhibited powdery fracture surface texture with micropores being evident.

• In general, the biofly brick matrix exhibited good compaction of materials, which is related to the fine particles of fly ash however in the clay/shale matrix there is less fine particles producing a matrix in which individual shale particles were weakly bonded.

• Thin sectioning for fired bricks confirmed the porosity as determined by water absorption testing indicated in Chapter 6. Absolute values of porosity, using thin section and point counting techniques, were not estimated due to lack of equipment such as an automatic point counter.

• Thin sectioning of fired bricks confirmed the irregular shapes of the pores which can be easily observed in clay/shale brick however enechelon types of pores can be easily detected in biofly brick. The ill-defined pore structure for clay/shale brick was highlighted and its coarse large-pored nature was obvious.
Chapter Eight

Leachability Studies

8.1. Introduction

Balanced against the positive benefits prospectively associated with biofly brick manufacture, concerns have been raised in regard to the fate of hazardous contaminants which might be introduced either to the brick manufacturing operation or the finished products through fly ash and sewage sludge addition. It might be reasonable to expect that thorough combustion of the sewage sludge at 1100°C all volatile organics would have been expelled as flue gas. However, the fate of toxic and hazardous inorganics, and particularly heavy metals, will remain within the brick matrix which may be of some concern.

Hence, this chapter will examine the fate of metal contaminants introduced into biofly brick by fly ash and sludge additions. Two such “fates” will be specifically addressed, the prospective loss via emission of metals during firing (in chapter 9) and subsequent metal losses due to natural weathering of an exposed brick surface using an available leaching test.

8.2. Leachability testing an overview

A number of generally stringent leaching tests have been developed that generate leachates from wastes under standardised conditions. Tests that are recognised by Environment Protection Authority of New South Wales include the USEPA’s Toxicity Characteristics Leaching Procedure (TCLP) and the American Society for Testing and Materials method ASTM D-3987 (1993).

In short, TCLP and ASTM tests consist of shaking the waste with a leaching medium for 18 hours and then filtering the leachate. The longer the duration of a leaching test, the more closely the concentration of the contaminants approaches a measurement of
their equilibrium concentration. This concentration is a thermodynamically constant value for the particular conditions and represents the upper level of solubility.

This is important because it means that such an equilibrium concentration is the highest level that will be obtained under those conditions. In many cases a standard leaching test should give results approaching the equilibrium concentrations and are thus "worst case" values, in others the concentrations would be limited by the rate of dissolution. The test, therefore, is a stringent one.

This equilibrium solubility of a contaminant is directly related to the "fugacity" also called "Gibbs free energy" of that contaminant. Fugacity is the potential for the contaminant to "flee" or "escape", its availability. Clearly the more available or soluble the contaminant, the greater its potential to harm. Most of the earth's rocks and soils are not very soluble, they have a low fugacity and are said to be geochemically stable. When wastes are able to be treated so that potentially hazardous contaminants have a low concentration in the leachate, they have a low potential for harm with a geochemical stability similar to the earth's rocks and soil (Fred Koo, 1993).

Hence, Toxicity Characteristics Leaching Procedure (TCLP) approved by Environment Protection Authority of New South Wales to define whether a leachate waste should be classified as hazardous or non-hazardous, was chosen as the appropriate leachate test (chapter 4).

8.3. Leachability of metals in sewage sludge ash

Bridle et al, (1990) investigated the leachate properties of the bed sewage sludge ash from the trial run at 786°C obtained from the oil from sewage sludge process. The USEPA toxic characteristic leaching procedure (TCLP), method #1310 was used. If leachate is classified non hazardous, the waste is considered suitable for disposal in a conventional sanitary landfill. Results from the TCLP for sludge ash are shown in Table 8.1. The data shown in Table 8.1 indicated that the leachate readily meets NSW EPA criteria and that the sewage sludge ash will be classified as non-hazardous.
Table 8.1. Sludge ash leachability results using TCLP (Bridle et al, 1990)

<table>
<thead>
<tr>
<th>Element</th>
<th>TCLP leachate (mg/L)</th>
<th>NSW EPA limit (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.07</td>
<td>5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.005</td>
<td>1</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.085</td>
<td>5</td>
</tr>
<tr>
<td>Copper</td>
<td>0.430</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;0.001</td>
<td>5</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.00005</td>
<td>0.2</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.17</td>
<td>50</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.0025</td>
<td>1</td>
</tr>
</tbody>
</table>

8.4. Leachability of sewage melted slag

In Japan, melting plants for sewage sludge are attracting great attention for their capability to produce molten slag and the possibility for their effective application as brick making material. Several plants have already commenced operation. Oku et al, (1990) have developed a new sewage sludge melting system, a melting after carbonizing sludge system, using a swirling flow melting furnace.

In this melting system the dewatered sludge cake is stored in a conical-silo type hopper, delivered quantitatively and fed to a fluidized-bed carbonising furnace. The sludge cake is carbonized in the furnace and the residue is separated by a cyclone. The separated residue is immediately charged into a swirling flow melting furnace in order to effectively utilize the heat of the separated residue. Slag discharged from the swirling flow melting furnace is cooled and solidified by an air/water-cooled slag removing device.

Oku et al., conducted leachate test using Japanese standard for different types of melting slag. Table 8.2 shows leachate test results of the slag. All the slag showed no leaching of harmful substances above detection limits.
Table 8.2. Sewage slag leachate test results (Oku et al, 1990)

<table>
<thead>
<tr>
<th>Element</th>
<th>Air rapidly cooled slag</th>
<th>Air slowly cooled slag</th>
<th>Water cooled slag</th>
<th>Detection limit (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl Mercury</td>
<td>below detection limit</td>
<td>below detection limit</td>
<td>below detection limit</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Total Mercury</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Lead</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Hax. Chromium</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Total Chromium</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Arsenic</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>PCB</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
</tr>
</tbody>
</table>

8.5. Leachability of sludge amended bricks

Alleman et al. (1990) have reported the successful laboratory and field scale production of bricks made from sewage sludge. The sludge used has a solids content of 35% by volume and is mixed with clay in varied proportions.

Spiked metal additions were incorporated in order to achieve final metal levels including background presence ranging from 0 to 1000 ppm, measured as mg metal/kg dry brick. The chemicals used for these spiked additions were first solubilized in a known volume of water and then blended with the clay/shale sludge mixture in the Hobart mixer. Final metal analyses were conducted using an atomic absorption spectrophotometer.

The potential for post firing leachate metal losses from these amended bricks was investigated by their repeated submergence, drying cycling in acetic acid baths held at pH levels of 2.5. This exposure was continued for a 7 day period, using a repetitive 2 hr soak and 2 hr dry cycle. Experimental results are given in Table 8.3.

The listed EPA maximum values given in table 8.3 are provided only for comparative purposes. Currently no defined criteria is available to determine permissible levels of metal leachate from these sludge amended bricks. However, the levels of most metals being released at pH 2.5 are low. The exceptions to this generalization would appear to be arsenic and selenium whose leachate losses were both in the parts per million range and cadmium which tended to be leached in the range of 1 ppm for heavily spiked brick.
### Table 8.3. Metal leachate losses with amended brick at pH 2.5

<table>
<thead>
<tr>
<th>Pre fired metal level (mg/kg)</th>
<th>As</th>
<th>Se</th>
<th>Cd</th>
<th>Zn</th>
<th>Pb</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.01*</td>
<td>2.00*</td>
<td>0.05*</td>
<td>0.18*</td>
<td>0.07*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.13</td>
<td>2.80*</td>
<td>0.96*</td>
<td>0.08</td>
<td>0.19*</td>
<td>0.13*</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>0.28</td>
<td>0.55*</td>
<td>3.90*</td>
<td>0.13</td>
<td>0.09*</td>
<td>0.25</td>
<td>0.24</td>
</tr>
<tr>
<td>40</td>
<td>0.40</td>
<td>0.35*</td>
<td>0.23*</td>
<td>0.16</td>
<td>0.11*</td>
<td>0.99</td>
<td>0.60</td>
</tr>
<tr>
<td>2.7</td>
<td>0.40</td>
<td>0.23*</td>
<td>0.38</td>
<td>0.11*</td>
<td>0.07</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>3.9</td>
<td>0.67</td>
<td>1.30*</td>
<td>0.44</td>
<td>0.16*</td>
<td>0.88</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.85</td>
<td>0.52*</td>
<td>0.75</td>
<td>0.21</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>0.92</td>
<td>0.36*</td>
<td>0.05</td>
<td>0.23</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>0.73</td>
<td>0.63*</td>
<td>0.06</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>0.88</td>
<td>0.55*</td>
<td>0.03</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>1.10</td>
<td>0.24*</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>1.00</td>
<td>0.88</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.40</td>
<td>0.37*</td>
<td>0.14</td>
<td>0.15</td>
<td>0.12</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>40.0</td>
<td>1.00</td>
<td>0.18*</td>
<td>0.10</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8</td>
<td></td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Brick not spiked with this metal•
USA Environmental Protection Agency, Maximum Limit •

As for the sludge used during this study, the majority was obtained from Indianapolis, Indiana's Belmont Advanced Wastewater Treatment Facility. This material had been previously dewatered to 26-28% solids. Indianapolis receives a mixed domestic and industrial wastewater and produces a sludge whose metal content is given in Table 8.4.

### Table 8.4. Indianapolis Sludge Metal Composition (Barr, 1984)

<table>
<thead>
<tr>
<th>Metal Species</th>
<th>Concentration (mg metal/kg dry TSS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>7.6</td>
</tr>
<tr>
<td>Cadmium</td>
<td>46.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>98.2</td>
</tr>
<tr>
<td>Lead</td>
<td>245.6</td>
</tr>
<tr>
<td>Chromium</td>
<td>394.0</td>
</tr>
<tr>
<td>Copper</td>
<td>563.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>2467.1</td>
</tr>
</tbody>
</table>

TSS: Total Suspended Solids
It is clear from Table 8.4 that the contaminant levels in raw sludge for Arsenic and Cadmium should be in the low spiked range. However for all other heavy metals it should be in the heavy spiked range, except Zinc over the heavy spiked range of 1000 mg/kg.

The overall findings suggest that standard sewage sludge, laden with normal metal levels, can be incorporated within commercial brick manufacturing operations without any leachate problems. This statement would similarly appear warranted for industrially contaminated sludge residues. The contained metals were believed to be physicochemically locked inside the vitrified brick, possibly due to a silicate-based entrapment mechanism. For sludge heavily contaminated with hazardous metals, leachate concentration of arsenic, selenium, and cadmium needs further investigation.

8.6. Leachate from fly ash

Three samples of bituminous coal fly ash, lignite coal fly ash and subbituminous coal fly ash were sent to laboratories across the USA by the Electric Power Research Institute (1979), where they were subjected to the various extraction procedures and the extract was analyzed according to standard ASTM procedures. The range of values from these analyses is presented in Table 8.5. One important fact is evident from this data. The variation in test results among the laboratories performing the same extraction procedure on the same waste sample is, in some cases, rather large. The results of the analysis presented are a function of many factors including;

- type of coal and geographical source
- degree of coal preparation, cleaning and pulverization
- design, type and operation of the power plant boiler unit
- collection, handling and disposal methods
- sample size

Due to the above factors, power plant ash will display a high degree of variability in its properties. Not only will the properties of an ash vary from power plant to power plant, but they will also vary from boiler to boiler at a particular and within an individual boiler at various times.
Table 8.5. Results of Leachate Tests on Fly Ash

<table>
<thead>
<tr>
<th>Analysis (mg/l)</th>
<th>ASTM &quot;A method&quot;</th>
<th>ASTM &quot;B method&quot;</th>
<th>EPA Extraction Procedure</th>
<th>Regulatory limits (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bituminous Coal Fly Ash</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.0004-0.045</td>
<td>0.0003-0.06</td>
<td>0.0001-0.04</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>0.0021-2.11</td>
<td>0.87-7.3</td>
<td>0.00059-2.046</td>
<td>5</td>
</tr>
<tr>
<td>Ba</td>
<td>&lt;0.02-79</td>
<td>0.11-1.0</td>
<td>&lt;0.02-0.5</td>
<td>100</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.0002-0.04</td>
<td>0.002-0.05</td>
<td>&lt;0.00005-0.06</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.008-0.23</td>
<td>0.04-0.74</td>
<td>0.008-0.39</td>
<td>5</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.00005-0.020</td>
<td>0.000011-0.5</td>
<td>&lt;0.000001-25.0</td>
<td>0.200</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.001-0.09</td>
<td>&lt;0.001-0.2</td>
<td>&lt;0.00001-0.7</td>
<td>5</td>
</tr>
<tr>
<td>Se</td>
<td>0.14-1.25</td>
<td>0.1-1.41</td>
<td>0.0001-1.56</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis (mg/l)</th>
<th>ASTM &quot;A method&quot;</th>
<th>ASTM &quot;B method&quot;</th>
<th>EPA Extraction Procedure</th>
<th>Regulatory limits (mg/l)</th>
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<tr>
<td></td>
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<tr>
<td><strong>Lignite Coal Fly Ash</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.009-0.04</td>
<td>0.007-0.04</td>
<td>&lt;0.009-0.04</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.01-0.2</td>
<td>&lt;0.01-0.65</td>
<td>0.004-1.8</td>
<td>5</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1-1.069</td>
<td>0.1-1.31</td>
<td>0.01-1.98</td>
<td>100</td>
</tr>
<tr>
<td>Cd</td>
<td>0.006-&lt;0.5</td>
<td>0.0013-&lt;0.5</td>
<td>&lt;0.01-0.58</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.01-0.78</td>
<td>&lt;0.01-0.56</td>
<td>0.031-0.15</td>
<td>5</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.001-&lt;0.005</td>
<td>&lt;0.0001-&lt;0.005</td>
<td>&lt;0.0001-&lt;0.005</td>
<td>0.200</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.00972-&lt;0.1</td>
<td>0.0047-&lt;0.1</td>
<td>&lt;0.001-0.4</td>
<td>5</td>
</tr>
<tr>
<td>Se</td>
<td>0.0693-1.0</td>
<td>0.06-1.5</td>
<td>0.0176-1.0</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis (mg/l)</th>
<th>ASTM &quot;A method&quot;</th>
<th>ASTM &quot;B method&quot;</th>
<th>EPA Extraction Procedure</th>
<th>Regulatory limits (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>Sub-bituminous Coal Fly Ash</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;0.01-0.09</td>
<td>&lt;0.01-0.08</td>
<td>&lt;0.01-0.08</td>
<td>5</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.002-0.03</td>
<td>0.003-0.4</td>
<td>&lt;0.002-0.5</td>
<td>5</td>
</tr>
<tr>
<td>Ba</td>
<td>0.1-100</td>
<td>0.4-125</td>
<td>0.3-0.94</td>
<td>100</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.01-&lt;0.05</td>
<td>&lt;0.01-&lt;0.05</td>
<td>&lt;0.01-&lt;0.05</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.01-0.10</td>
<td>&lt;0.01-&lt;0.25</td>
<td>&lt;0.01-0.39</td>
<td>5</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0001-0.08</td>
<td>&lt;0.0001-0.11</td>
<td>&lt;0.0001-0.08</td>
<td>0.200</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.01-0.1</td>
<td>&lt;0.01-0.2</td>
<td>&lt;0.01-0.3</td>
<td>5</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;0.01-&lt;0.5</td>
<td>0.032-0.3</td>
<td>&lt;0.002-0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Source: The Electric Power Research Institute, USA (1979)

The data shown above indicated that the leachate readily meets regulation criteria and hence, the fly ash will be classified as non-hazardous.
8.7. Results and discussion of biofly leachate tests

The biofly leachate samples were collected as described in research method Chapter 4. These samples were then analysed to determine the concentration of nine metals. The detailed table of the test results are provided in Volume 2 Appendix 2 (Tables 2.1-2.36) and discussion in the following sections.

In each batch, approximately 100 bricks were made and fired in the gas kiln. The sampling was carried out with the intention of determining the presence of metal concentration in the biofly leachate as shown in Table 8.6. It was initially assumed that the metal leaching rates would increase as particle size decreased due to an increase in available surface area for leaching. To verify this, various size ranges of particles of biofly bricks were created by grinding and sieving solidified brick specimens. Size ranges tested were 4.75-9.5 mm, 0.2-0.6 mm and 75 μm. For comparison purposes, the raw materials were also sieved and similar tests were performed. As all raw materials were less than 4.75 mm, no comparison was made in this range.

Table 8.6. Summary of metal concentrations in the leachate

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal</th>
<th>Metals leached concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sieve 4.75-9.5 mm</td>
</tr>
<tr>
<td>1</td>
<td>Aluminium</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cadmium</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Chromium</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Copper</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Iron</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Manganese</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Nickel</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Zinc</td>
<td></td>
</tr>
</tbody>
</table>

The list of metals selected were based on a review of other brick making processes using sludge and fly ash as partial brick material. Samples of burnt brick were prepared to test leaching properties of nine metals, including 7 heavy metals (Cd, Cr, Cu, Fe, Pb, Ni and Zn), and five of these metals (Cd, Cr, Cu, Pb and Mn) are associated with the USEPA'S criteria for classifying hazardous wastes via the extraction test procedure, two of these metals (Cd and Zn) have elemental boiling points (765 and 906°C) below the vitrification temperature and five of these metals have melting points (660, 320, 1083, 327 and 419°C) below vitrification temperature used with the brick production. Three of
these metals (Al, Fe, Mn) are related to the refractory materials especially in brick vitrification.

At present there is no defined criteria for permissible levels of metal leachate from these type of bricks. Hence, the results obtained from the analysis of each sample are presented below for each metal and a discussion is provided using "maximum" permissible values for leaching criteria, listed in US. Code of Federal Regulations (CFR) Standard (1988) and Victoria EPA Standard (1986) for landfill disposal.

8.7.1. Aluminium

The variation of leachate of aluminium from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.1, 8.2 and 8.3 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of aluminium ranges between 0.002 and 0.01125 mg/l and the data clearly show that leachate concentration from reference materials is higher than the level of leachate concentration from biofly bricks. This indicates the great ability of the biofly brick process to keep even the small amount of aluminium within the matrix.

It was initially thought that as the particle size decreased, which increases the surface area, the magnitude of metal leaching would increase. This was not the case with the aluminium samples where the metals remained “locked up” even in the small particles of size 75 μm. This may be due to the greater ion exchange capacity of the smaller particles which prevents significant leaching of the metals.

There is no conclusive evidence available that leachate of aluminium changes with increases in waste material replacement within 50-70%. Also the effect of sludge type on leachate concentration is not clear.
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Figure 8.1. Variation of Aluminium leachate with waste materials replacement

Figure 8.2. Variation of Aluminium leachate with waste materials replacement
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8.7.2. Cadmium

The variation of leachate of cadmium from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.4, 8.5 and 8.6 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of cadmium ranges between 0.000485 and 0.0025875 mg/l for most of the biofly samples. One sample from 75 μm particle size was over the range of 0.001 mg/l, and considering the other data this is considered to be an outlier.

The figures clearly show that leachate concentration from reference bricks is lower than the level of leachate concentration from biofly bricks. This is expected because 100% clay/shale sample contains less cadmium than the three materials combined in biofly bricks, chapter four. Compared to the raw materials the leachate of cadmium for biofly bricks are marginally small. There is no significant evidence available that cadmium gets locked up in biofly bricks. It also appears that the cadmium is unaffected by percentage waste material replacement. On the other hand, the maximum leachate level of the biofly brick samples is well below the US. CFR Standard of 0.066 mg/l.

Figure 8.3. Variation of Aluminium leachate with waste materials replacement
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Figure 8.4. Variation of Cadmium leachate with waste materials replacement

Figure 8.5. Variation of Cadmium leachate with waste materials replacement
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8.7.3. Chromium

The variation of leachate of chromium from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.7, 8.8 and 8.9 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of chromium ranges between 0.000125 and 0.002 mg/l.

The leachate concentration level of raw materials were above the leachate concentration level of the biofly brick replacement, clearly indicating that chromium is well trapped in the biofly bricks. Silica is believed to be involved in the binding of the heavy metals, particularly with chromium and lead as suggested by Bishop , (1988).

The chromium leachate concentration from biofly bricks are higher than this clay/shale sample indicating the availability of chromium for leachate from wastes. However, the variation of chromium leachate with percentage material replacement show that the leachate level of chromium does not vary proportionally with the various
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Figure 8.7. Variation of Chromium leachate with waste materials replacement

Figure 8.8. Variation of Chromium leachate with waste materials replacement
addition of sludge and fly ash. The level of concentration of chromium was well below the US. CFR Standard level of concentration 0.094 mg/l.

It is to be noted that some of the leachate concentration from reference bricks may not be detected with some particle sizes because it is below the detection limit of the instrument used.

8.7.4. Copper

The variation of leachate of copper from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.10, 8.11 and 8.12 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of copper ranges between 0.000125 and 0.0035 mg/l. The lowest value of copper concentration shown in Fig. 8.10 for 60% waste replacement is an outlier.

The figures clearly show that the raw materials leachate concentration level were higher than the biofly brick leachate concentration level. However, the reference brick
samples have less leachate concentration level than both the raw materials and the biofly materials. This was expected because the raw materials of clay contained 0.005% of copper, however the fly ash contained 0.0016% of copper and Bellambi, Wollongong, Shellharbour and Port Kembla sludges contained 0.044, 0.083, 0.063 and 0.076% of copper, respectively (section 4.2, chapter 4).

The level of the leachate concentration for all the biofly brick materials were under the maximum permissible value of Victoria EPA Standard (1 mg/l). This data indicates that the vitrification of biofly brick has the potential to decrease the copper leachate by "locking up" the metals even with the fine particles of 75 μm. This may be related to the greater ion exchange capacity of the particles which directly prevents leaching of metals.

From the graphs it can be inferred that the leachate of copper is not directly proportional to the percentage of sludge and fly ash added. No relationship has been found between the particle size and the level of copper leachate.

![Figure 8.10. Variation of Copper leachate with waste materials replacement](image)

Figure 8.10. Variation of Copper leachate with waste materials replacement
Chapter 8: Leachability studies

Figure 8.11. Variation of Copper leachate with waste materials replacement

Figure 8.12. Variation of Copper leachate with waste materials replacement
8.7.5. Iron

Iron is the refractory type constituent which gives the brick the red colour and also part of the strength. The leachate concentration level of iron ranges between 0.0005 and 0.1515 mg/l, illustrated in Figures 8.13, 8.14 and 8.15.

The figures clearly show that leachate concentration from laboratory reference brick is higher than the level of leachate concentration from biofly bricks, except Bellambi mix. This may be because the metals are bound into the solid mix differently. Compared to the raw materials the leachate of iron from biofly bricks are marginally higher. No significant evidence is available to indicate that iron gets locked up in biofly bricks.

The variation of the quantity of the sludge and the fly ash has no effect on the proportional of the metal concentration, however it is clearly exhibited in the Figures that leachate variation of iron with addition of different types of sludge to the mixes are varied with the sludge type. Iron invariably leached at a much greater rate than did any other metal and this may indicate that the metals are bound into the solid differently. The level of concentration was well below the Victoria EPA Standard of 1 mg/l.

![Figure 8.13. Variation of Iron leachate with waste materials replacement](image-url)
Chapter 8: Leachability studies

Figure 8.14. Variation of Iron leachate with waste materials replacement

Figure 8.15. Variation of Iron leachate with waste materials replacement
It is to be noted that some of the leachate concentration from reference bricks was not detected with some particle sizes because they were below the detection limit of the instrument used.

### 8.7.6. Manganese

The leachate concentration of manganese illustrated in Figures 8.16, 8.17 and 8.18 is within the range 0.000125 and 0.001875 mg/l. The leachate concentration of raw materials were above the leachate concentration level of the biofly brick replacement, clearly indicating that manganese is trapped within the biofly bricks.

The variation of manganese leachate with percentage material replacement showed that the leachate level of manganese does not vary proportionally with the addition of sludge and fly ash, and no correlation was found between the particle size and the leachate concentration.

Reference samples concentration were slightly lower than the level of concentration of biofly brick samples. This is expected because the 100% clay/shale sample contains less manganese than the three waste materials combined together (chapter 4).

---

**Figure 8.16. Variation of Manganese leachate with waste materials replacement**
Figure 8.17. Variation of Manganese leachate with waste materials replacement.

Figure 8.18. Variation of Manganese leachate with waste materials replacement.
The leachate of biofly brick materials was well below the Victoria EPA Standard 0.5 mg/l. It is concluded that the biofly brick process encapsulates the manganese within the solid silica matrix.

8.7.7. Nickel

The variation of leachate concentration of nickel from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.19, 8.20 and 8.21 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of nickel ranges between 0.0005 and 0.00975 mg/l.

The figures clearly show that leachate concentration from reference bricks is lower than the level of leachate concentration from biofly bricks. This is expected because 100% clay/shale sample contains less nickel than the three materials combined in biofly bricks (section 4.2 chapter four). Compared to the raw materials the leachate of nickel for biofly bricks are marginally small. However it appears that nickel does get locked up in biofly bricks.

It should be noted that the leachate concentration from factory brick with particle size 0.2-0.6 mm and 4.75-9.5 mm were not available. leachate values for nickel were not detected for the above particle sizes because they were below the detection limit of the instrument used.

The variation of nickel leachate concentration with percentage material replacement shows that the leachate concentration level of nickel does not vary proportionally with the addition of sludge and fly ash. Also no correlation has been found between the particle size and the leachate concentration.

The leachate concentration of biofly brick materials was well below the US. CFR Standard value of 0.048 mg/l. It is concluded that the biofly brick process encapsulate the nickel within the silica matrix.
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**Leachability studies**

**Figure 8.19. Variation of Nickel leachate with waste materials replacement**

**Figure 8.20. Variation of Nickel leachate with waste materials replacement**
8.7.8. Lead

The variation of leachate concentration of lead from 4 types of biofly bricks with waste materials replacement is shown in Figures 8.22, 8.23 and 8.24 for particle sizes 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, respectively. For comparison, leachate from clay/shale and raw material samples are also shown on the same graphs. The leachate concentration of lead ranges between 0.00025 and 0.002 mg/l. However, it is noticed that the average leachate concentration of the biofly brick samples was of the order of 0.001 mg/l.

The figures clearly show that leachate concentration from reference bricks is lower than the level of leachate concentration from biofly bricks. This is expected because 100% clay/shale sample contains less lead than the three materials combined in biofly bricks (chapter four). Compared to the raw materials, the leachate of lead for biofly bricks are considerably reduced. Results indicate that lead gets locked up in biofly bricks. This shows the ability of the biofly brick to solidify the lead through the matrix.
Figure 8.22. Variation of Lead leachate with waste materials replacement

Figure 8.23. Variation of Lead leachate with waste materials replacement
The figures 8.22-8.24 have shown that the leachate variation of lead does not vary with the replacement of waste materials. Also results indicate that there no relationship exists between the particle size and the concentration of leachate from lead. The level of the leachate concentration was well below the US. CFR Standard of 0.180 mg/l.

8.7.9. Zinc

The variation of the analysis for the determination of zinc leachate concentration from 4 types of biofly bricks are shown in Figures 8.25, 8.26 and 8.27. The range of leachate concentration was between 0.0013 and 0.0382 mg/l. This is higher than most of the heavy metals concentration and it is similar in behaviour to that found for aluminium.

The figures indicated that some of the samples give slightly higher results than the reference concentration, but were lower than the raw materials concentration and were well below the Victoria EPA Standard of 1 mg/l.
Figure 8.25. Variation of Zinc leachate with waste materials replacement

Figure 8.26. Variation of Zinc leachate with waste materials replacement
No relationship has been found between the quantity of the sludge and fly ash added and the concentration of lead leachate, except Shellharbour bricks has a tendency to increase zinc leachate with percentage materials replacement. No relationship was found between the particle size and the level of concentration. From these results it can be inferred that the biofly brick material are trapped most of the heavy metals within the matrix.

8.8. Summary

- The solidification/stabilization, or chemical fixation, process may be defined as a process to limit or minimize the movement of contaminants away from the disposal site and to improve the physical characteristics of the waste.

- The overall findings suggest that typical sewage sludge, laden with normal metal levels, can be incorporated within commercial brick manufacturing operations. The contained metals were believed to be physicochemically locked inside the vitrified brick, possibly due to a silicate-based entrapment mechanism. For sludge heavily contaminated
with hazardous metals, leachate concentration of arsenic, iron, selenium, cadmium and similar metals may warrant further investigation.

- The fly ash leachate concentration data indicated that the leachate readily meets regulation criteria and hence, will be classified as non-hazardous.

- In this investigation, biofly brick materials were ground to specified size ranges 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, before contact with a mild acetic acid for 24 hours, after which the leachate was analyzed for nine metals, aluminium, cadmium chromium, copper, iron, manganese, nickel, lead, and zinc.

- The heavy metal leachate from the Biofly bricks in general was similar or lower than that of the conventional clay brick except in the case of cadmium and iron, and it was well within the Standard limits.

- Even though the raw materials used for making the Biofly bricks had a higher concentration of heavy metals, the leachate rates are comparatively low. This proves that the Biofly brick process has the potential to reduce the heavy metal leachate. This also proves that the heavy metals in the sludge and fly ash are trapped inside the brick during the encapsulation process.

- It is expected that the concentration of metals in the leachate should be increased with the increased exposed surface area of the smaller particles. This was not the case, the metals remained “locked up” even in the small particles. This may be due to the greater ion exchange capacity of the smaller particles which prevents significant leaching of the metals.

- For the iron samples, the leachate concentration behaviour is different from most of the other metals. The variation of the quantity of the sludge and the fly ash has no effect on the proportional of the metal concentration, however it is clearly exhibited that leachate variation of iron with addition of different types of sludge to the mixes are varied with the sludge type. Iron invariably leached at a much greater rate than did any other metal and this may indicate that the metals are bound into the solid differently.
Chapter Nine

Gas Consumption and Flue Gas Analysis

9.1. Introduction

"Biofly" brick process is a new process in which the two waste materials, sewage sludge and fly ash are combined with clay/shale to make bricks for the first time on a pilot scale. The two waste materials contain varying compositions of pollutants and there is no data available on the characteristic of pollutants that could be emitted from the brick firing. Balanced against the positive benefits prospectively associated with biofly brick manufacture, concerns have been raised in regard to the fate of hazardous contaminants which might be introduced either to the brick manufacturing operation or the finished products. On one hand, it might be reasonable to expect thorough combustion of the sludge's constitutive organics due to the extreme firing temperature of 1100°C which may yield an exothermic heat release and, consequently, reduce the energy required for firing of the biofly brick. Hence the biofly brick will not contain any pathogens. However, the fate of toxic and hazardous inorganics, particularly heavy metals, represents a considerably more significant concern. In addition, in some countries there have been concerns of fluorine emissions from brick manufacturing plants. Fluorine is a cumulative pollutant. To determine the nature of pollutants that could be emitted, an overview of similar high temperature processes involving sewage sludge and clay/shale have been investigated in sections 9.2-9.5. In addition, a comprehensive flue gas analysis of the biofly process has been undertaken and presented in sections 9.7-9.9.

9.2. Emission of fluorine from manufacture of brick

Fluorine has been reported to be emitted during the manufacture of bricks. Konrad (1957) cites a report of tree damage by fluorine emitted from a brickworks. Subsequently Konrad reported fluorosis in cattle in the vicinity of a brick works in Bedfordshire, England. Brandt and Anderson (1972) stated that brick manufacturing was responsible for the bulk of fluorine emission from industrial sources in USA. National academy of Sciences (1971) attributes a significant proportion of atmospheric fluorine to brick
manufacturing. All these publications were based on the values calculated from the average fluorine content of the clay, rather than the actual stack gas analysis. Hence fluorine measurement is warranted in the flue gas analysis of the biofly process.

9.3. Sludge incinerator emissions

Incineration offers the opportunity to reduce sludge to a sterile landfill and remove offensive odours, but it also has the potential to be a significant contributor to the air pollution problem in an urban community. The pollutants include particulate and gaseous compounds.

9.3.1. Particulate pollutants

The quantity and size of particulate emissions leaving the furnace of an incinerator vary widely depending on such factors as the sludge being fired, operating procedures and completeness of combustion. Incomplete combustion can form objectionable intermediate products such as hydrocarbons and carbon monoxide. There is also a potential for the discharge of air pollutants such as sulphur dioxide, nitrous oxides, and metals such as mercury. The particulate content in sludge incinerator gases is given in Table 9.1.

<table>
<thead>
<tr>
<th>Type of incinerator</th>
<th>Particulate content gr/dscm</th>
<th>US NPS gr/dscm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiple hearth</td>
<td>0.0005759-0.0025653</td>
<td>-</td>
</tr>
<tr>
<td>Fluidised bed</td>
<td>0.0008551-0.0014204</td>
<td>0.0053</td>
</tr>
</tbody>
</table>

gr/dscm: Grains/Dry Standard Cubic Meter

The above values correspond to about 15 kg of particulates per tonne of sludge burnt for multiple hearth incinerator and 20 kg of particulates per tonne of sludge burnt for fluidised bed incinerator. These emission data meet the National Performance Standard US NPS (1971).

9.3.2. Gaseous pollutants

The highest average air pollutants emitted from one of the sludge incinerators are listed in Table 9.2.
Table 9.2. Air pollutants emitted from a sludge incinerator (US. EPA., 1975)

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Unit</th>
<th>Average</th>
<th>US NPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>% by volume</td>
<td>10.1</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>% by volume</td>
<td>7.5</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>% by volume</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>SO₂</td>
<td>ppm</td>
<td>14.2</td>
<td>300</td>
</tr>
<tr>
<td>NOₓ</td>
<td>ppm</td>
<td>163</td>
<td>100</td>
</tr>
<tr>
<td>HCl</td>
<td>ppm</td>
<td>2.72</td>
<td>-</td>
</tr>
</tbody>
</table>

Consideration of the possibility of SO₂ and NOₓ emission is aided by examination of the sulfur and nitrogen content of sludges. Sulfur content is low in most sludges unless it is heavily contaminated from a particular industry. In addition, much of this sulfur is in the form of sulphate, which originated in the wastewater. Sludge typically has a high nitrogen content from proteinaceous compounds and ammonium ion. Hence, sulfur dioxide is not expected to be a serious problem. The discharge concentration was found to be 14.2 ppm as compared to 300 ppm standard. The concentration of oxides of nitrogen from sludge incineration should be less than 100 ppm from a properly operated incinerator, and were observed to be higher.

9.3.3 Metals

Wastewater sludges contain metals that could be hazardous if discharged into the atmosphere. Unfortunately, there are very few published data available on the metals being discharged to the atmosphere from municipal sludge incineration. The forms in which metals are found in sludge will influence their behaviour on incineration. It is believed that most of the hazardous or potentially hazardous metals, with the exception of mercury, will not disproportionately appear in the stack gases because of volatilization, but will be converted to oxides and appear in the particulates removed by scrubbers in the ash. The metal emission rates from incinerators with emission control are given in Table 9.3. Mercury presents special problems during incineration. High temperatures during incineration decompose mercury compounds to volatile mercuric oxide or metallic mercury.
Table 9.3. Metal emission rates from incinerators with emission control
(US. EPA., 1975)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Emission factor range mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.223-0.714</td>
</tr>
<tr>
<td>Ni</td>
<td>0.089-3.661</td>
</tr>
</tbody>
</table>

9.3.4 Organics

In addition to the major air pollutants resulting from the burning of sludge, toxic substances can arise because of the content of pesticides or other organic compounds in the sludge. Unfortunately, again very limited data are available on the concentration of these materials in the municipal sludges and their fate in an incinerator. Data reported in Table 9.4 by US. EPA. (1975) in a random selection of sludges, showed the following organic materials were present in the raw sludges.

Table 9.4. Organic content of raw sludges (US. EPA., 1975)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>16</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.08-2.0</td>
</tr>
<tr>
<td>Chlordane</td>
<td>3.0-32</td>
</tr>
<tr>
<td>DDD</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>DDT</td>
<td>&lt; 1.1</td>
</tr>
<tr>
<td>PCB’s</td>
<td>1.2-2.5</td>
</tr>
</tbody>
</table>

Pesticides and PCB’s were found only in the raw sludges. They were not found in the ash from either type of incinerator, nor in the inlet or outlet scrubber water. Ash can be analyzed for these materials to the same degree of sensitivity as the sludge. A level of 0.1 ppm could easily have been detected in the ash. It is quite certain that these materials are not being carried out in the ash. Rapid thermal degradation of most pesticides has been shown to begin at approximately 500°C with near total destruction at 900°C. It has also been shown that 99% destruction of PCB’s is possible at 870-980°C in two seconds.
### 9.4. Oil from sludge process (OFS) emissions

The OFS technology reported by Bridle, et al., (1990) is a thermochemical process whereby organics in sludge are converted to oil having properties similar to diesel fuel. The process operates at a moderate temperature of 450°C. The characteristics of the municipal sludge used and the products produced in the process are shown in Table 9.5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sludge</th>
<th>Oil</th>
<th>Char</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>33.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Arsenic</td>
<td>3.1</td>
<td>0.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Cadmium</td>
<td>44</td>
<td>0.7</td>
<td>69</td>
</tr>
<tr>
<td>Chromium</td>
<td>615</td>
<td>2.1</td>
<td>977</td>
</tr>
<tr>
<td>Copper</td>
<td>1187</td>
<td>4.0</td>
<td>1934</td>
</tr>
<tr>
<td>Lead</td>
<td>267</td>
<td>1.1</td>
<td>412</td>
</tr>
<tr>
<td>Mercury</td>
<td>7</td>
<td>&lt;1</td>
<td>1.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>198</td>
<td>0.9</td>
<td>307</td>
</tr>
<tr>
<td>Zinc</td>
<td>1999</td>
<td>8.7</td>
<td>3142</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>1.3</td>
<td>1.0</td>
<td>&lt;0.004</td>
</tr>
<tr>
<td>Polychlorinated Biphenyls</td>
<td>0.32</td>
<td>0.48</td>
<td>&lt;0.012</td>
</tr>
</tbody>
</table>

Numerous organochlorine contaminants were found in the sludge, albeit at very low concentrations. Only Hexachlorobenzene and Polychlorinated Biphenyls were in measurable concentrations.

During the trials, the fate of heavy metals and organochlorines were monitored across all unit operations and the results were obtained. Belt filter press dewatering does not alter heavy metal and organochlorine content of the sludge. Thermal drying does have the potential to release metals and organochlorine’s from the sludge.

Mass balance conducted around reactor products revealed that, with the exception of arsenic and mercury, heavy metals are essentially retained in the Char. Reactor off gas analysis indicated presence of 3% of mercury fed to the reactor and did not detect any organochlorines. The contaminant concentration in the sludge and the reactor products are listed in Table 9.5.
The Char, non-combustible gases and reaction water from the reactor were combusted to provide the energy required for sludge drying and reactor heating. A fluidised bed combustor was used and the bed temperature was in the range of 789°C-876°C. Heavy metal and organochlorine’s analysis was conducted on the Char feed, ash products and flue gas. The results are listed in Table 9.6.

Table 9.6. Analysis of heavy metal concentrations of OFS process run at 786°C (Bridle et al, 1990)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Char mg/kg</th>
<th>Bed ash mg/kg</th>
<th>Cyclone Fines mg/kg</th>
<th>Filter Fines mg/kg</th>
<th>Flue gas mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>7.5</td>
<td>11.5</td>
<td>12.4</td>
<td>27.5</td>
<td>ND</td>
</tr>
<tr>
<td>Cadmium</td>
<td>63.3</td>
<td>83.9</td>
<td>53.7</td>
<td>153</td>
<td>4</td>
</tr>
<tr>
<td>Chromium</td>
<td>930</td>
<td>867</td>
<td>1249</td>
<td>5311</td>
<td>ND</td>
</tr>
<tr>
<td>Copper</td>
<td>1942</td>
<td>2424</td>
<td>2888</td>
<td>3605</td>
<td>6</td>
</tr>
<tr>
<td>Lead</td>
<td>174</td>
<td>251</td>
<td>334</td>
<td>688</td>
<td>ND</td>
</tr>
<tr>
<td>Mercury</td>
<td>1.64</td>
<td>0.04</td>
<td>0.03</td>
<td>14.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Nickel</td>
<td>284</td>
<td>233</td>
<td>380</td>
<td>5010</td>
<td>10</td>
</tr>
<tr>
<td>Zinc</td>
<td>2909</td>
<td>3169</td>
<td>4049</td>
<td>3334</td>
<td>4</td>
</tr>
</tbody>
</table>

ND: not detected

The data shows that with the exception of mercury, heavy metals are concentrated in the Char, bed ash and cyclone/filter fines. Extremely low concentrations of metals were detected in the flue gas. Organochlorine compounds were not detected either in the Char or in the flue gas.

9.5. Gas emissions from sludge amended brick

The fate of metals contained within the sludge used for brick making relative to the vitrification process was studied by Alleman et al (1990). It appears from his results that most metals have been trapped within the sludge amended brick, both during firing and weathering. This behaviour appears to be related to a silicate based physico-chemical containment mechanism. Alleman et al (1990) were concerned about the fate of toxic and hazardous inorganics, and particularly heavy metals.

The following section outlines the detailed studies undertaken by Alleman et al (1990) with reference to metal retention in sludge bricks. The prospective loss via emission of metals during firing and subsequent metal losses due to natural weathering of an exposed brick surface were studied. Eight metals were selected for study, including six heavy metals (cadmium, chromium, iron, lead, nickel and zinc) and two transition metals
arsenic and selenium). Five of these metals (arsenic, cadmium, chromium, lead and selenium) are associated with USEPA's criteria for classifying hazardous wastes via the extraction procedure and five of these metals (arsenic, selenium, cadmium, lead, nickel and zinc) have elemental boiling points which are below the vitrification temperature commonly used with conventional brick production at 1100°C. Furthermore, two of these metals (arsenic and selenium) have extremely low permissible extraction procedure contaminant concentrations. Several of these metals warrant extreme attention with respect to their potential release and fate, either during firing of the brick or subsequent weathering of the finished product.

As for the sludge used during this study, the majority was obtained from Indianapolis, Indiana's Belmont Advanced Wastewater Treatment Facility. This material had been previously dewatered to 26-28% solids. Indianapolis receives a mixed domestic and industrial wastewater and produces a sludge whose metal content is given in the following Table (Barr, 1984).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Concentration mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>7.6</td>
</tr>
<tr>
<td>Cadmium</td>
<td>46.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>98.2</td>
</tr>
<tr>
<td>Lead</td>
<td>245.6</td>
</tr>
<tr>
<td>Chromium</td>
<td>394.0</td>
</tr>
<tr>
<td>Copper</td>
<td>563.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>2467.1</td>
</tr>
</tbody>
</table>

It is noticed from Table 9.7 that the contaminant levels in raw sludge indicate that Arsenic and Cadmium are likely to be in the low range (0-80 mg/kg). However all other heavy metals are likely to be in the heavy range (>80-1000 mg/kg), except Zinc which is over the heavy range (>1000 mg/kg).

**Bench scale brick manufacturing procedure**

Volumetric addition of dry sludge averaging 28% were added to the raw clay/shale and then blended in a mixer. This blend was then manually compressed into a hand packed brick mould. Following one week of air drying at room temperature, it was oven
dried at 105°C for 36 hours. Brick firing was conducted in a computer controlled muffle furnace with ramped heating to 1050°C and cooling cycles covering a total of 50 hours.

**Spiked metal concentrations**

Spiked metal additions were incorporated in order to achieve final metal levels including background presence ranging from 0-1000 mg/kg dry brick weight. The chemicals used for these spiked additions were first solubilized in a known volume of water and then blended with clay/shale and sludge in a mixer.

**Metal emissions testing**

An attempt was made to measure off gas metals losses during firing of the sludge amended brick. The kiln employed was enclosed within a glass vault and a controlled portion of the ventilating gas stream was successively passed through a paper fibre filter and liquid impinger. An effort was also made to quantify the metal deposition within the interior or immediate exterior of the kiln by placing high temperature metal alloy disks in or adjacent to the kiln and swabbing their surfaces with acid following every brick firing run.

**Constitutive brick metal testing**

Both green and fired bricks were subjected to destructive constitutive metal testing in order to quantify their pre and post firing metals composition. Powdered samples were taken from each brick for this purpose using a tungsten drill bit. The metals contained within known quantities of this powder were then extracted using one of several alternative procedures:

a) gold cup fusion digestion  
b) microwave parr bomb digestion with nitric acid  
c) microwave parr bomb digestion with hydrofluoric acid  
d) microwave parr bomb digestion with hydrofluoric acid and aqua-regia.

**Metals emission behaviour during firing**

Originally, it was believed that the low boiling point metals (arsenic, cadmium and selenium) might be released from these bricks at some point during the high temperature
firing and vitrification process, however, this was not observed. At no time was there any sign of particulate metal emission from the sludge amended metal spiked brick. Similarly, there was little evidence to demonstrate the loss of metals during firing due to gaseous emissions. In only one instance during which selenium had been added to the brick to a level of 1000 ppm was there any indication of gas phase metal loss. It was observed that a thin film was deposited on the upper edge of the kiln door. This material likely occurred in this location due to immediate cooling and condensation of the gaseous selenium.

**Pre/Post firing constitutive metal change**

Metal levels within green and fired bricks were compared on a basis of relative percentile change. Table 9.8 contains the analytical results of pre and post firing testing for brick spiked with the various metal species and concentrations.

**Table 9.8. Change in constitutive metal content of amended brick (Alleman et al, 1990)**

<table>
<thead>
<tr>
<th>Pre-fired metal level (mg/kg)</th>
<th>Metal</th>
<th>Metal change percent during change firing</th>
<th>Brick weight change (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>Se</td>
<td>Cd</td>
<td>Zn</td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>-5a</td>
<td>+16a</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>-11c</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>+133a</td>
<td>+2c</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>+2a</td>
<td>+62a</td>
<td>+85a</td>
</tr>
<tr>
<td>60</td>
<td>+58c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>+4c</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td>+11c</td>
</tr>
<tr>
<td>200</td>
<td>0c</td>
<td>+19c</td>
<td>+16d</td>
</tr>
<tr>
<td></td>
<td>+9d</td>
<td>+8a</td>
<td>+3a</td>
</tr>
<tr>
<td></td>
<td>+11a</td>
<td>+13a</td>
<td>+50a</td>
</tr>
<tr>
<td>400</td>
<td></td>
<td>-9a</td>
<td>+29a</td>
</tr>
<tr>
<td>500</td>
<td>+19a</td>
<td>+9a</td>
<td>+34a</td>
</tr>
<tr>
<td>1000</td>
<td>+17a</td>
<td>+33a</td>
<td>+32a</td>
</tr>
</tbody>
</table>
Mostly, the fired brick metal levels increased relative to the pre fired levels in apparent correlation with the increased density and decreased weight of the brick. This indicates that most metals are locked up in the burnt brick and so it is unlikely to result in higher concentration of emissions. Unfortunately the table showed, only a nominal amount of data collected on the arsenic and selenium species, due to severe analytical interference with these metals during pretreatment methods employed for metals extraction.

It is concluded, that these results did not reveal any indication whatsoever that metals were being released in the flue gas during the brick firing process. The fact that hydrofluoric acid was able to release these metals, suggests that the metals were being physiochemically bonded and fused within the silicate based matrix of the vitrified brick (Alleman et al, 1990).

9.6 Gas emission for melting system for sewage sludge

Melting plants for sewage sludge are attracting great attention for their capability to produce molten slag and the possibility for their effective application. Melting treatment reduces the sludge volume, stabilizes chromium and other harmful substances, and enables effective utilisation of generated slag for construction material.

Oku, et al. (1990), conducted a study on a sewage sludge melting system. In this system dewatered cake is stored in a conical silo type hopper, delivered quantitatively and fed to the fluidized bed carbonizing furnace. In the carbonizing furnace, dewatered cake is carbonized at a combustion air ratio of 1.0 or less and the residue is separated by the cyclone with a slight amount of carbon remaining. The separated residue is immediately charged into the swirling flow melting furnace in order to effectively utilize the heat of the separated residue. Slag discharged from the swirling flow melting furnace is cooled and solidified by an air/water cooled slag removing device.

Exhaust gas from the swirling flow melting furnace is mixed with that from the carbonizing furnace in the secondary combustion chamber, and is completely burnt. Exhaust gas is recovered as heat by the combustion air preheater and white smoke
prevention air preheater, and discharged into the atmosphere after treatment in the scrubber absorption tower. Table 9.9 shows properties of exhaust gas.

**Table 9.9 Exhaust gas analysis (Oku et al, 1990)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Carbonizing furnace</th>
<th>Secondary combustion chamber</th>
<th>Stack</th>
<th>Japanese Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>730</td>
<td>790</td>
<td>124</td>
<td>-</td>
</tr>
<tr>
<td>Humidity, Nm³/h</td>
<td>4.240</td>
<td>5.440</td>
<td>11.900</td>
<td>-</td>
</tr>
<tr>
<td>Dryness, Nm³/h</td>
<td>2.320</td>
<td>3.440</td>
<td>9.210</td>
<td>-</td>
</tr>
<tr>
<td>Dust conc, g/m²³</td>
<td>-</td>
<td>-</td>
<td>0.019</td>
<td>-</td>
</tr>
<tr>
<td>NOx, ppm</td>
<td>30</td>
<td>25</td>
<td>23</td>
<td>&lt;250</td>
</tr>
<tr>
<td>CO₂, %</td>
<td>16.4</td>
<td>8.9</td>
<td>3.0</td>
<td>-</td>
</tr>
<tr>
<td>O₂, %</td>
<td>0.0</td>
<td>6.0</td>
<td>17.0</td>
<td>-</td>
</tr>
<tr>
<td>CO, %</td>
<td>0.5</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
</tr>
<tr>
<td>H₂, %</td>
<td>0.77</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
</tr>
<tr>
<td>SO₂, ppm</td>
<td>61</td>
<td>46</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>HCl, mg/m³</td>
<td>1.129</td>
<td>550</td>
<td>10</td>
<td>&lt;700</td>
</tr>
</tbody>
</table>

The NOx concentration is 20-30 ppm, which is greatly reduced when compared with NOx concentrations of 100-200 ppm in a conventional regular fluidized bed incineration. This is thought to result from the effects of the carbonizing secondary combustion system which combines the carbonizing furnace with the secondary combustion chamber.

**9.7 Gas analysis from the biofly brick process**

The gas samples were collected during the firing of biofly brick as per the methods described in Chapter 4. These samples were then analysed to determine the concentration of the pollutants. The results of these analyses are provided and discussed in the following sections. Three batches were selected for gas analysis. They are:

(I) 25 S/30 FA/ 45 C/S Shellharbour mix, provides information on biofly brick made from uncontaminated sewage sludge from Shellharbour. The mix composition also provides the highest sludge proportion.

(II) 25 S/30 FA/45 C/S Port Kembla mix is chosen to provide information on biofly brick made from possibly industry contaminated sewage sludge from Port Kembla. The mix composition also provides the highest proportion of sludge.
Laboratory clay/shale mix is chosen to obtain base line data on flue gas emitted from ordinary brick manufacturing.

For each batch, 24 bricks made of the same proportion of raw materials were fired in the kiln. The sampling was carried out with the intention of determining the concentration of the following pollutants namely, heavy metals, fluorides, chlorides and acid gases. These pollutants were selected based on the previous review. Since the firing temperature used in a batch process changed with time, it was decided to determine the concentration of the pollutants at each stage of firing. Hence, the firing process was divided into five different temperature ranges and gas samples were collected continuously within each temperature range.

The five temperature ranges are: 0 to 200°C; 200 to 400°C; 400 to 600°C; 600 to 800°C and 800 to 1100°C. Gas samples were collected for 3.25 hours per range for the first four ranges, and for 7.50 hours for the last range for biofly bricks. For the clay/shale brick the first four temperature ranges were the same and the fifth was between 800 to 1030°C. The time ranges however were different and they are 4.25 hours, followed by 21.25, 11.75, 3.25 and 7.50 hours, respectively.

The gas flow sampling rate was maintained constant at 0.023 m³/min during the sampling period for all the pollutants. So, for the first four ranges about 4.4 m³ of gas was sampled for each pollutant analysis and for the fifth temperature range about 11.3 m³ of gas was sampled for each pollutant for biofly bricks. For clay/shale brick the first range was about 5 m³ followed by 24, 13, 3.7 and 8.6 m³, respectively. Detailed data are summarized in Tables 9.10, 9.11 and 9.12 respectively for Shellharbour biofly mix, Port Kembla biofly mix and laboratory clay/shale for gas composition and flue gas emissions. Similarly Tables 9.13, 9.14 and 9.15 provides a summary of pollutant concentration in the flue gas from Shellharbour mix, Port Kembla mix, and Badgery’s Creek clay/shale respectively. The relevant Australian Standard value is shown on the right most column of the three tables.
### Table 9.10. Volume of gas collected during firing of 25 S/30 FA/45 C/S Shellharbour biofly brick

<table>
<thead>
<tr>
<th>Date/Time</th>
<th>Time Start/End</th>
<th>Acid gases reading m³</th>
<th>Hydrogen fluoride reading m³</th>
<th>Trace metals reading m³</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2/95</td>
<td>9.15</td>
<td>0000.230</td>
<td>0052.829</td>
<td>0000.480</td>
<td>0</td>
</tr>
<tr>
<td>1/2/95</td>
<td>12.30</td>
<td>0004.914</td>
<td>0057.229</td>
<td>0004.969</td>
<td>200</td>
</tr>
<tr>
<td>1/2/95</td>
<td>3.45</td>
<td>0009.375</td>
<td>0061.665</td>
<td>0009.462</td>
<td>400</td>
</tr>
<tr>
<td>1/2/95</td>
<td>7.00</td>
<td>0013.894</td>
<td>0066.167</td>
<td>0013.905</td>
<td>600</td>
</tr>
<tr>
<td>1/2/95</td>
<td>10.15</td>
<td>0018.056</td>
<td>0070.460</td>
<td>0018.029</td>
<td>800</td>
</tr>
<tr>
<td>2/2/95</td>
<td>5.45</td>
<td>0029.389</td>
<td>0081.806</td>
<td>0029.430</td>
<td>1100</td>
</tr>
<tr>
<td>3.25</td>
<td>9.15-12.30</td>
<td>4.684</td>
<td>4.400</td>
<td>4.489</td>
<td>0-200</td>
</tr>
<tr>
<td>3.25</td>
<td>3.45-7.00</td>
<td>4.519</td>
<td>4.502</td>
<td>4.443</td>
<td>400-600</td>
</tr>
<tr>
<td>3.25</td>
<td>7.00-10.15</td>
<td>4.162</td>
<td>4.293</td>
<td>4.124</td>
<td>600-800</td>
</tr>
<tr>
<td>7.50</td>
<td>10.15-5.45</td>
<td>11.333</td>
<td>11.346</td>
<td>11.401</td>
<td>800-1100</td>
</tr>
</tbody>
</table>

### Table 9.11. Volume of gas collected during firing of 25 S/30 FA/45 C/S Port Kembla biofly brick

<table>
<thead>
<tr>
<th>Date/Time</th>
<th>Time Start/End</th>
<th>Acid gases reading m³</th>
<th>Hydrogen fluoride reading m³</th>
<th>Trace metals reading m³</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4/5/95</td>
<td>18.19</td>
<td>0000.403</td>
<td>0099.038</td>
<td>0029.065</td>
<td>0</td>
</tr>
<tr>
<td>4/5/95</td>
<td>21.30</td>
<td>0003.875</td>
<td>0101.865</td>
<td>0032.570</td>
<td>200</td>
</tr>
<tr>
<td>4/5/95</td>
<td>00.31</td>
<td>0007.711</td>
<td>0104.958</td>
<td>0036.126</td>
<td>400</td>
</tr>
<tr>
<td>4/5/95</td>
<td>03.48</td>
<td>0011.242</td>
<td>0107.624</td>
<td>0039.541</td>
<td>600</td>
</tr>
<tr>
<td>4/5/95</td>
<td>07.00</td>
<td>0014.783</td>
<td>0110.097</td>
<td>0042.969</td>
<td>800</td>
</tr>
<tr>
<td>5/5/95</td>
<td>14.50</td>
<td>0024.851</td>
<td>0118.501</td>
<td>0051.585</td>
<td>1100</td>
</tr>
<tr>
<td>3.25</td>
<td>18.19-21.30</td>
<td>3.472</td>
<td>2.827</td>
<td>3.505</td>
<td>0-200</td>
</tr>
<tr>
<td>3.25</td>
<td>21.39-00.31</td>
<td>3.836</td>
<td>3.093</td>
<td>3.556</td>
<td>200-400</td>
</tr>
<tr>
<td>3.25</td>
<td>00.51-03.48</td>
<td>3.531</td>
<td>2.666</td>
<td>3.415</td>
<td>400-600</td>
</tr>
<tr>
<td>3.25</td>
<td>04.02-07.00</td>
<td>3.541</td>
<td>2.473</td>
<td>3.428</td>
<td>600-800</td>
</tr>
<tr>
<td>7.50</td>
<td>07.20-14.50</td>
<td>10.068</td>
<td>8.404</td>
<td>8.616</td>
<td>800-1100</td>
</tr>
</tbody>
</table>
Table 9.12. Volume of gas collected during firing of Badgery's Creek clay/shale brick

<table>
<thead>
<tr>
<th>Date/Time</th>
<th>Time Start/End</th>
<th>Acid gases reading</th>
<th>Hydrogen fluoride reading</th>
<th>Trace metals</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/5/95</td>
<td>16.30</td>
<td>0.026441</td>
<td>0.0119623</td>
<td>0.0052781</td>
<td>0</td>
</tr>
<tr>
<td>9/5/95</td>
<td>20.30</td>
<td>0.031079</td>
<td>0.0124927</td>
<td>0.0057792</td>
<td>200</td>
</tr>
<tr>
<td>9/5/95</td>
<td>17.45</td>
<td>0.055615</td>
<td>0.0149024</td>
<td>0.0082564</td>
<td>400</td>
</tr>
<tr>
<td>10/5/95</td>
<td>05.35</td>
<td>0.069279</td>
<td>0.0163387</td>
<td>0.0096201</td>
<td>600</td>
</tr>
<tr>
<td>10/5/95</td>
<td>09.00</td>
<td>0.073070</td>
<td>0.0166798</td>
<td>0.0100032</td>
<td>800</td>
</tr>
<tr>
<td>10/5/95</td>
<td>16.30</td>
<td>0.082063</td>
<td>0.0175459</td>
<td>0.0110579</td>
<td>1030</td>
</tr>
<tr>
<td>4.25</td>
<td>16.30-20.30</td>
<td>4.638</td>
<td>5.304</td>
<td>5.011</td>
<td>0-200</td>
</tr>
<tr>
<td>21.25</td>
<td>20.50-17.45</td>
<td>24.536</td>
<td>24.097</td>
<td>24.772</td>
<td>200-400</td>
</tr>
<tr>
<td>11.75</td>
<td>18.04-05.35</td>
<td>13.664</td>
<td>14.363</td>
<td>13.637</td>
<td>400-600</td>
</tr>
<tr>
<td>3.25</td>
<td>05.50-09.00</td>
<td>3.791</td>
<td>3.411</td>
<td>3.831</td>
<td>600-800</td>
</tr>
<tr>
<td>7.50</td>
<td>09.00-16.30</td>
<td>8.993</td>
<td>8.661</td>
<td>10.547</td>
<td>800-1030</td>
</tr>
</tbody>
</table>

Table 9.13. Summary of pollutant concentration in the gas sample 25 S/30 FA/45 C/S Shellharbour

<table>
<thead>
<tr>
<th>No</th>
<th>Pollutant</th>
<th>0-200 °C</th>
<th>200-400 °C</th>
<th>400-600 °C</th>
<th>600-800 °C</th>
<th>800-1100 °C</th>
<th>Australian Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>0.0040</td>
<td>0.0045</td>
<td>0.0045</td>
<td>0.0046</td>
<td>0.0016</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Cr</td>
<td>0.0008</td>
<td>0.0005</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0003</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Zn</td>
<td>0.0190</td>
<td>0.0137</td>
<td>0.0129</td>
<td>0.0140</td>
<td>0.0051</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>0.0050</td>
<td>0.0037</td>
<td>0.0038</td>
<td>0.0043</td>
<td>0.0009</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Mn</td>
<td>0.0020</td>
<td>0.0019</td>
<td>0.0015</td>
<td>0.0012</td>
<td>0.0006</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pb</td>
<td>0.0189</td>
<td>0.0104</td>
<td>0.0115</td>
<td>0.0095</td>
<td>0.0030</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>0.0701</td>
<td>0.0340</td>
<td>0.0392</td>
<td>0.0323</td>
<td>0.0130</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Al</td>
<td>0.0456</td>
<td>0.0161</td>
<td>0.0156</td>
<td>0.0186</td>
<td>0.0213</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Cd</td>
<td>0.0025</td>
<td>0.0018</td>
<td>0.0020</td>
<td>0.0016</td>
<td>0.0005</td>
<td>20</td>
</tr>
<tr>
<td>10</td>
<td>Fluoride</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>5.162</td>
<td>50</td>
</tr>
<tr>
<td>11</td>
<td>Chloride</td>
<td>0.2857</td>
<td>0.2862</td>
<td>0.8672</td>
<td>2.4933</td>
<td>1.3300</td>
<td>200</td>
</tr>
<tr>
<td>12</td>
<td>Acid gas</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.000001</td>
<td>0.000005</td>
<td>400</td>
</tr>
</tbody>
</table>

ND not detected
### Table 9.14. Summary of pollutant concentration in the gas sample

#### 25 S/30 FA/45 C/S Port Kembla

<table>
<thead>
<tr>
<th>No</th>
<th>Pollutant</th>
<th>Pollutant concentration after dilution ( \text{mg/m}^3 )</th>
<th>Australian Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0-200 °C</td>
<td>200-400 °C</td>
</tr>
<tr>
<td>1</td>
<td>Cu</td>
<td>0.0018</td>
<td>0.0009</td>
</tr>
<tr>
<td>2</td>
<td>Cr</td>
<td>0.0028</td>
<td>0.0002</td>
</tr>
<tr>
<td>3</td>
<td>Zn</td>
<td>0.0049</td>
<td>0.0042</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>0.0006</td>
<td>0.0006</td>
</tr>
<tr>
<td>5</td>
<td>Mg</td>
<td>0.0003</td>
<td>0.00006</td>
</tr>
<tr>
<td>6</td>
<td>Pb</td>
<td>0.0002</td>
<td>0.0028</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>0.0062</td>
<td>0.0028</td>
</tr>
<tr>
<td>8</td>
<td>Al</td>
<td>0.0031</td>
<td>0.0006</td>
</tr>
<tr>
<td>9</td>
<td>Cd</td>
<td>0.0001</td>
<td>0.00007</td>
</tr>
<tr>
<td>10</td>
<td>Fluoride</td>
<td>0.0760</td>
<td>0.0460</td>
</tr>
<tr>
<td>11</td>
<td>Chloride</td>
<td>0.5275</td>
<td>0.9785</td>
</tr>
<tr>
<td>12</td>
<td>Acid gas</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND not detected

### Table 9.15. Summary of pollutant concentration in the gas sample of

#### Badgery's Creek Clay/Shale

<table>
<thead>
<tr>
<th>No</th>
<th>Pollutant</th>
<th>Pollutant concentration after dilution ( \text{mg/m}^3 )</th>
<th>Australian Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0-200 °C</td>
<td>200-400 °C</td>
</tr>
<tr>
<td>1</td>
<td>Cu</td>
<td>0.0149</td>
<td>0.0030</td>
</tr>
<tr>
<td>2</td>
<td>Cr</td>
<td>0.0093</td>
<td>0.0017</td>
</tr>
<tr>
<td>3</td>
<td>Zn</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>Ni</td>
<td>0.0122</td>
<td>0.0026</td>
</tr>
<tr>
<td>5</td>
<td>Mn</td>
<td>0.0009</td>
<td>0.0002</td>
</tr>
<tr>
<td>6</td>
<td>Pb</td>
<td>0.9978</td>
<td>0.0040</td>
</tr>
<tr>
<td>7</td>
<td>Fe</td>
<td>0.0098</td>
<td>0.0035</td>
</tr>
<tr>
<td>8</td>
<td>Al</td>
<td>0.0301</td>
<td>0.0091</td>
</tr>
<tr>
<td>9</td>
<td>Cd</td>
<td>0.0001</td>
<td>0.00005</td>
</tr>
<tr>
<td>10</td>
<td>Fluoride</td>
<td>1.1102</td>
<td>0.1889</td>
</tr>
<tr>
<td>11</td>
<td>Chloride</td>
<td>0.4879</td>
<td>0.0801</td>
</tr>
<tr>
<td>12</td>
<td>Acid gas</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND not detected

As shown in Chapter 4, the gas kiln exhaust was situated immediately above the kiln cavity but there was an air gap of 200 mm between the kiln and the knobby, when hot gases for kiln exhaust, they get diluted from atmospheric air and escape into the flue pipe. Hence calculation of a dilution factor is important. A dilution factor of 10 have
been calculated and used to correct the emissions throughout the entire gas sampling run. Further details on the dilution factor calculation are found in Appendix 3.

9.7.1. Heavy Metals

The samples were analysed to determine the concentration of Cadmium, Chromium, Lead, Manganese, Aluminium, Iron, Copper, Zinc and Nickel. Four of these metals (aluminium 660.2°C, cadmium 320.9°C, lead 327.4°C and zinc 419.46°C) have elemental melting point below the vitrification temperature. For example, if cadmium is present in the sludge and fly ash in solution as cadmium chloride, it could volatilize during firing. On the other hand, if it is present as a precipitated hydroxide, it would probably decompose to the oxide, but would not volatilize at the temperature of firing. It is believed, however, that most of the hazardous or potentially hazardous metals, will not disproportionately appear in stack gases because of volatilization, but will be converted to oxides and appear in the liquid collected according to the method mentioned in Chapter 4. These metals warrant extreme attention with respect to their potential release, during firing of the brick.

The raw materials used in the biofly brick process, clay/shale, fly ash and sewage sludge, contain heavy metals of varying proportions. As it was decided to determine the concentration of the heavy metals that could potentially be emitted during the firing of the bricks, the concentrations of the heavy metals in the raw material was also determined. The concentrations of these heavy metals in the raw materials are given in Table 9.16. Comparison of the metal concentrations in sludges and fly ash with available literature (US EPA, 1975, Bridle et al, 1990, Alleman et al, 1990, Oku et al, 1990) indicated that although wide variability exist, in general the concentration value shown in Table 9.16 are within acceptable range.
The variation of aluminium emissions are illustrated in Figure 9.1. From the graph it can be seen that the aluminium emissions do not change significantly with firing temperature changes in all cases which may be due to the change towards the vitrified state while the temperature increased gradually.

Aluminium levels in Shellharbour and Port Kembla mixes are approximately the same, but emissions are different. Aluminium levels in both mixes are low compared to clay/shale, emissions between Port Kembla and Badgery's Creek clay/shale reflect this, but not Shellharbour and Badgery's Creek clay/shale. One possible reason is that aluminium is likely to solidify differently throughout the matrix.

Aluminium emission seems to be affected by the percent of aluminium in different sludge but it is not conclusive. Considering the high aluminium content in the raw materials the emissions are very low possibly due to a silicate-based entrapment mechanism.

The aluminium emissions in the flue gas vary with the temperature of firing and above 400°C, the level of aluminium concentration increases up to 800°C and subsequently it drops. It should be noted that the maximum concentration of 0.1140
mg/m$^3$ aluminium, was emitted during the firing of the reference brick in the temperature range of 600 to 800°C.

![Figure 9.1. Concentration of Aluminium Emission in Different Temperature Ranges](image)

Cadmium

The variation of cadmium emission is illustrated in Figure 9.2. From the graph it can be noted that the emission of cadmium does vary proportionally with the addition of sludge, 800 and 600 mg/kg for Shellharbour and Port Kembla, respectively.

Also from the graph it can be noted that the emission of cadmium does vary proportionally with the addition of the waste materials, 403 and 353 mg/kg for Shellharbour and Port Kembla mixes respectively.

Cadmium is high in Badgery's Creek clay/shale compared to Shellharbour and Port Kembla mixes. However the graph shows that the emission behaviour is different, one possible reason that cadmium is likely to be solidify differently through the matrix. It is
clear from the graph that maximum emissions is well below the Australian standard of 20 mg/m³.

![Figure 9.2. Concentration of Cadmium Emission in Different Temperature Ranges](image)

**Figure 9.2. Concentration of Cadmium Emission in Different Temperature Ranges**

**Chromium**

The maximum concentration of chromium 0.01305 mg/m³, was emitted during the firing of the reference brick in the temperature range of 600 to 800°C. However Shellharbour and Port Kembla mixes show a trend of decreasing chromium emissions with increasing temperature.

The variation of chromium emissions within the different temperature ranges is illustrated in Figure 9.3. From the graph it can be inferred that reference emission levels against biofly emissions shows the dependence of chromium emission levels on chromium concentration levels of raw materials.

There is no standard available for chromium emission. However the graph shows that the emission of chromium from biofly bricks were lower than the reference sample.
Copper

The copper emission trend is similar to that observed for chromium. The maximum concentration of copper, 0.0326 mg/m$^3$, was emitted during the firing of the reference brick in the temperature range of 600 to 800°C.

The variation of copper emission within the different temperature ranges is illustrated in Figure 9.4. From the graph it can be inferred that the emission of copper is not directly proportional to the concentration of copper in the raw sludge added, 630 and 760 mg/kg for Shellharbour and Port Kembla, respectively.

Although there is a significant difference in copper concentration between clay/shale and biofly brick raw materials, the emission is of the same magnitude. This indicates that the firing of the biofly brick has the potential to "lock up" the copper throughout the matrix. Further this amount of "lock up" seems to dependent on the type of sludge.
In general both clay/shale and biofly copper emissions are well below the Australian standard for stationary sources of 3 mg/m$^3$.

![Figure 9.4. Concentration of Copper Emission in Different Temperature Ranges](image)

**Iron**

The variations of iron emission are illustrated in Figure 9.5. From the graph it can be seen that the iron emission is not proportional to the sludge addition, 9300 and 11900 mg/kg for Shellharbour and Port Kembla, respectively.

The iron emissions show that for both Port Kembla and clay/shale, maximum concentration occurs around 800°C and is also found that their behaviour seems to be similar at all other temperature as well.

The iron emission for Shellharbour mix is similar to other metal emissions. In general all metal emissions from Shellharbour mix are marginally higher than for Port Kembla mix. This trend shows that "locking up" of metals may be different within different types of sludges.
No Australian Standard is available for iron emissions from stationary sources. But considering the high content of iron in the raw mix, 58650 and 65150 mg/kg for Shellharbour and Port Kembla respectively, the emissions are very low.

![Figure 9.5. Concentration of Iron Emission in Different Temperature Ranges](image)

**Figure 9.5. Concentration of Iron Emission in Different Temperature Ranges**

**Manganese**

All the stack gas samples analysed for biofly and clay/shale bricks contained some quantity of manganese. The maximum concentration of manganese, 0.0024 mg/m³, was emitted during the firing of Port Kembla brick in the temperature range of 600 to 800°C.

The variation of manganese emission within the different temperature ranges is illustrated in Figure 9.6. From the graph it can be inferred that the emission of manganese is not directly proportional to the concentration of manganese in the raw sludge added, 540 and 590 mg/kg for Shellharbour and Port Kembla, respectively.

The emission of manganese reaches the same emission in the temperature range 600 to 800°C for all the bricks. The manganese emissions show that for Shellharbour and Port Kembla, maximum concentration occurs around 800°C and it is also found that at this temperature, their behaviour is similar.
No Australian Standard is available for manganese emissions from stationary sources. But considering the high content of manganese in the raw mix, 640.5 and 625.5 mg/kg for Shellharbour and Port Kembla respectively, the emissions are very low.

![Graph showing manganese concentration in different temperature ranges](image)

**Figure 9.6. Concentration of Manganese Emission in Different Temperature Ranges**

**Nickel**

When compared with nickel concentration of raw clay/shale, the biofly mix concentrations are slightly lower. However the nickel emission levels from biofly are lower than clay/shale. This gives support to the previous conclusion that the metals are locked up in the biofly brick.

The variation of nickel emission with the addition of sludge is shown in Figure 9.7. From the graph it can be seen that the emission of nickel indicates that the firing of the biofly brick has the potential to decrease the nickel emission. No clear trend is visible with reference to the effect of temperature on nickel emissions for all samples.
No absolute Standard is available for nickel emissions from stationary sources. But considering the content of nickel in the raw mix, 49.6 and 49.6 mg/kg for Shellharbour and Port Kembla respectively, the emissions are very low.

![Graph showing concentration of nickel emission in different temperature ranges](image)

**Figure 9.7. Concentration of Nickel Emission in Different Temperature Ranges**

**Lead**

It can be seen from the results in Table 9.16 that the concentration of lead is quite low when compared with other heavy metals. The clay/shale lead emissions are, in general higher than biofly brick emissions. This gives further support to the theory of locking up of the heavy metals in the waste materials throughout the matrix.

The variation of lead emission is shown in Figure 9.8. From this graph, it can be seen that the lead emission varies proportionally with the addition of sewage sludge, 160 and 40 mg/kg for Shellharbour and Port Kembla, respectively.

It appears that there is a decreasing trend of lead emission levels for Shellharbour and Port Kembla mixes with increases in temperature between 400 and 1100°C. This may be due to the change towards the vitrified state while temperature increased gradually.
No absolute Standard is available for lead emissions from stationary sources. But considering the content of lead in the raw mix, 68.5 and 38.5 mg/kg for Shellharbour and Port Kembla respectively, the emissions are very low.

![Graph showing concentration of lead emission in different temperature ranges](image)

**Figure 9.8. Concentration of Lead Emission in Different Temperature Ranges**

**Zinc**

It can be seen from Table 9.16 that sludge has more influence on the emission of zinc than clay/shale. This is proved by the zinc emissions from the biofly brick in different ranges. However the emissions of clay/shale brick were detected only in the range 600 to 800°C.

The variation of zinc emissions is shown in Figure 9.9. From this graph it can be seen that, zinc emissions have been found to be very low particularly in clay/shale. However biofly brick zinc emissions are very similar in both Shellharbour and Port Kembla mixes, and they are higher than clay shale.

The zinc concentration is very high in the raw materials and that values are 2034.5 and 1602 mg/kg for Shellharbour and Port Kembla respectively. However the emission
of zinc at all temperatures was far lower than the Standard value of 10 mg/m³.

![Zinc Concentration Chart]

**Figure 9.9. Concentration of Zinc Emission in Different Temperature Ranges**

**Fluorides**

From the literature review it was found that the major air pollution problem for the clay/shale brick was the emission of fluorides. As a result the stack gas resulting from firing of the brick was sampled and analysed for fluoride concentration. From the results illustrated in Figure 9.10 it can be seen that the maximum emission of 5.162 mg/m³ occurred during the firing of Shellharbour biofly brick sample. It can also be seen that fluoride emissions are comparatively higher for the reference brick between 0-800°C.

The biofly bricks emit lower concentrations of fluoride during firing between 0-800°C and hence might prove to be a good solution for the fluoride emission problems faced by the conventional clay brick. However fluoride emissions were very high in comparison with the other pollutant concentrations and was comparatively higher in the temperature range of 800-1100°C for the biofly brick samples. In comparison with the Australian Standard, the emissions were very low.
Acid gases (HCl)

Acid gas emission has been a problem in the manufacture of the clay/shale bricks and also in sludge incineration and sludge melting processes. Since the biofly brick process involves clay/shale, sewage sludge and fly ash as raw materials, it is necessary to determine the acid gas emissions.

Figure 9.11 shows that acid gas emissions were relatively very low in comparison to the other pollutants. It can be observed from the results presented here that there is little variation in the emission of acid gases between the different brick samples.

The maximum emission was observed in the temperature range of 800-1100°C from Port Kembla mix. At the same time the emission concentration were below detection limit within the ranges of 200-400°C and 400-600°C in all the samples. Comparison with the Standard, the emissions are negligible.
Chloride

The emission of chloride is a problem faced by sludge incineration and sludge melting processes. However the emission of chloride is mainly based on the source and the type of the sludge. So the emission samples were collected and analysed for chloride concentration.

It can be observed from the results illustrated in figure 9.12 that there is some variation in the emission of chloride among the samples and the highest concentration detected was in the temperature range of 600-800°C for all samples.

A general increase in chloride emissions with temperature increase up to 800°C is observed which may be due to the heat work during firing. In general there is similarity in behaviour between Shellharbour and Port Kembla mixes and clay/shale. However, the amount of chloride emissions from Port Kembla mix is slightly higher than clay/shale brick.
In comparison with the Standard, the emissions are negligible. Hydrogen chloride, which would be generated by decomposition of certain plastics from sewage sludge, is not a significant problem at concentrations currently observed.

The following observations are made based on flue gas analysis of heavy metals and acid gases.

- The heavy metal emission from the biofly bricks was less than that of the conventional clay bricks and is well within the standard limits.
- Even though the raw materials used for making the biofly bricks had a very high concentration of heavy metals, the emission rates are comparatively low. This proves that the biofly brick process has the potential to reduce the heavy metal emission. This also proves that the heavy metals in the sludge and fly ash are trapped inside the brick during the solidification process.
- The fluoride emission at different temperatures was comparatively low in the case of the biofly bricks. This indicates that by substituting the clay/shale with sewage sludge...
and fly ash, the fluoride emission from brick kilns can be reduced except at 1100°C. However the total emission from biofly is lower than clay/shale.

- The pollutant emission varied with firing temperature. When bricks of the same composition 25 S/30 FA/45 C/S were fired the concentration of pollutants in the stack gas varied with increasing temperature.

- The emission of heavy metals does vary directly with the quantity of heavy metals in the sludge in the case of Zn, Mn, Pb, Al and Cd, however it does not vary directly with Cu, Cr, Fe and Ni. From this it can be concluded that other factors could be involved in the process, such as kiln temperature and other raw materials fly ash and clay/shale used in the brick making.

**9.7.2. Gaseous Pollutants**

Gaseous pollutants that could be released by the biofly brick during firing are: hydrogen chloride, fluoride and acid gases as discussed earlier, and other gases such as sulfur dioxide, oxides of nitrogen, carbon monoxide, carbon dioxide and combustible gases. Data are presented in Table 9.17 of gaseous pollutant emission detected from the brick samples during firing including different temperature levels and pollutant concentration for SO₂, NOₓ, CO, CO₂ and combustible gases. The emissions are also compared with Victorian Standard values, for emission levels for stationary sources. The data are provided for biofly brick mix proportional of 25 S/30 FA/45 C/S Shellharbour, Port Kembla biofly brick and clay/shale laboratory brick. The detailed analysis of individual parameters are summarized below, whereas the raw data is presented in appendix 3.
### Table 9.17. Average gaseous pollutant emission detected from the brick samples

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Average Pollutant Concentration mg/m³</th>
<th>Overall average mg/m³</th>
<th>Victorian Standard mg/m³</th>
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<tbody>
<tr>
<td><strong>Badgery's Creek</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂ mg/m³</td>
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<tr>
<td>NOₓ mg/m³</td>
<td>4.09</td>
<td>2.54</td>
<td>27.46</td>
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<tr>
<td>CO mg/m³</td>
<td>2.28</td>
<td>3.87</td>
<td>8.28</td>
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<tr>
<td>CO₂%</td>
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<td>0.79</td>
</tr>
<tr>
<td>CG%</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Shellharbour</strong></td>
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<td></td>
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<tr>
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<tr>
<td>NOₓ mg/m³</td>
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<tr>
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<td>0.91</td>
<td>60.29</td>
</tr>
<tr>
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<td>0.04</td>
<td>0.23</td>
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<tr>
<td>CG%</td>
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</tr>
<tr>
<td><strong>Port Kembla</strong></td>
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<td>SO₂ mg/m³</td>
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</tr>
<tr>
<td>NOₓ mg/m³</td>
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<tr>
<td>CO mg/m³</td>
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<tr>
<td>CO₂%</td>
<td>0.92</td>
<td>0.95</td>
<td>2.32</td>
</tr>
<tr>
<td>CG%</td>
<td>0</td>
<td>0.03</td>
<td>0.16</td>
</tr>
</tbody>
</table>

CG: Combustible gases

**Sulfur dioxide**

Table 9.17 illustrates that some of the gas samples detected contained small quantities of sulfur dioxide. The reference brick sample, emitted some sulfur dioxide at a concentration of 30.62 mg/m³ (10.56 ppm) during firing within the temperature range 800-1030°C.

The maximum average concentration of sulfur dioxide of 379.11 mg/m³ (130.73 ppm), was emitted during the firing of Port Kembla biofly brick in the temperature range 800-1100°C, and it is attributed to the industrial type of sludge.

Most of the sulfur dioxide emission seems to have occurred during the vitrification process except for some traces emitted during the firing of Shellharbour biofly brick. The trace concentration were 9.07 and 0.81 mg/m³ (3.13 and 0.28 ppm) respectively which occurred within the first two temperature ranges 0-400°C during the dehydration stage.
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All emission values detected were below the Victorian Standard volume of 5600 mg/m³. Figures 9.13, 9.14 and 9.15 illustrate the dynamic change of SO₂ concentration with varying temperature for Shellharbour biofly brick, Port Kembla biofly brick and clay/shale brick, respectively.

In general it is noticed that sulfur concentration from Port Kembla increases with increasing temperature. However the Shellharbour mix emitted only trace quantities which is completely different in behaviour to Port Kembla samples. The clay/shale emits small amount of SO₂ only after 850°C. It is clear from the figures that sulfur dioxide emission are dependent on sludge type.

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**Figure 9.13. Sulfur Dioxide Emission of Shellharbour Biofly Brick**
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Figure 9.14. Sulfur Dioxide Emission of Port Kembla Biofly Brick

Figure 9.15. Sulfur Dioxide Emission of Badgery’s Creek Clay/Shale Brick
Nitrogen oxides

The emission concentration change during firing of Shellharbour, Port Kembla bricks and clay/shale brick are illustrated respectively in Figures 9.16, 9.17 and 9.18. The concentration of nitrogen oxides detected in all samples were below the Victorian Standard value of 350 mg/m³. The maximum average emission was 98.07 mg/m³ (46.70 ppm) from the firing of Port Kembla sample and may be due to the sludge type.

Nitrogen oxide emission in Port Kembla mix increased with increases in temperature. The Shellharbour mix behaviour is different from Port Kembla. The Shellharbour mix emissions start at 500°C and proceeding to 1100°C, with the maximum average emission of the sample being 25.11 mg/m³ (11.96 ppm). However the clay/shale emissions is sporadic, and in general increase with increases in temperature, the maximum average emission of the sample being 50.67 mg/m³ (24.13 ppm).

The maximum average emission detected for Port Kembla and Shellharbour were below the Victorian limit of 350 mg/m³. The above limit is similar to the Standard limit set by US. EPA (1975). It was expected that the clay/shale brick would be far below the Victorian limit which was the case.

Figure 9.16. Nitrogen Oxides Emission of Shellharbour Biofly Brick
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Figure 9.17. Nitrogen Oxides Emission of Port Kembla Biofly Brick

Figure 9.18. Nitrogen Oxides Emission of Badgery’s Creek Clay/Shale Brick
Carbon monoxide

The range of CO₂ emission concentration detected for Shellharbour and Port Kembla biofly bricks and clay/shale brick respectively are illustrated in Figures 9.19, 9.20 and 9.21. The maximum average emission detected during the firing of Port Kembla brick was 108.40 mg/m³ (83.39 ppm). Results for Shellharbour and clay/shale were 60.29 mg/m³ and 8.28 mg/m³ (46.38 and 6.37 ppm), respectively. These emissions are well below the Australian Standard value of 2500 mg/m³.

The maximum average emission for all the samples appears to be in the temperature range of 400-600°C during dehydration and oxidation stages. Further with increasing temperature, the emissions detected decreased gradually from dehydration stage to vitrification stage.

![Figure 9.19. Carbon Monoxide Emission of Shellharbour Biofly Brick](image-url)
Figure 9.20. Carbon Monoxide Emission of Port Kembla Biofly Brick

Figure 9.21. Carbon Monoxide Emission of Badgery’s Creek Clay/Shale Brick
Combustible gases

The concentration range detected for biofly bricks and clay/shale brick are respectively illustrated in Figures 9.22, 9.23 and 9.24. The maximum average emission detected was 0.17 % which occurred during the firing of Port Kembla biofly brick. This is associated with the industrial type of sludge.

The maximum average emission detected for the clay/shale brick is 0.13 % which was slightly less than the level detected in Port Kembla brick. The maximum average combustible gases occur in most of the samples within the range 800-1100°C during the vitrification stage. There is no detection limit found for combustible gases in any Australian Standard.

![Figure 9.22. Combustible Gases Emission of Shellharbour Biofly Brick](image)
Figure 9.23. Combustible Gases Emission of Port Kembla Biofly Brick

Figure 9.24. Combustible Gases Emission of Badgery's Creek Clay/Shale Brick
**Carbon dioxide**

The concentration range detected for biofly bricks and clay/shale brick are illustrated respectively in Figures 9.25, 9.26 and 9.27. The maximum average detection for all the samples were within the range 800-1100°C during the vitrification stage.

The maximum average concentration detected during firing of Port Kembla brick is 4.97 %, which was expected due to sludge type. The reference brick indicate a concentration of 2 % less than half of the biofly brick emissions. This was expected due to the sludge content of the biofly brick.

The trend observed for all the samples was that the content of emission increased gradually with increasing the temperature from 0-1100°C and it reached the maximum average at 1100°C. It is also noticed that overall average detection from the reference brick was >1% however for Shellharbour and Port Kembla bricks the values were < 1%.

These results reflect the difference between the two types of sludge used in the mixes namely the Shellharbour and Port Kembla brick. The Australian standard do not recommend a detection limit for CO2 emission.

**Figure 9.25. Carbon Dioxide Emission of Shellharbour Biofly Brick**
Figure 9.26. Carbon Dioxide Emission of Port Kembla Biofly Brick

Figure 9.27. Carbon Dioxide Emission of Badgery’s Creek Clay/Shale Brick
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• In summary it can be concluded that, the gaseous pollutants emission from Port Kembla biofly bricks was higher than that of the conventional clay bricks, however Shellharbour biofly bricks emission was lower than the clay bricks. This certainly indicates the effect of the type of sludge used in the manufacture of biofly bricks. The sludge of Port Kembla is contaminated with industrial sources whereas Shellharbour consists of sludge of municipal origin.

• In general the gaseous pollutants emission appears to vary with increasing firing temperature. This is particularly evident for Port Kembla mix brick emissions.

9.8. Mass balance of heavy metals in the biofly and clay/shale bricks

Heavy metals balance was conducted to confirm the entrapment of heavy metals in the brick sample. The exact volume of gas discharged from the bricks during firing could not be determined due to the type of flue system in the kiln. The approximate volume of gas discharged was calculated based on the sampling rate, which was maintained constant during the sampling period for all the pollutants, and the time elapsed for firing the bricks. The calculations for heavy metals balance is tabulated in Tables 9.18, 9.19 and 9.20 for Shellharbour, Port Kembla and clay/shale brick mixes respectively. The detailed discussion of the tabulated data are presented below.

Copper

The amount of copper in the raw materials of Shellharbour mix, Port Kembla mix and clay/shale are 5539, 6707 and 4800 mg respectively. When fired, the total emission of copper from these three brick types were found to be 0.96, 0.22 and 4.75 mg respectively. Despite the fact that biofly mix have higher content of copper present than clay/shale brick, the copper emission levels were lower than the reference brick. This is clearly indicates that the copper is trapped at a higher percentage level in the biofly brick than clay/shale brick during firing. The amount of retention is estimated to be 99.982, 99.996 and 99.901 percent for Shellharbour, Port Kembla mixes and clay/shale respectively. These values also illustrate the general concept of solidification of waste materials as a monolithic solid such as a brick which has been shown to have the potential to trap a high percentage of metals.
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## Table 9.18. Heavy Metals Balance of 25 S/30 FA/45 C/S Shellharbour biofly brick

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Total mass of wet bricks kg</th>
<th>Mass of dry sludge kg</th>
<th>Mass of fly ash kg</th>
<th>Mass of clay kg</th>
<th>Total mass of HM in bricks kg</th>
<th>Total HM in bricks mg</th>
<th>Total HM in fly ash mg</th>
<th>Total HM in clay mg</th>
<th>Total HM conc. O°C</th>
<th>HM conc. O°C</th>
<th>Total HM conc. O°C</th>
<th>Total HM conc. O°C</th>
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Table 9.19. Heavy Metals Balance of 25 S/30 FA/45 C/S Port Kembla biofly brick

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<th>Mass of clay (kg)</th>
<th>HM in sludge (mg/kg)</th>
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<td>0.003854</td>
<td>0.000285</td>
</tr>
<tr>
<td>Fe</td>
<td>96</td>
<td>24</td>
<td>5.376</td>
<td>28.8</td>
<td>43.2</td>
<td>11900</td>
<td>31000</td>
<td>58000</td>
<td>0.003854</td>
<td>0.000285</td>
</tr>
<tr>
<td>Al</td>
<td>96</td>
<td>24</td>
<td>5.376</td>
<td>28.8</td>
<td>43.2</td>
<td>29000</td>
<td>222000</td>
<td>17100</td>
<td>0.003854</td>
<td>0.000285</td>
</tr>
<tr>
<td>Cd</td>
<td>96</td>
<td>24</td>
<td>5.376</td>
<td>28.8</td>
<td>43.2</td>
<td>600</td>
<td>0.2</td>
<td>450</td>
<td>0.003854</td>
<td>0.000285</td>
</tr>
</tbody>
</table>

Average 99.998
<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Total mass of bricks</th>
<th>HM in clay</th>
<th>Total HM in bricks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg</td>
<td>mg/kg</td>
<td>mg</td>
</tr>
<tr>
<td>Cu</td>
<td>96</td>
<td>50</td>
<td>4800</td>
</tr>
<tr>
<td>Cr</td>
<td>96</td>
<td>70</td>
<td>6720</td>
</tr>
<tr>
<td>Zn</td>
<td>96</td>
<td>110</td>
<td>10560</td>
</tr>
<tr>
<td>Ni</td>
<td>96</td>
<td>60</td>
<td>5760</td>
</tr>
<tr>
<td>Mn</td>
<td>96</td>
<td>590</td>
<td>56640</td>
</tr>
<tr>
<td>Pb</td>
<td>96</td>
<td>10</td>
<td>960</td>
</tr>
<tr>
<td>Fe</td>
<td>96</td>
<td>58000</td>
<td>5568000</td>
</tr>
<tr>
<td>Al</td>
<td>96</td>
<td>171000</td>
<td>16416000</td>
</tr>
<tr>
<td>Cd</td>
<td>96</td>
<td>450</td>
<td>43200</td>
</tr>
</tbody>
</table>

Average: 99.920
Chromium

The behaviour of chromium emissions is similar to copper. The amount of chromium in the raw materials for the Shellharbour, Port Kembla mixes and clay/shale are 4165, 4318 and 6720 mg respectively. However the firing total emission levels were 0.14, 0.05 and 2.95 mg. The percentage retention of chromium in all bricks were significantly higher with marginally higher retention achieved in the Port Kembla mix. Hence it appears that the percentage retention may be a function of the sludge type.

Zinc

The zinc emission characteristics are slightly different to copper and chromium. The raw mixes have 110092, 104065 and 10560 mg of zinc for Shellharbour, Port Kembla mixes and clay/shale respectively. The total emission levels from the three mixes were 3.22, 1.15 and 0.5 mg respectively. The amount of emission was proportional to the quantity of zinc in the raw materials. The amount of retention was 99.999, 99.998 and 99.995 respectively. These values are proportional to the raw materials, and in general support the concept of solidification when the brick has the potential to trap high percentage of zinc metal.

Nickel

The amount of nickel in the raw materials of Shellharbour mix, Port Kembla mix and clay/shale were 3405, 3457 and 5760 mg respectively. When fired, the total emission of nickel from these three brick types were found to be 0.85, 0.11 and 2.56 mg respectively. The amount of emission was not proportional to the quantity of zinc in the raw materials. The amount of retention was estimated to be 99.974, 99.996 and 99.955 percentage for Shellharbour, Port Kembla mixes and clay/shale respectively. These values are the reverse of the nickel content in raw materials.

Manganese

The amount of manganese in the raw materials for the Shellharbour, Port Kembla mixes and clay/shale were 51029, 51108 and 56640 mg respectively. However the firing total emission levels were 0.375, 0.115 and 0.283 mg, with marginally higher emission noticed in the Shellharbour mix. The amount of emission does not match the quantity of manganese in the raw materials. The percentage retention of manganese in all three...
bricks are significantly higher than 99.999. Hence it appears that the percentage retention may be a function of either complicated physiochemically bonded process or due to the sludge type.

**Lead**

The lead emission characteristics are completely different to zinc. The raw mixes contained 3477, 2951 and 960 mg of lead from Shellharbour, Port Kembla mixes and clay/shale respectively. The total emission levels from the three mixes are 2.57, 0.05 and 5.0 mg respectively, with marginally higher emission occur during the firing of the reference sample. The amount of emission was not proportional to the quantity of lead in the raw material. The amount of retention was 99.926, 99.998 and 99.479 respectively. These values were proportional to the total emission levels. In general the retention values support the concept that the metals were being physiochemically bonded and fused within the silicate based matrix of the vitrified brick.

**Iron**

The behaviour of iron emissions is similar to aluminium. The amount of iron in the raw materials of Shellharbour mix, Port Kembla mix and clay/shale were 3829176, 4038144 and 5568000 mg respectively. When fired, the total emission of iron from these brick types were found to be 9.24, 2.29 and 4.13 mg respectively, with marginally higher emission occurring during the firing of the Shellharbour sample. However the emission of iron was not directly proportional to the mass of the raw materials. The percentage retention of iron in all the three bricks was significantly higher than 99.999. These retention values illustrate the general concept of solidification of waste materials as a monolithic solid such as a brick which is shown to have the potential to trap a high percentage of iron metal.

**Aluminium**

The behaviour of aluminium emissions is similar to iron. The amount of aluminium in the raw materials for the Shellharbour, Port Kembla mixes and clay/shale were 1397071, 1393670 and 16416000 mg respectively. However the maximum emission level was found in the reference sample 12.2725 mg which was the highest emission during firing. The second highest emission was during the firing of Shellharbour sample 6.6775 mg and the last with marginally lower emission occurring during the firing of the Port Kembla
sample of 0.38 mg. These values indicate that the biofly brick emits less aluminium than
the normal brick during firing. The percentage retention of aluminium in all the three
bricks are significantly higher 99.999. In general the retention values support the concept
that the metals were being physiochemically bonded and fused within the silicate based
matrix of the vitrified brick.

**Cadmium**

The cadmium emission characteristics were slightly different to chromium. The raw
mixes had 23151, 22671 and 43200 mg of cadmium from Shellharbour, Port Kembla
mixes and clay/shale respectively. The total emission levels from the three mixes were
0.418, 0.022 and 0.08 mg respectively, with marginally higher emission occurring during
the firing of the Shellharbour sample. The amount of emission was not proportional to
the quantity of cadmium in the raw materials. The amount of retention was 99.998,
99.999 and 99.999 percent respectively. The percentage retention of aluminium in all
three bricks were significantly higher. Hence it is felt that the percentage retention may
be a function of the sludge type. In general the retention values support the concept of
solidification when the brick has the potential to trap high percentage of cadmium metal.

- From the material balance it can be concluded that even though a high mass of heavy
metal were fired in the kiln, the mass of heavy metals discharged in the stack was very
low. This proves that the heavy metals get entrapped in the bricks during calcination and
they are not released even at high temperature irrespective of the type of brick. This show
that this type of solidification process can entrap metals which may have significant
application in solidifying sludge with higher heavy metals.

- The amount of retention does seem to depend on the type of metal. For some metals
the amount of retention was higher with Shellharbour than with Port Kembla mixes and
vice versa. In general, the average percentage of retention of metals was 99.985, 99.998
and 99.920 respectively for Shellharbour, Port Kembla and clay/shale mix.

- In Chapter eight, the leachate analysis indicated that the amount of leachate of
various metals from the Shellharbour, Port Kembla and clay/shale mixes were extremely
small. Hence for the combined mass balance and leachate analysis, it can be concluded
that biofly bricks indeed entrap the heavy metals within the matrix presumably bonded
and fused physiochemically during the solidification process.
9.9. Biofly Brick Gas Consumption

9.9.1. Firing the brick

Clay bricks made in factories are usually fired in two different types of kilns, namely intermittent and continuous tunnel kilns. Sinclair (1987) found that the average fuel consumption using tunnel kiln was 9.9 MJ/brick and for intermittent kiln to be 21.1 MJ/brick showing that the intermittent kilns have twice the energy requirement to tunnel kilns. Most kilns are fired by either natural gas or coal however wood, saw dust and waste oil are being used as a supplementary fuel source by some manufacturers. A typical firing cycle for clay brick will be in the range of 48 to 72 hours from the time the brick enters the kiln until the time they are removed from the kiln.

In the Biofly process, the addition of sludge and fly ash to the manufacturing process should not prove to be a hindrance. In fact, the firing characteristics of the clay bricks have been altered significantly by the addition of sludge and fly ash. The dry sludge (solids content about 20%) contains an estimated energy value of 10 MJ/kg. Assuming an organic content of 60% and a sludge content of 20% in the Biofly brick the potential source of energy in the raw material is 4.2 MJ/brick based on an assumption for wet brick weight of 3.5 kg. This estimate is almost half the energy required for firing in a tunnel kiln for a single brick showing the greatest potential in energy savings. Hence sludge with a high organic and solids content will substitute half of the energy required for the Biofly brick plant.

Fly ash is a glassy pre-fired raw material which can be fired very rapidly in comparison to clay because fly ash does not undergo abrupt crystalline phase changes during firing as clay does. Therefore less time will be required for firing the Biofly brick.

A reduction in the amount of clay contained within a green brick should also reduce the energy requirement during firing. The addition of sludge and fly ash will accomplish this by partially replacing the volume normally occupied by the clay. This will increase kiln throughput and effectively save on fuel consumption.

The specific fuel consumption can be defined as the amount of heat in the fuel used per thousand bricks. For the intermittent and tunnel kilns the values reported by Sinclair
(1987) are 21.1 and 9.9 GJ/thousand bricks respectively with an overall average of 17.3 GJ/thousand bricks for all types of kilns.

9.9.2. Theoretical fuel availability:

In the case of Biofly brick heat energy is available from the sludge and a limited amount from the carbon content from the shale.

Table 9.21. Heat available from shale (Theoretical)

<table>
<thead>
<tr>
<th>Clay/Shale% by weight</th>
<th>Shale weight in brick kg</th>
<th>Heat given off KJ/brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.32</td>
<td>52</td>
</tr>
<tr>
<td>45</td>
<td>0.29</td>
<td>47</td>
</tr>
<tr>
<td>40</td>
<td>0.26</td>
<td>41</td>
</tr>
<tr>
<td>35</td>
<td>0.23</td>
<td>36</td>
</tr>
<tr>
<td>30</td>
<td>0.19</td>
<td>31</td>
</tr>
</tbody>
</table>

Table 9.22. Heat available from sludge in Biofly brick (Theoretical)

<table>
<thead>
<tr>
<th>Sludge% by weight</th>
<th>Sludge weight in brick kg</th>
<th>Heat given off KJ/brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.53</td>
<td>3180</td>
</tr>
<tr>
<td>20</td>
<td>0.70</td>
<td>4200</td>
</tr>
<tr>
<td>25</td>
<td>0.88</td>
<td>5280</td>
</tr>
</tbody>
</table>

• Assume sludge organic content 60%

Table 9.23. Total heat available in Biofly brick (Theoretical)

<table>
<thead>
<tr>
<th>Brick proportions %</th>
<th>Sludge heating value KJ/brick</th>
<th>Shale heating value KJ/brick</th>
<th>Total heating value MJ/brick</th>
<th>Energy saving %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20S/50FA/30C/S</td>
<td>4200</td>
<td>31</td>
<td>4.231</td>
<td>42.7</td>
</tr>
<tr>
<td>15S/50FA/35C/S</td>
<td>3180</td>
<td>36</td>
<td>3.216</td>
<td>32.4</td>
</tr>
<tr>
<td>20S/40FA/40C/S</td>
<td>4200</td>
<td>41</td>
<td>4.241</td>
<td>42.8</td>
</tr>
<tr>
<td>25S/30FA/45C/S</td>
<td>5280</td>
<td>47</td>
<td>5.327</td>
<td>53.8</td>
</tr>
<tr>
<td>20S/30FA/50C/S</td>
<td>4200</td>
<td>52</td>
<td>4.252</td>
<td>42.9</td>
</tr>
</tbody>
</table>
Assuming that the moist green brick contains 81.5% clay and 18.5% shale with a heating value of 0.16 MJ/kg, Table 9.21, 9.22 and 9.23 have been constructed to illustrate the theoretical heat given off by the shale and sludge for varying proportions in a Biofly brick using an assumption for wet brick weight of 3.5 kg.

The data shown on Tables 9.21, 9.22 and 9.23 also illustrate that the shale dissipates very little energy during the firing process in comparison to the available energy from sludge. In fact for 25% sludge in Biofly brick a 53.8% energy saving can be obtained.

9.9.3. Gas Consumption of Biofly Brick

The accumulative and instantaneous gas consumption for the Biofly brick and clay/shale mixes is shown in Figure 9.28 and 9.29 respectively. Figure 9.28 shows that the accumulative gas consumption of biofly brick mixes was 22.611, 22.744, 22.594 and 23.138 m³ for Shellharbour, Port Kembla, Bellambi and Wollongong respectively. The accumulative gas consumption rate was low during the first 9 hours due to water smoking stage and the first half of the dehydration stage (0-600°C). The rate increased exponentially after the first 9 hours during the second half of the dehydration stage, oxidation and vitrification stages due to the heat work to solidify the brick (600-1100°C).

However the accumulative gas consumption of clay/shale laboratory brick was found to be 40.940 m³ and it was significantly higher than all the biofly brick mixes. The accumulative gas consumption rate was low during the first 24 hours of water smoking stage between (0-400°C). The rate increased rapidly between (400-1030°C) during dehydration, oxidation and vitrification stage which attributed to the extensive heat work.

Within the first 24 hours during the water smoking stage of clay/shale mix gas consumption was low, however it was higher than the consumption of all biofly brick mixes. During the dehydration, oxidation and vitrification stages of clay/shale mix the rate increased rapidly for the second period of 24 hours, the gas consumption was high and again higher than the consumption of the biofly brick mixes.
Figure 9.28 shows the similarity between the accumulative gas consumption for the biofly brick proportions Shellharbour (15 S/50 FA/35 C/S), Port Kembla (15 P/50 FA/35 C/S), Bellambi (25 B/30 FA/45 C/S) and Wollongong (25 W/30 FA/50 C/S) respectively. By simple calculation, the data in Table 9.24 show that for 15% Shellharbour sludge (65S), 15% Port Kembla sludge (65P), 25% Bellambi sludge (55B) and 25% Wollongong sludge (55W) respectively, the percentage of energy savings were 44, 44, 44 and 43 respectively.

The data in Table 9.24 shows that there was no difference in energy consumption between 15% and 25% sludge replacement from different sources, as well as there was no difference in energy consumption between 55% and 65% replacement with waste materials.

![Figure 9.28. Accumulative Gas Consumption of Biofly Brick and Clay/Shale Mixes](image)

The instantaneous gas consumption for the Biofly brick and clay/shale mixes is shown in Figure 9.29. This Figure shows that the maximum peak gas consumption of biofly brick mixes was 5 m$^3$/h. The biofly brick mixes spikes shown corresponds to plateau in the firing curve where the gas consumption is excessive during soak time at different temperature levels of 200, 400, 600, 800 and 1100°C respectively.
Figure 9.29 shows that the maximum peak gas consumption of clay/shale brick was 2.4 m³/h. This is significantly lower than all the biofly brick mixes, however it is due to the long time of firing to a total of 48 hours. The clay/shale brick spikes shown corresponds to a plateau in the firing curve where the gas consumption is excessive during soak time at different temperature levels of 200, 400, 600, 800 and 1030°C respectively.

The instantaneous gas consumption rate is low during the first 24 hours of water smoking stage between (0-400°C). The rate increased exponentially between (400-600°C) during the first half of dehydration stage which attributed to the heat work for 12 hours.

During the second half of dehydration and first half of oxidation stages between (600-800°C), the instantaneous gas consumption rate was low for 5 hours. The rate increased exponentially between (800-1030°C) during the second half of oxidation stage and vitrification stage which attributed to the extensive heat work for 8 hours.

Figure 9.29. Instantaneous Gas Consumption of Biofly Brick and Clay/Shale Mixes
A summary of total gas consumption and energy saving using different biofly brick proportions with different types of sludge in comparison with clay/shale brick are shown in Table 9.24. In fact for a 55 or 65% waste in Biofly brick a 44.377% energy saving has been achieved. This is indeed very significant which implies that slightly more than a half of the external form of fuel is needed for firing the Biofly bricks. This compares quite well with the work reported by Slim and Wakefield (1991) during manufacture of stock bricks using sludge only with energy savings of the order of 65% for 30% sludge by volume.

9.10. Summary

• The gas consumption and flue gas analysis of the biofly and clay/shale bricks have been presented.

• A review of literature concluded that the fate of toxic and hazardous inorganics, particularly heavy metals, represents considerably more significant concern. In addition, there have been concerns of fluorine emissions from brick manufacturing plants. Fluorine is a cumulative pollutant. To determine the nature of pollutants that could be emitted, an overview of similar high temperature processes involving sewage sludge and clay/shale have been investigated.

• It is concluded from the literature, that the results did not reveal any indication whatsoever that metals were being released during the brick firing process. It appears
that the metals were being physiochemically bonded and fused within the silicate based matrix of the vitrified brick.

• "Biofly" brick process is a new process and the three materials, sewage sludge, fly ash and clay/shale have been combined to make bricks for the first time in pilot scale. There is no data available on the characteristic of pollutants that could be emitted from the brick firing.

• The biofly and clay/shale brick gas samples were collected during the firing of biofly brick as per the methods described in Chapter 4. These samples were then analysed to determine the concentration of heavy metals and other gas pollutants.

Gas emission

• The heavy metal emission from the biofly bricks was found to be lesser than that of the conventional clay bricks and was well within the standard limits adapted to the Australian Standard.

• Even though the raw materials used for making the biofly bricks had a very high concentration of heavy metals, the emission rates are comparatively low. This proves that the biofly brick process has the potential to reduce heavy metal emission. This also proves that the heavy metals in the sludge and fly ash are trapped inside the brick during the solidification process.

• The fluoride emission was comparatively low in the case of the biofly bricks. This indicates that by substituting the clay/shale with sewage sludge and fly ash, the fluoride emission from brick kilns can be reduced.

• The pollutant emission varied with firing temperature. When bricks of the same composition were fired the concentration of pollutants in the stack gas varied with increasing temperature.

• The emission of heavy metals does vary directly with the quantity of some heavy metals in the sludge, however does not vary directly with some other heavy metals in the sludge. From this it can be concluded that other factors could be involved in the process
like kiln temperature and other raw materials fly ash and clay/shale used in the brick making also influencing the emission of pollutants.

• The gaseous pollutants emission from Port Kembla biofly bricks was higher than that of the conventional clay bricks, however Shellharbour biofly bricks was less than the clay bricks. This certainly indicates the effect of the type of sludge, varied between industrial sludge of Port Kembla to domestic sludge of Shellharbour. however the emissions are well within the standard limits.

• The gaseous pollutants emission varied with firing temperature. When biofly bricks were fired the concentration of pollutants in the stack gas varied with increasing temperature.

Material balance

• Heavy metals balance was conducted to confirm the entrapment of heavy metals in the brick sample. From the material balance it can be found that even though a high mass of heavy metals were fired in the kiln, the mass of heavy metals discharged in the stack was very low. This proves that the heavy metals get entrapped in the bricks during calcination and are not released even at high temperature.

• From the material balance results it can be observed that most of the heavy metals are retained in the biofly brick. However, it was detected that the emission from clay/shale in most of the metals was higher than the biofly brick. It can be concluded that these metals get entrapped inside the Biofly bricks by some mechanism during the solidification process.

• These research findings suggest that sewage sludge with heavy metals, can satisfactorily be incorporated within commercial brick manufacturing operations. The contained metals were believed to be physico-chemically locked inside the vitrified brick, possibly due to a silicate-based entrapment mechanism.

• Since the pollutant emissions are well within the standards, the biofly brick process seems to be a viable alternative for the present day sewage sludge and fly ash disposal options.
Energy saving

- It is concluded that very significant energy savings about 44%, easily can be achieved during firing of biofly brick, since biofly brick also fired in approximately less than one half the time required for firing clay brick. This will increase the kiln throughput by almost 100%.
Chapter Ten

Materials Handling and Health Precautions

10.1. Introduction:

The “Biofly” brick being a new process and the three materials, clay/shale, fly ash and sewage sludge being combined to make a brick for the first time. Consideration of the possible impact of working with sludge, fly ash and clay/shale on health and safety is an important aspect of this project. Health and safety issues need to be considered in the light of available information and experience. Moreover, the composition and properties of sludge, fly ash and clay/shale need to be reviewed at a fundamental level. Widespread prejudice and suspicion concerning the possible ill effects of working with these materials are understandable because of lack of adequate information. On the basis of published facts and accumulated experience such perceptions can be removed and the health impacts can be considered rationally. At the very outset, it must be stated that hygienic and other normal precautions are always emphasized in the literature. Observance of good hygiene will continue to be emphasised in the future.

The purpose of this review is to assess the potential health risks associated with the use of sludge products from wastewater treatment plants. Sludge products from different plants will vary depending on wastewater and sludge treatments but for assessing the risks this review concentrated on mesophilic anaerobic digested sludge which have been used during the Biofly brick project. Two types of risk assessments are carried out. Firstly the risks are assessed by looking at the following questions:

1. Which groups of people could be at risk from exposure to sludge?
2. What densities of pathogens have been found in wastewater sludge?
3. What is the infectious dose for these pathogens?
4. Therefore what are the risks to people who are likely to get exposed?
A separate assessment of risk based on the incidence of disease in Australia, estimated excreted loads, persistence of pathogens in the environment and infectious doses is also conducted. Epidemiological studies are also summarised.

It is recognized that the major route of infection for most enteric pathogens is person to person contact. However this does not negate the possibility that exposure to wastewater sludge may be another potential route of infection.

10.2. People at risk from exposure to sludge:

People at risk from direct exposure to wastewater sludge might include wastewater and sludge treatment plant workers, sludge transporters and handlers. People directly exposed to wastewater sludge could ingest pathogens through contaminated hands or clothes. The following discussion will concentrate on direct exposure to wastewater sludge.

10.3. Pathogen densities in wastewater sludge:

A major public health concern is the risk of spread of human diseases by microorganisms from human excreta in the sewage sludge. The pathogens associated with sewage sludge fall into four categories.

**Virus**—A virus is any group of ultramicroscopic agents that reproduce only in living cells. This characteristic of viruses is important because they cannot reproduce without a host cell and, therefore, will not reproduce in wastewater. The major source of viruses that are infectious to man is from human waste that has been discharged to the sewer.

**Bacteria**—Bacteria do not require a living host cell to reproduce. Pathogenic bacteria are microscopic in size and are common in waste water. Because bacteria can reproduce outside the body, they can be present in large quantities in the collection system.

**Protozoan**—Protozoans may be present in sewage sludge. They are much larger than bacteria and viruses but are still single celled organisms. These organisms cause disease in humans. They are able to exist in the form of a cyst or spore which allows the organism to survive for prolonged periods in sewage sludge.
Parasite - A parasite lives on or in another organism of a different species, from which it derives its nourishment. The organism is called the parasite's host. Parasites normally do not kill their hosts, because the life of the parasite would also be terminated.

Pathogenic microorganisms in sewage sludge can cause disease if they come into contact with humans. This contact can occur by inhaling sludge aerosols or dust during the work with Biofly brick.

During an extensive literature search very few information about pathogen densities in Australian sludges is found. A limited number of studies have been carried out using anaerobic digested sludge in the USA and UK and the results are summarised in Table 10.1.

Anaerobic digestion process involves biological degradation of complex organic substances present in sludges in the absence of free oxygen. Primary or secondary sludge, or a mixture of both, is fed continuously or intermittently into an airtight vessel and retained for varying periods of time. Retention times can vary from 30 to 60 days in low-rate reactors and from 10 to 20 days in high-rate reactors which are mixed and heated to either mesophilic 30 to 38°C or thermophilic 50 to 60°C temperatures. The digester's performance is indicated by the percent of volatile solids (VS) destroyed. Reduction of VS usually ranges between 35% and 60%, depending on the character of the sludge, detention time and temperature.

The enteric viruses shown in Table 10.1. are probably from the enterovirus group which includes poliovirus, echovirus and coxsackieviruses. Other viruses reported by Fradkin et al., (1985) are to be present in wastewater and sludge, but for which no quantifiable densities are found, included rotavirus, hepatitis type A, reovirus, adenovirus and parvovirus. Other bacteria reported to be present were Shigella, enteropathogenic E. coli, Yersinia enterocolitica, Vibrio cholerae and Leptospira.

Aerobic digestion process produce reduction in pathogenic bacteria and viruses as well. The minimum effectiveness depends on the processes being carried out, this type of stabilization process appears to be particularly ineffective for inactivating parasite organisms.
Pathogen densities in sludge will vary seasonally and from community to community. Two factors affect pathogen densities in sludge. They are the numbers of pathogens excreted by infected individuals and persistence of these pathogens in the environment.

Table 10.1. Summary of pathogen densities in anaerobic digested wastewater sludge

<table>
<thead>
<tr>
<th>Group</th>
<th>Pathogen</th>
<th>No. of organisms/L</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>Viruses</td>
<td>Enteric viruses</td>
<td>30</td>
<td>0-60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>550</td>
<td>10-5859</td>
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<tr>
<td></td>
<td></td>
<td>1900</td>
<td>300-4100</td>
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<td>200</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>810</td>
<td>&lt;0.9-7500</td>
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<tr>
<td></td>
<td>Salmonella</td>
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<td>3-1100</td>
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<tr>
<td>Bacteria</td>
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<td>16</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Campylobacter</td>
<td>620</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>0-95</td>
</tr>
<tr>
<td>Protozoa</td>
<td>Entamoeba</td>
<td>NS</td>
<td>0-3720</td>
</tr>
<tr>
<td></td>
<td>Giardia</td>
<td>832</td>
<td>70-3.0x10^4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.9x10^4</td>
<td>3000-1.23x10^5</td>
</tr>
<tr>
<td>Helminths</td>
<td>Nematodes</td>
<td>95</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Ascaris</td>
<td>410</td>
<td>25-775</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2030</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9700</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Trichuris</td>
<td>5100</td>
<td>2785-6415</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1400</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Toxocara</td>
<td>410</td>
<td>0-230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1730</td>
<td>125-695</td>
</tr>
<tr>
<td></td>
<td>Toxascaris</td>
<td>1200</td>
<td>1010-3400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>480</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Cestodes</td>
<td>10</td>
<td>0-160</td>
</tr>
<tr>
<td></td>
<td>Taenia</td>
<td>2200</td>
<td>1250-3150</td>
</tr>
</tbody>
</table>

NS: Not Stated

The types of pathogens in Australian sludges likely to be similar to those from the USA, UK. An example of what might be expected in Australian sludges is shown in Table 10.2, which shows the number of reported cases infections caused by different
pathogens in Western Australia in 1991. Complete data is not available for the whole of Australia so Western Australia is used as an example.

It appears that in the case for Western Australia, there were more reported cases caused by the bacterial pathogens Campylobacter, Clostridium difficile and Salmonella, and the protozoa Giardia than by any other enteric pathogens. The numbers of reported helminth infections are relatively low.

Table 10.2. Number of persons infected by enteric pathogens in Western Australia in (1991)

(Public health and enteric diseases unit of state health laboratory services, 1992)

<table>
<thead>
<tr>
<th>Group</th>
<th>Pathogen</th>
<th>No. of cases reported</th>
<th>Excreted load*</th>
<th>Persistence</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Metro Area</td>
<td>State Total</td>
<td>No.</td>
</tr>
<tr>
<td>Viruses</td>
<td>Rotavirus</td>
<td>NS</td>
<td>259</td>
<td>10^6</td>
</tr>
<tr>
<td></td>
<td>Adenovirus</td>
<td>NS</td>
<td>206</td>
<td>10^5</td>
</tr>
<tr>
<td></td>
<td>Enteroviruses</td>
<td>NS</td>
<td>194</td>
<td>10^6</td>
</tr>
<tr>
<td></td>
<td>Hepatitis A</td>
<td>NS</td>
<td>142</td>
<td>10^7</td>
</tr>
<tr>
<td>Bacteria</td>
<td>Campylobacter species</td>
<td>1156</td>
<td>1579</td>
<td>10^7</td>
</tr>
<tr>
<td></td>
<td>Salmonella species</td>
<td>376</td>
<td>785</td>
<td>10^8</td>
</tr>
<tr>
<td></td>
<td>Clostridium difficile</td>
<td>438</td>
<td>520</td>
<td>10^8</td>
</tr>
<tr>
<td></td>
<td>Shigella species</td>
<td>49</td>
<td>285</td>
<td>10^7</td>
</tr>
<tr>
<td></td>
<td>Aeromonas species</td>
<td>35</td>
<td>54</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Enterotoxigenic E.coli</td>
<td>0</td>
<td>27</td>
<td>10^8</td>
</tr>
<tr>
<td>Protozoa</td>
<td>Giardia intestinalis</td>
<td>514</td>
<td>1014</td>
<td>10^5</td>
</tr>
<tr>
<td></td>
<td>Blastocystis hominis</td>
<td>353</td>
<td>494</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Cryptosporidium species</td>
<td>67</td>
<td>273</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Entamoeba species</td>
<td>49</td>
<td>70</td>
<td>10^5</td>
</tr>
<tr>
<td>Helminths</td>
<td>Hymenolepis nana</td>
<td>25</td>
<td>178</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Strongyloides stercoralis</td>
<td>14</td>
<td>132</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Trichuris trichiura</td>
<td>115</td>
<td>127</td>
<td>10^3</td>
</tr>
<tr>
<td></td>
<td>Hookworm ova</td>
<td>26</td>
<td>125</td>
<td>10^2</td>
</tr>
<tr>
<td></td>
<td>Ascaris lumbricoides</td>
<td>12</td>
<td>16</td>
<td>10^4</td>
</tr>
<tr>
<td></td>
<td>Taenia saginata</td>
<td>1</td>
<td>1</td>
<td>10^4</td>
</tr>
</tbody>
</table>

* Typical number of organisms per gram of faeces

NS: Not Specified

To assess how representative results from metropolitan area are for the rest of Australia, the incidences of notifiable enteric diseases in Perth, Melbourne and the
Kimberley region of Western Australia are compared. Data was not available for all enteric pathogens but for those shown in Table 10.3, the incidence of reported enteric infections in Melbourne is approximately half that for Perth. This may have reflected the true incidence but is more likely to have been due to differences in notification rates. The relative infection rates for different pathogens in Perth and Melbourne are similar.

The dominant enteric pathogens are Campylobacter, Giardia and Salmonella species. Infection rates for notifiable helminths are low. In the Kimberley region infection rates are considerably higher than in the cities due to high aboriginal population. Giardia is the dominant enteric pathogen. It appears that results from Perth may be representative of other cities but not necessarily of regional areas, particularly northern parts of Australia.

**Table 10.3. Incidence of enteric infectious diseases per 100 000 population in 1991**

*Public health and enteric diseases unit of state health laboratory services, 1992*

<table>
<thead>
<tr>
<th>Pathogen</th>
<th>Incidence/100 000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melbourne</td>
</tr>
<tr>
<td>Hepatitis A</td>
<td>14</td>
</tr>
<tr>
<td>Campylobacter species</td>
<td>58</td>
</tr>
<tr>
<td>Giardia species</td>
<td>20</td>
</tr>
<tr>
<td>Salmonella species</td>
<td>23</td>
</tr>
<tr>
<td>Shigella species</td>
<td>2</td>
</tr>
<tr>
<td>Taenia saginata</td>
<td>0.2</td>
</tr>
<tr>
<td>Echinococcus species</td>
<td>0.03</td>
</tr>
</tbody>
</table>

NS: Not Specified

The incidences of enteric infectious diseases in Perth and Melbourne contain low concentrations of helminths compared to the other countries. For the helminths Hymenolepis nana, Ascaris lumbricoides and Strongyloides stercoralis, which only have a human host, the numbers of cases and numbers of pathogens excreted by infected individuals in Perth are such that they couldn’t give the concentrations shown in other countries unless the number of people with unreported infections is very high. Taenia saginata eggs which originate from infected humans will not infect other people but may present a risk to cattle. However based on Table 10.1 and Table 10.2, it might be expected that the Australian sludges likely to present a risk.
10.4. Infectious doses:

Risk of infection during working with bio-fly brick may exist from exposure to wet sludge during handling and mixing operations. Workers handling and processing dried sludge at the top of the pile may risk infection from inhaled dust. There is a risk of inhaling fungal spores when working with dried sludge.

Infectious dose information is scarce because infectious dose studies depend on human volunteers. There are also problems with using infectious dose information. Some of these problems are:

1. Infectious doses vary depending on the health of the individual.

<table>
<thead>
<tr>
<th>Pathogen</th>
<th>Probability of infection from exposure to 1 organism</th>
<th>Dose to cause incidence of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1%*</td>
</tr>
<tr>
<td>Enteroviruses</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Poliovirus 1</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>Poliovirus 3</td>
<td></td>
<td>0.32</td>
</tr>
<tr>
<td>Echovirus 12</td>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td>Rotavirus</td>
<td></td>
<td>3.1x10^{-1}</td>
</tr>
<tr>
<td>Norwalk Agent</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Hepatitis A virus</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Salmonella species</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>Salmonella typhi</td>
<td></td>
<td>263</td>
</tr>
<tr>
<td>Salmonellanewport</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Salmonella derby</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Salmonella pullorum</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Shigella dysenteriae</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Shigella flexneri</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Vibrio cholera</td>
<td></td>
<td>1428</td>
</tr>
<tr>
<td>Escherichia coli</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Clostridium perfringens</td>
<td></td>
<td>1.4</td>
</tr>
<tr>
<td>Campylobacter</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Entamoeba histolytica</td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Giardia lambia</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Ascaris lumbricoides</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Ancylostoma duodenale</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Trichuris trichiura</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

* from Rose and Gerba (1991)  ** from Shuval et al., (1986)

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2. Infection can be measured in different ways including clinical symptoms, shedding of pathogens in faeces and serological response, so data from different studies may not be comparable.

3. Ingestion of laboratory grown organisms may not replicate ingestion of organisms in environmental samples.

Rose and Gerba (1991) and Shuval et al., (1986) summarised infectious doses for different organisms and these are shown in Table 10.4. In interpreting this data, the above problems associated with using infectious dose information need to be kept in mind. Table 10.4 shows that the probability of becoming infected by consuming one organism is higher for viruses, protozoa and helminths than for bacteria, and the number of organisms required to cause infection in a certain percentage of the population is less for viruses, protozoa and helminths than for bacteria.

10.5. Risks from exposure to fresh sludge:

Ingestion is generally the major route of infection during Biofly brick work. The common practice of touching the mouth with the hand may contribute to the possibility of infection. Studies conducted by Sydney Water Board (1993) indicate that infections from specific biological agents are not common, however it is noticed that new workers in their first few years of employment have been shown to experience increased rates of gastrointestinal or upper respiratory illnesses.

Tables 10.2 and 10.4 are used to quantify the health risks of direct exposure to pathogens in wastewater sludge. The risk assessment is based on exposure to fresh sludge which have been used during Biofly brick work, rather than treated or stored sludge. Two assumptions are made. Firstly it is assumed that pathogen densities in Australian sludges are similar to those from other countries. As discussed above, this may not be true for helminths. Secondly for the purposes of estimating the risk, it is assumed that the maximum amount of sludge that any individual would ingest at one time is 1 g however a more realistic amount that an individual might ingest is 0.1 g.

In the worst case it is assumed that Australian sludges contain the maximum numbers of enteric pathogens found in any of the studies from other countries and that an
individual handling sludge would ingest 1 g of sludge. The results of this calculation made by Gibbs and Ho (1993) are shown in Table 10.5.

The percentage of individuals likely to become infected with the worst case dose is taken from the infectious dose information given in Table 10.4, and this is also shown in Table 10.5. A slightly more realistic infection rate is calculated by assuming that sludge contains the mean number of pathogens shown in Table 10.4, and that an individual might consume 0.1 g of sludge when handling sludge. This is still likely to be an overestimate as it is unlikely that many people will ingest 0.1 g of sludge. This estimate also does not take into account protozoa and helminth viability. Keeping the assumptions in mind it can be seen from these estimates that for an individual handling sludge and consuming 0.1 g of sludge then there is an approximately 1% chance of becoming infected with an enteric virus, less than 1% chance of contracting a Salmonella infection, greater than 1% chance of contracting a Giardia infection and less than 25% chance of contracting a helminth infection.

### Table 10.5. Estimated infection rate from handling sludge (Gibbs & Ho, 1993)

<table>
<thead>
<tr>
<th>Pathogen</th>
<th>Worst case</th>
<th>Average case</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number in 1.0 g</td>
<td>Percentage of exposed people infected</td>
</tr>
<tr>
<td>Enteric viruses</td>
<td>7.5</td>
<td>1-25</td>
</tr>
<tr>
<td>Salmonella</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Giardia</td>
<td>123</td>
<td>1-25</td>
</tr>
<tr>
<td>Ascaris</td>
<td>9.7</td>
<td>26-50</td>
</tr>
<tr>
<td>Trichuris</td>
<td>5.1</td>
<td>26-50</td>
</tr>
</tbody>
</table>

These calculations suggest that if Australian sludges contain the concentrations of enteric pathogens found in digested sludge in the USA and UK, then they pose a risk to the health of people handling sludge which has not been treated further than mesophilic anaerobic digestion. The greatest risk appears to arise from Giardia and helminths in USA and UK sludge.

A qualitative risk assessment is also carried out. Rather than using data from other countries the assessment is based on reported infection rates in Western Australia. This is used in conjunction with estimated excreted loads and persistence of pathogens in the
environment as shown in Table 10.2. Information in Table 10.2 is classified into low, medium or high as outlined in Table 10.6.

Table 10.6. Criteria used to classify number of cases in Western Australia excreted load and pathogen persistence

<table>
<thead>
<tr>
<th>Classification</th>
<th>No. of cases</th>
<th>Excreted load</th>
<th>Persistence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Less than 100</td>
<td>$10^5$ and less</td>
<td>1 month and less</td>
</tr>
<tr>
<td>Medium</td>
<td>100 to 500</td>
<td>$10^4$ and $10^5$</td>
<td>Greater than 1 month to 3 months</td>
</tr>
<tr>
<td>High</td>
<td>Greater than 500</td>
<td>Greater than $10^5$</td>
<td>Greater than 3 months</td>
</tr>
</tbody>
</table>

• Typical number of organisms per gram of faeces

Infectious dose classifications are taken from Shuval et al. (1986). The classifications are then combined to rank the pathogens into five groups. Group 5 contains the pathogens which present the most risk with the risks decreasing to group 1 which contains the pathogens of least risk. The classifications and groups of pathogens are shown in Table 10.7.

Table 10.7. Relative health risks of different groups of pathogens

<table>
<thead>
<tr>
<th>Group</th>
<th>Pathogen</th>
<th>No. of cases in Western Australia in 1991</th>
<th>Excreted load</th>
<th>Persistence</th>
<th>Infectious dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 5</td>
<td>Rotavirus</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Adenovirus</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Enterovirus</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Hepatitis A</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Salmonella</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Giardia intestinalis</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Trichuris trichiura</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Group 4</td>
<td>Campylobacter</td>
<td>High</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Shigella</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td></td>
<td>Cryptosporidium</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Hookworm ova</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Group 3</td>
<td>Hymenolepis nana</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Entamoeba</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>Strongyloides stercorealis</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>Enterotoxigenic E. Coli</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Group 2</td>
<td>Ascaris lumbricoides</td>
<td>negligible risk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 10: Materials Handling and Health Precautions

This risk assessment is obviously very general and is based on a number of assumptions. Some of the assumptions are:

1. Each of the different factors, number of cases, excreted load, persistence and infectious dose had equal weight
2. Reported cases reflected symptomless
3. Input into wastewater from infected animal waste is not significant
4. Where data is not available it is estimated from data for similar pathogens
5. Any pathogen which resulted in less than 2 cases per 100,000 people per year is considered to present negligible health risk in wastewater sludge
6. Levels of immunity to viruses are not significantly higher than for other pathogens
7. Salmonella regrowth potential is not significant.

Based on the qualitative risk assessment and with the above assumptions in mind, the pathogens of most concern in Western Australian sludges are enteric viruses. The next group of pathogens which are of concern are Salmonella, Giardia intestinalis and Trichuris trichiura. Most of the Trichuris trichiura infections are associated with travellers and recent immigrants, so infection rates in the resident population appear to be low. This organism is therefore not considered to present a major risk from transmission through sludge. Most of the hookworm, Hymenolepis nana and Strongyloides stercoralis infections reported in Western Australia are from patients in the Kimberley region. The risk of infection from helminths in Perth sludges would therefore appear to be low. This may be similar in other cities in Australia.

The qualitative risk assessment using infection rates in Western Australia gave a different result to the quantitative risk assessment based on pathogen densities in sludge in other countries. The quantitative risk assessment suggested that Giardia and helminths presented more of a risk than enteric viruses and Salmonella. One reason for the differences may be that poor recoveries of pathogens in sludge resulted in an underestimation of pathogen densities in sludge in other countries. Measured enteric virus concentrations in sludge may have been particularly low. Another reason is that the methods used to detect Giardia did not assess viability. However the differences may also underline the general uncertainty attached to the results due to the assumptions made and lack of data which could be used in the risk assessment.
The conclusions of the qualitative risk assessment differ from those of Shuval et al., (1986). They proposed a model to predict the relative infectiveness of pathogens in causing infections through wastewater irrigation in developing countries. The risks from pathogens are ranked in the following way:

1. High Helminths
2. Lower Bacterial infections
   Protozoan infections
3. Least Viral infections

In contrast, the ranking developed in this study shown in Table 10.7 suggests that viruses present the highest risk, followed by bacteria and protozoa with helminths presenting the least risk. There are probably two main reasons for the difference which are due to Shuval and his college (1986) model being developed for developing countries. First Shuval et al., assumed that the prevalence of helminth infections is very high. They used figures of 60% prevalence for both Ascaris and Trichuris. Based on reported cases of the prevalence of Ascaris and Trichuris in the Perth area in 1991 is 0.001 and 0.01% respectively. These are very small. The second reason is that Shuval et al., assumed that due to poor hygiene most infants would be exposed to enteric viruses and subsequently immune to enteric virus infections. This assumption is not made for this study so immunity is not treated as a significant factor in the risk assessment.

10.6. Epidemiology:

Epidemiological studies are another way of assessing the risks from pathogens in sludge. However epidemiological information is limited because the costs involved in epidemiological studies are extremely high. There are a greater number of studies involving exposure to wastewater and these are summarised by Shuval et al. (1986).

Clark et al. (1984) reported a study of exposure to sludge rather than exposure to wastewater. This was related to a study of sludge compost workers. Workers directly involved in composting showed evidence of an immune response to antigens which is higher than groups not involved with compost activities. More symptoms of burning eyes and skin irritation are also reported among compost workers. However these may have been associated with high dust levels rather than the sludge. Jakubowski (1986) described an epidemiological study of farm residents on farms using anaerobically
digested sludge spread on their fields. No significant differences are observed between the test and control groups for reported illness and serology. However health risks might have been higher with a higher rate of exposure. Another study described by Block (1986) reported hepatitis A infections in four men who spread wastewater sludge on farmland. It is probable that these men were infected during the course of their work.

In a review of the epidemiology of Salmonella, Pike (1986) found only one published outbreak of salmonellosis which involved the use of sludge. This involved 98 human cases drinking unpasteurised milk from a farm in Scotland. Sludge containing effluent from a chicken factory had been sprayed on grassland and cattle reintroduced shortly afterwards. Cows, calves and domestic pets are found to be infected with S. typhimurium. Another milk borne epidemic in Czechoslovakia appeared to have been caused by sludge spread on land (Raska et al. 1966). Cesspool wastewater is spread on fields and this resulted in contamination of the water supply into a dairy. This appeared to lead to contamination of the milk and an infectious hepatitis A epidemic.

In 1986, the European Community round table discussions are held on the risks associated with the agricultural use of wastewater sludge. A Salmonella panel stated that wastewater and wastewater sludge are the source of infection in 12 reported outbreaks of salmonellosis. How many of these outbreaks are actually associated with municipal wastewater sludge is not clear. At least three of them which occurred in the UK are associated with animal wastes, wastewater or septic tanks rather than municipal sludge. The conclusions of the panel are that sludge presented a hazard to the health of animals and men and that it should be treated to destroy pathogens or restrictions imposed on the use of land after sludge is applied. A parasite panel agreed that sludge spread on land can act as a vector of Ascaris and Taenia saginata. A virus panel concluded that there are only two relevant reports of wastewater sludge acting as a source of infection for the spread of enteric viruses. These are the two hepatitis A outbreaks described above.

On the basis of the limited number of studies that have been carried out it appears that human infection has occurred through handling of sludge or the use of wastewater sludge in agriculture. However if guidelines are followed which include sludge treatment or restrictions on the use of sludge amended soil and public access, then the health risks appear to be low.
10.7. Sludge Guidelines

As shown above epidemiology has not provided enough information to state conclusively whether past sludge management practices have resulted in any disease in exposed humans. There does seem to be some evidence that sewage sludge has been associated with a few cases of infection, but not in cases where the sludge had been treated or where use restrictions were imposed after sludge was applied to land. Studies in the USA and UK have demonstrated that sludge which has not been treated past mesophilic anaerobic digestion may contain pathogenic viruses, bacteria, protozoa and helminths. Estimated infection rates among exposed populations consuming 0.1g of sludge were approximately 1% for enteric viruses, <1% for pathogenic bacteria, >1% for Giardia and <25% for heminth ova. The epidemiological information and reported pathogen densities from other countries therefore suggest that sludge which has only been treated by mesophilic anaerobic digestion is not safe for unrestricted use by the public.

Legislators in US EPA and UK have adopted this philosophy and responded to it in two ways. The first is by requiring that sludge undergo further sludge treatment before unrestricted use. The second is by imposing restrictions on the use of partially treated sludge. These restrictions include requirements such as subsurface injection or tilling of sludge into soil, limitations on access and withholding periods for sludge amended soil. The following discussion concerns issues which are likely to be related to the biofly brick project.

10.7.1. Pathogens of Concern

The qualitative risk assessment based on the incidence of disease in Western Australia Table 10. 2 produced a ranking of the relative risks of different pathogens in sewage sludge Table 10. 7. Enteric viruses were considered to present the greatest health risk in sewage sludge. Also of concern were Salmonella and Giardia. Pathogens such as Campylobacter, Shigella and Cryposporidium presented a lower risk. The risk of infection from helminths in municipal sludge was considered to be low.
10.7.2. Indicator Organisms as Predictors of Pathogen Densities in Sewage Sludge

Lewis-Jones and Winkler (1991) indicated that faecal streptococci may be useful indicators of enteric virus densities in sludges. Faecal and total coliforms did not appear to be good indicators which suggests that Escherichia coli may also be a poor indicator. However the results were not conclusive. No studies were available which examined the relationship between faecal indicators and parasites. This is an area where more investigation is needed as the risk assessment suggested that Giardia may be a pathogen of major concern in sludge. The reviewed studies do not provide any basis for using the densities of faecal indicator bacteria in sludge to predict the presence or absence of enteric pathogens.

10.7.3. Salmonella Regrowth in Composted Sewage Sludge

Laboratory studies have demonstrated that Salmonella can regrow in composted sewage sludge (Yanko, 1988). The results of a field study also suggest this. The author measured Salmonella levels in blending products and concluded that nutrient related regrowth of Salmonella was the only explanation for these high levels. In the described study Salmonella was regularly detected in composted sludge meeting US EPA criteria. These studies suggest that mixing with other products and bagging seemed to be conditions which favoured regrowth. Additional research to better understanding of what conditions give rise to Salmonella regrowth is warranted.

An epidemiological review and assessment of the health risks associated with municipal sewage sludge suggested that untreated digested sluges are not suitable for unrestricted marketing due to unacceptably high risks associated with enteric viruses, Salmonella, Giardia and some helminths. However both epidemiological information and studies of pathogen concentrations in sludge were scarce. The risk assessment was based on data from other countries so a qualitative risk assessment based on reported cases in Western Australia was carried out. This suggested that enteric viruses in sludge present the greatest risk followed by Salmonella and Giardia. Two issues are of concern for biofly brick project guidelines. Firstly the use of faecal indicator bacteria to predict pathogen densities in sludge was not supported by the literature. Secondly there is regrowth potential of Salmonella in sludge treated by composting or other forms of further treatment.
10.8. Sources and control of odour emissions from biofly brick processing

Biofly brick processing operations may cause nuisance odour problems in nearby communities. Public awareness of odours is on the increase as the expansion of urban development occurs in the vicinity of the once isolated brick factories.

Odours from biofly brick processing may originate from such diverse sources as raw materials, during mixing and extruding. Produced during anaerobic degradation of complex organic compounds during drying of the raw brick, and during firing.

There are three general approaches for the control and treatment of odours originating from biofly brick processing operations. Odorous emissions can be prevented, collected and treated, or modified by masking with chemicals. Claims have also been made for the prevention and treatment of odours by bioaugmentation, where proprietary bacterial cultures are added to odour-generating units.

The human olfactory system is extremely sensitive to a wide range of odorous chemical compounds. An individual’s response to any particular compound is determined by the intensity, detectability, and character of the perceived odour. Odours compounds in biofly brick processing include both inorganic and organic compounds, the majority of which are produced by biological activity. With the exception of hydrogen sulfide (H₂S), the compounds of most concern are typically formed through the anaerobic or anoxic decomposition of proteins and carbohydrates that are abundant in biofly raw brick.

10.8.1. Control of odour emissions during dry stage

Odours associated with the biofly brick processing can be reduced or eliminated with various techniques. Some controls are aimed at the removal and/or elimination of odours from raw materials. These are called source control, one of those techniques used with biofly brick raw materials include in the section 10.10. Others are for the removal of odours from the atmosphere in a confined area where the biofly brick get processed. These include:

- atmospheric dilution
- masking, modification, and counteraction
Chapter 10: Materials Handling and Health Precautions

• absorption
• adsorption
• biological methods
• incineration and afterburners

One of those techniques used during storage, mixing and extruding of biofly brick raw materials was the atmospheric dilution. This is probably the most common and oldest method of dealing with odour problems. The odorous gas is diluted with fresh air to such an extent that sub-odour-threshold levels have been reached. This is basically a physical phenomenon and there is no intent to remove, or even to change the characteristics, of the odorous materials. The odorous substances are no longer a nuisance if their concentrations are below their odour detection limits.

Fans were used to reduce odour during storage, mixing and extruding of biofly brick raw materials. The use of the fans are mechanical means to increase the speed of airflow so that the odorous gases can be released higher into the atmosphere. Performance of that dilution technique is dependent very much upon the weather conditions. It is expected that efficiency would be lower during temperature inversions, where the rate of temperature change with altitude is too low to allow the exhaust odorous gases to rise and disperse. Temperature inversions happen normally in calm, clear nights and may persist longer in the fall.

The dilution technique is simple and straightforward. Operational costs are much lower than those associated with the use of chemicals and/or sorbents. This technique is, however, very much dependent upon atmospheric conditions. It may be difficult, if not impossible, to provide a guaranteed elimination of the odour problems during storage, mixing and extruding of biofly brick raw materials, by using this technique alone.

One of those techniques used during drying of biofly raw bricks was the absorption technique. In this process, the odorous gas is brought into contact with a liquid absorbent whereby the odour-producing substances are removed through dissolution and chemical reactions as shown in Eq. 10.2. Some typical chemical reactions for different techniques are as follows:
• the absorption of ammonia in sulfuric acid solution

\[2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4\] \hspace{1cm} (10.1)

• the absorption and neutralization of sulfur dioxide with sodium hydroxide solution

\[\text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}\] \hspace{1cm} (10.2)

• the oxidation of hydrogen sulfide with chlorine

\[\text{H}_2\text{S} + 4\text{Cl}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 8\text{HCl}\] \hspace{1cm} (10.3)

• the oxidation of formaldehyde with potassium permanganate

\[3\text{HCHO} + 4\text{KMnO}_4 \rightarrow 4\text{MnO}_2 + 2\text{K}_2\text{CO}_3 + 3\text{H}_2\text{O} + \text{CO}_2\] \hspace{1cm} (10.4)

Absorption using scrubbers and washers has been a very effective odour control practice during drying biofly raw bricks. However the effectiveness of using scrubbers and washers may vary depending upon the type of odorous compounds present, the device used, the ratio of liquid to gas flow rates, and the concentration of the chemical solution.

For biofly raw brick process, pilot tests are generally required to develop the design criteria, which may include the selection of chemicals, the depth of absorbing chamber, air flow rate, and the ratio of liquid to gas flow rates.

10.8.2. Control of odour emissions during “Firing” stage

The most important factor in sludge firing is the burning temperature. Sludge will normally burn quite well at temperature of 430 to 480°C, but up to 760 and 820°C is required to eliminate odours and smoke (WPCF, 1988). It has been reported that vapours generated from the firing of most anaerobically digested sludges requires a temperature of 700 to 750°C to deodorize, and a few require 760°C. A temperature of 740 to 770°C would be needed to destroy odours from volatile fatty acids (Sawyer and Kahn, 1960). It has also been reported that a minimum temperature of 680°C is needed to deodorize the
dewatered sludge cakes (Laboon, 1961). The biofly brick process reached 1100°C during firing, which has eliminated all the odours.

Hydrocarbon odours have been recognised during firing of biofly brick between 0 and 430°C. Both the height of the exhaust stack and the weather conditions will then influence the efficiency of odour removal through firing. The odour removal performance is therefore difficult to predict, but the experience is that, the higher the temperature, the higher the removal would be (USEPA, 1985). Very often, separate scrubbers are still needed for a more reliable control of the odours.

10.9. Health risk associated with handling fly ash and clay/shale:

10.9.1. The silicosis danger:

It is generally accepted that the silicosis danger is created by the uptake of silicogenic matter such as fly ash and clay/shale in lung macrophages. The lung macrophages try to neutralise the particles but are unable to do so. So the macrophage dies and breaks open. The macrophages contain a protein which is a signal matter to make connective tissue fibrose. The silicogenic matter is again free and the second lung macrophage will do the same with the same consequence of production of connective tissue. The connective tissue reduces the flexibility of the lung tissue so the respirable lung volume is reduced.

One of the possible causes that lung macrophages are unable to neutralise silicogenic matter, is outlined by Raaske (1980). The fly ash or clay/shale silanol structure OH-groups on the surface of the α quartz or tridimite or cristobalite could be the cause. By heating the α quartz the OH-groups disappear as water vapour and the siloxane structure will be left. Heating quartz over 500°C reduces the silicogenic activity.

Beretka and Mathew (1984) tested Australian fly ash with an extreme high SiO₂ content of 75%. The fraction smaller than 10 µm was separated by sedimentation in water and later on also a fraction of 5 µm. The grain sizes were checked, and the α quartz contents measured by X-ray diffraction as:

- in the average ash > 10 µm 19%
- in the fraction 10 µm 18%
- in the fraction 5 µm 15%
The following question is: Can these fractions be harmful for fly ash workers?

A double check has been made by Zarkower et al (1982) for lung macrophage test and haemolysis test. Both tests gave the same result. No silicogenic activity on the lung macrophages of rats or cows were found. The haemolysis test was carried out with human blood. No significant human cell membrane reaction was determined.

Raaske (1980) checked the silicogenic activity on respirable fly ash quartz in an autoclave after 3 hours in wet conditions over 100°C. No silicogenic effect or citotoxicity was measured, even the citotoxicity was reduced probably due to washing off all heavy metals from the fly ash.

Maxcy and Rosenau (1993) reported that approximately 40 percent of the particles between 1 and 2 μm in size are retained in the bronchioles and alveoli. Particles ranging in size from 0.25 to 1 μm show a decrease in retention, because many particles in this range are breathed in and out again. However, particles below 0.25 μm show another increase in retention because of Brownian motion, which results in impingement.

During the biofly brick process, Eraring fly ash and Badgery’s Creek clay/shale raw materials have been used. Eraring fly ash particles were very small and they vary in size between <1 μm to >100 μm with a median size 12.8 μm. Badgery’s Creek clay/shale particles vary in size between <75 μm to 4.75 mm with average particle size is about 2.36 mm. It is likely that the average particle size used during the biofly brick process has no silicogenic effect.

10.9.2. Mutagenic and carcinogenic properties:

In 1978, Chrisp et al reported that serum extracts of fly ash were mutagenic when tested in the Ames salmonella assay by Ames et al (1975). The fly ash samples were collected downstream of the electrostatic precipitator. The serum extracts did not require metabolic activation with rat liver enzyme and were mutagenic to S. typhimurium TA 1538, TA 98 and TA 100. No activity was found with strain TA 1535. Fly ash from an electrostatic precipitator was not found to be mutagenic in the Ames test reported by Fisher et al., (1979). Since this work, further extensive studies of fly ash have shown
that no mutagenic activity in the Ames salmonella assay at any particle size (Raabe, 1981).

Cytotoxicity of fly ash to alveolar macrophages in vitro has been examined by Hill and Hobbs (1982) by measuring the release of lactate dehydrogenase into the culture media. Fly ash was not found to be cytotoxic. Aranyi and Bradof (1981) measured the effect on adenosine triphosphate in macrophage cell lines with similar results.

In a mouse inhalation study reported by Zarkower et al., (1982) and Eskew et al., (1982) in which mice were exposed to fly ash for variable amounts of time they found that in the exposed animals macrophages had a reduced ability to phagocytose bacteria but that fly ash had little effect on cellular immune responses. Fisher (1980) states that no significant changes were observed on the function of lung macrophages from rat exposed continuously for up to 180 days to 4mg/m³ of fly ash.

De Nicola (1981) reported that in acute inhalation studies of six hours duration of female Syrian hamsters, no histological differences were found between exposed and control animals although macrophages filled with dark cytoplasmic granules were observed in terminal bronchioles or adjacent alveoli.

Schiff et al., (1981) exposed Syrian hamsters to 1-2 mg/m³ fly ash for 3 hours per day on 9 hours over a two week period. In the tracheal epithelium stratified metaplastic changes and basal cell hyperplasia were observed.

The results of these extensive international studies on fly ash consistently demonstrate that fly ash biological activity should be regarded in the same category of the inert dusts. The ASTM present exposure limit of 10 mg/m³ of total dust is appropriate.

10.10. Effects of fly ash on municipal sewage sludge:

From the epidemiological review conclusions stated in section 10.7.3, it was thought that an admix of sewage sludge with fly ash could produce, deodorized and sterile product which might be valuable for the Biofly brick process. The success of the process would seem to depend upon the reaction of alkalinity of fly ash with the odoriferous acids of sulphur and phosphorous present in sewage sludges thus rendering them
innocuous. The success of the process might also be dependent upon the action of earth oxides present in the fly ash, together with increased temperature resulting from the exothermic reaction of these oxides with water present in the sludges in effecting to kill the fecal coliform, and other bacteria.

Laboratory studies were conducted to determine some of the consequences of mixing fly ash with municipal sewage sludge. Three different municipal sludges were used in this study. They were primary sludge, secondary activated sludge, and 50/50 mixture of primary and secondary. One hundred grams of the fly ash was placed in a beaker and then 100, 200, and 300 mL of the sewage sludge was added and mixed with the fly ash. Subsequent samples were then taken at regular intervals for fecal coliform analysis.

The results of the fecal coliform analysis are shown in Table 10.8. It is seems that the 1:1 and 2:1 mixtures of secondary sludge resulted in an immediate kill of all fecal coliforms. All other mixtures showed some immediate kill. All mixtures showed 100% kill of fecal coliforms 24 hours after mixing the fly ash with the sludge.

### Table 10.8. Results of fecal coliform count

<table>
<thead>
<tr>
<th>Type of sludge</th>
<th>Sludge/fly ash mixture</th>
<th>Initial counts Number/mL</th>
<th>24 hours after initial counts Number/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>1:0</td>
<td>3.1x10^5</td>
<td>No counts Detected</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>1.0 x 10^4</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>1.0 x 10^5</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>2.1 x 10^5</td>
<td>&quot;</td>
</tr>
<tr>
<td>Secondary</td>
<td>1:0</td>
<td>6.0x10^4</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>0</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>2.0 x 10^3</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mixture of primary and secondary</td>
<td>1:0</td>
<td>6.5x10^4</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>1.0 x 10^3</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>4.5 x 10^3</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>3:1</td>
<td>9.0 x 10^3</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

An important observation during these studies was the elimination of odors after the fly ash was mixed with the sewage sludge. The sewage sludge was quite odorous before
being mixed with the fly ash. More work is needed on the physical properties of the resulting mixture, however preliminary results indicate that such continuous investigation may be worth the effort.

Figure 10.1. diagrammatically shows a sequence of a preferred method for using sludge/fly ash/clay/shale for making brick using the idea in thoughts. Sludge and fly ash are fed from their respective sources of supply to a mixer. After mixing, the mixture is conveyed to a silo for storage of the mixture for 24 hours between the mixing and extruding steps to insure deodorized and sterile material, storing helps stabilize the mixture to insure that the extrusion process will be trouble-free. Clay/Shale added to the stored mixture of sludge/fly ash and conveyed to a conventional extruder and former, and the articles so formed are then conveyed on to a dryer. As shown in dotted line, the exhaust gases from the dryer may be vented to the kiln as combustion gas for the kiln. After drying, the articles are conveyed to the kiln for firing.

![Figure 10.1. Sequence for a preferred method for making brick](image-url)
10.11. Health concerns of biofly brick raw materials

10.11.1. Health hazard

The biofly brick raw materials when come in contact with eyes may cause infection. Breaks in the skin will increase the risk of infection. Workers handling raw materials may risk infection from inhaled dust. There is a risk of inhaling fungal spores when working with raw materials. Ingestion is generally the major route of infection. The common practice of touching the mouth with dirty hand will contribute to the possibility of infection. Workers who eat or smoke without washing their hands have a much higher risk of infection. A good rule of thumb to follow is to never touch yourself above the neck whenever there is contact with raw materials. Although most health effects studies indicate that infections from specific biological agents in raw materials are not common, operations and maintenance personnel must presume that biological hazards will exist at any location within facilities where raw materials are present. Water Board NSW Studies have indicated that new workers in their first few years of employment have been shown to experience increase rates of gastrointestinal or upper respiratory illnesses within facilities. Workers handling raw materials should be immunised for tetanus and hepatitis B.

First aid: Flush eye with fresh potable water. Broken skin and abrasions, use soap and water to clean up. An antibiotic ointment or disinfectant should be applied to the wound after thorough washing.

10.11.2. Health precautions

Biofly materials are a mixtures of sludge/fly ash/clay/shale. Health hazards may exist, for specific components in raw materials. The most important precautions are follow:

In a confined space raw materials decomposition products can lead to hazardous atmospheres. Safe working regulations in a confined space using musk’s need to be followed when entering a confined space.

Avoid breathing dust containing pathogenic organisms. Fungal spores exist within raw materials on top of the pile. Avoid breaking the surface of raw materials because this releases spores which readily become airborne and pose an inhalation risk. Workers
and the surrounding population can be affected by airborne spores. Keeping raw materials moist will prevent release of spores.

10.11.3. Personal hygiene

The most important consideration is the use of good workplace practices and good personal hygiene guidelines.

- Wash hands with soap and water after contacting with raw materials, before going to the toilet, before eating, drinking, or smoking, and at end of the work shift.

- Wear heavy duty gloves and boots that are waterproof and puncture resistant. Discard torn gloves. Do not submerge hand below top of glove.

- Wear aerosol respirators and goggles and faceshields where prolonged exposure to aerosols would occur.

- Change work clothing as soon as the job is completed.

- Shower before changing into clean work clothes and shoes.

- Launder work clothes at work not at home.

- Handle sharp items with extra care to prevent accidental injuries.

- Clean contaminated tools after use.

- Whenever possible, use separate lockers to separate work and street clothes.

- Promptly clean body parts that become contaminated.

10.11.4. Transport, handling and storage of sewage sludge

Sewage sludge should be transported to the site in covered, water tight trucks and stockpiled on site. It is best handled by conveyor belt or auger. If front end loader used, dust, odour and spillage must be minimised.
Sewage sludge should not be stockpiled on slope of less than 5%. Drainage controls should be provided upslope to prevent uncontaminated run-off entering the stockpile area. Downslope run-off controls such as silt traps, will prevent sludge contaminated run-off from entering surface waters. Sandy soils are unsuitable for stockpile areas.

Effluent from cleaning of silos and other equipment, should be returned to the sewer via a normal trash waste arrangement and leachability must be avoided.

Storage method: Sludge and fly ash are fed from their respective sources of supply to a mixer. After mixing, the mixture is conveyed to a silo for storage of the mixture for 24 hours between the mixing and extruding steps to insure deodorized and sterile material, storing helps stabilize the mixture to insure that the extrusion process will be trouble-free. Clay/Shale added to the stored mixture of sludge/fly ash and conveyed to a conventional extruder and former.

10.12. Summary

- Literature concerning pathogen densities in untreated wastewater sludge was reviewed to aid an assessment of the health risks associated with the use of sewage sludge. No information on pathogen densities in Australia sludges was found, so risks were assessed using pathogen densities in other countries and infection rates in Western Australia. Based on information from other countries it was estimated that an individual handling sludge and ingesting 0.1 g of sludge would have a greater than 1% chance of becoming infected with giardia, less than 25% chance of contracting a helminth infection, approximately 1% chance of contracting a salmonella infection. However a qualitative risk assessment based on reported infection rates in Western Australia suggested that enteric viruses in sewage sludge pose the most risk followed by salmonella and giardia. These risk assessments and a limited amount of epidemiological evidence suggest that digested sewage sludge is not suitable for unrestricted use. Two issues of concern for Biofly brick project are the use of indicator organisms to predict pathogen densities and the possibility of salmonella regrowth in the raw materials.

- Odours associated with the biofly brick processing can be reduced or eliminated with various techniques described, some controls are aimed at the removal and/or elimination
of odours from green materials. These are called source control, one of those techniques used with biofly brick raw materials was the absorption. Others are for the removal of odours from the atmosphere in a confined area where the biofly processed, those have been discussed.

- The results of mutagenicity and animal studies in the published literature demonstrate that fly ash has low biological activity. Clinical studies have not revealed any pathological chest lesions which can be attributed to exposure to fly ash. There is no evidence to support any change in the exposure ASTM limit value of 10 mg/m³ of total dust.

- A preliminary experiment was run using an admix of fly ash and sewage sludge, which produced, deodorized and sterile material free of fecal coliform suitable for use with Biofly brick without risk. This experimental needs further work to confirm this finding.

- Guidelines for the use of sewage sludge with brick making have been prepared. It is felt that basic sanitary and health precautions need to be followed by all the workers in accordance with clearly established guidelines.
Chapter Eleven

Conclusion

11.1. Introduction

In view of the disposal problems associated with fly ash and wastewater sludge and the trends toward greater quantities of these wastes becoming available in the near future, the investigation into safe and reliable reuse and disposal alternative was undertaken. Since fly ash and wastewater sludge have some mutually complementary characteristics, it was proposed that these two waste products could be beneficially combined with clay/shale to create a material which would be suitable for structural brick making. Potential advantages of this technique include:

- the reuse and utilisation of two waste products
- environmentally safe waste disposal
- waste products become assets instead of liabilities
- light weight brick
- significant energy savings during brick making
- no loss of strength.

Two broad objectives were established for this investigation:

- To determine whether the two waste materials can be successfully combined to produce actual size bricks, that could be suitable for use as a building brick.

- To determine the extent of adverse environmental effects, especially leaching/gas emission of potentially harmful trace elements.

11.2. Material characterestics

Particle size analysis for Eraring fly ash, the four types of sludges Bellambi, Wollongong, Shellharbour and Port Kembla respectively and Badgery's Creek clay/shale showed that the volumetric mean diameter can be classified as equivalent to
the category of medium silt. The particle sizes are similar hence good and uniform mixing can be achieved with clay/shale acting as a binder for sewage sludge and fly ash waste materials to make the biofly brick.

Fly ash exhibited the finest range of particle size which may likely to enhance the durability and strength of the biofly brick.

The chemical analysis showed that the percentage content of the silica, alumina and iron in both fly ash and clay/shale is nearly the same, and hence fly ash can replace or combine with other materials readily to make biofly brick.

11.3. Firing curve

A total 18 firing trials were conducted using over 500 bricks over a period of six months. It took 8 such trials to establish a suitable firing curve for the biofly brick. However, it took ten trials to develop the firing curve for clay/shale brick. During the firing of biofly bricks, several composition of waste material have been used with a total maximum waste material replacement of 70%. It is concluded that the change of composition did not affect the optimum firing curve.

The colour of all the successful biofly bricks are orange. It is felt that this is the common colour of the biofly bricks. One possible reason may due to the effect of adding the sludge and fly ash to the clay which has made the biofly brick this colour. However, the fired clay/shale bricks were found to be brown in colour. This colour was consistent for bricks with and without holes.

The trials with clay/shale indicates that good quality bricks can be obtained by keeping the dehydration stage for 36 hours and vitrification for 12 hours.

It is clear that there is often a limit to the finishing temperature which can be employed and sufficient time has to be allowed at a suitable firing temperature to develop the desired properties. During these successful trials, temperature was raised to the maximum of 1030 °C as recommended for the Sydney area Wianamatta Group of clays and shales.
The total firing time is 20.5 hours to fire biofly brick in comparison to 48 hours to fire clay/shale factory or laboratory brick. Hence, it is concluded that utilisation of fly ash, sewage sludge and a small amount of clay for making the biofly brick can significantly reduce the total firing time.

11.4. Structural characteristics

The waste materials sewage sludge and fly ash were mixed with clay/shale, in different proportions by weight in "as received" condition. The amount of water added to get the desired optimum mix varied between 24 to 33%. It has been found that the amount of water added for the mix varied with the sludge type primarily due to the difference in moisture content of the source of various sludges.

"Biofly" bricks specifications relate to twelve of the tests performed on the actual size bricks namely dimensions, transverse strength, compressive strength, characteristic expansion, efflorescence, pitting due to lime particles, initial rate of absorption, water absorption properties, resistance to salt attack, linear shrinkage and weight loss. The Australian Standard AS 1226 specifies acceptable values for the dimensions, transverse strength, compressive strength, resistance to salt attack, efflorescence and pitting due to lime particles. No recommended values are available for the rest of the properties.

Results of tests on bricks exhibited general similarities between Shellharbour mix, Port Kembla mix, Bellambi mix and Wollongong mix. Biofly bricks had very similar physical features and colour, although the Wollongong mix was much lighter in external colour. Shellharbour and Port Kembla mixes exhibited uniform colour throughout the thickness whereas Bellambi mix exhibited dark coloured core and exterior. All biofly brick specimens were found to satisfy dimensional tolerance as specified by Australian Standard 1226.

The strength of the bricks was measured as transverse strength and compressive strength. All the biofly brick samples have characteristic transverse strength in excess of the standard value of 1 MPa and exceed the clay/shale bricks by 37, 21, 18, and 36% respectively for Shellharbour, Port Kembla, Bellambi and Wollongong mixes. However it was observed that the characteristic transverse strength of factory clay/shale bricks fell below the standard and this can be attributed to the effects of perforations present. The transverse strengths of the biofly bricks were found to be vary with the type of sludge.
added. The mixes show both increasing and decreasing trends in the characteristic transverse strength values for waste material additions between 50% and 70%.

The overall average characteristic compressive strength value of 25 MPa for biofly bricks indicated that it is higher than laboratory and factory clay/shale brick values by 10% and 7% respectively. The characteristic compressive strength values of biofly bricks also varied with the type of sludge addition. The Shellharbour and Wollongong mixes generally show an increasing trend in the characteristic compressive strength values with increasing percentage of waste material addition. These two mixes produced the highest average strength of 24.5% and 25% respectively, more than laboratory clay/shale brick. The Port Kembla and Bellambi mixes show a generally decreasing trend and this is primarily attributed to the type of sludge used.

Efflorescence tests indicated some efflorescence were present in bricks made from the Bellambi mix, whereas no efflorescence was detected for any other mix. Salt deposits were very light, and in most cases could only be detected as a very slight staining or colour change on the surface of the brick. No pitting due to lime particles was detected in bricks made from any mix.

An overall average value of 0.64 kg/m²/min was found for the initial rate of absorption of biofly bricks. This value is within the recommended optimum range of 0.5-1.5 kg/m²/min. The initial rate of absorption values of biofly bricks and clay/shale bricks are very similar. In general the average values obtained in the laboratory are approximately half of the average values of Australian extruded bricks. It was found that the addition of waste materials as well as the type of sludge affects the initial rate of absorption.

Resistance to salt attack measurements indicate that biofly bricks, and clay/shale laboratory bricks have survived the 40 cycles durability test. However, the clay/shale factory brick has failed at 14 cycles due to its porous nature.

The overall average characteristic expansion of the biofly mixes ranged between 0.62 to 1.74 mm/m which falls into the medium to high category. The biofly brick made from Bellambi sludge exhibited expansion values in the medium category primarily due to the high silica, alumina and iron content. The Shellharbour, Wollongong and Port Kembla mixes show expansion values in the high category. The biofly bricks in general have
less characteristic expansion compared with clay/shale bricks fired in the laboratory. However the absolute values for thermal expansion of clay/shale bricks fired in the laboratory are higher than those observed in the factory bricks. This may be attributed to the different firing characteristics and type of extrusion used in the laboratory.

The biofly bricks in general have less linear shrinkage compared with clay/shale bricks fired in the laboratory. The biofly bricks have higher weight loss compared with clay/shale bricks fired in the laboratory. Hence, it is concluded that the addition of fly ash and sewage sludge tends to decrease the linear shrinkage and increase the weight loss of the bricks.

It is has been found that the addition of waste material decreases the bulk density. The change in bulk density of bricks from each mix appears to vary with the quantity of silica+alumina+iron present in the sludge. The overall average bulk density of the biofly bricks is 1629 kg/m3 which is 25% lighter than clay/shale brick, and is primarily attributed to the volatile organic content of the sludge. This is indeed one of the main advantage of biofly bricks.

The overall average of cold and hot water absorption values of 15.0% and 15.3% for biofly bricks are respectively higher than the laboratory clay/shale brick values of 3.9% and 4.9%. However, the biofly values are comparable to average values for other waste bricks produced in South Africa. In addition, the higher water absorption property may be a useful feature especially if the bricks are used as pavers. High water absorption may give rise to better mortar adhesion. Further, the saturation coefficient values for biofly bricks of 0.96 are found to be similar to clay/shale brick values of 0.97 and 1.13 respectively. These results reflect the porosity measurements determined for the bricks by thin sectioning, which indicated the porous type of material.

The analysis of structural and related properties of full size biofly bricks and its comparison with clay/shale bricks made under similar condition indicate that:

- The addition of waste materials as well as the type of sludge affect the biofly brick without altering the visual properties.
• The biofly bricks can be made 10-25% stronger than clay/shale bricks which indicate that the addition of two waste materials does not affect but increases the compressive strength of bricks.

• The biofly bricks are 25% lighter than clay/shale bricks. This is a significant advantage for storage, transport and handling. It may also give superior thermal properties.

• The durability of the biofly brick is shown to be better than clay/shale brick.

• The type of sludge affect the colour, the strength and other properties. An industrial type sludge such as for Port Kembla may produce unusual structural characteristic which need further investigation.

• The optimum waste mix brick is likely to be 15% sludge, 50% fly ash and 35% clay/shale.

11.5. Thin sectioning and X-Ray diffraction

From X-Ray diffraction technique, it has been found that after firing, the Kaolinite has transposed to Mullite + Cristobalite. The recrystalisation of the minerals to Mullite was common in fired brick. The presence of Cristobalite gives rise to increase strength and durability of the biofly brick.

Thin sectioning of fired bricks confirmed the irregular shapes of the pores which can be easily observed in clay/shale brick however enechelon types of pores were detected in biofly brick.

Thin sectioning illustrated that the biofly brick contained micropores and microcracking in the matrix. In addition some poorly bonded inclusions were observed. Generally the matrix for the biofly brick exhibited smooth type of fracture. In comparison, clay/shale brick exhibited rough fracture and texture with large pores being evident. This may explain the reason for better durability, resistance to salt attack and strength of the biofly brick in comparison to clay/shale brick.
11.6. Leachability studies

The biofly brick materials were ground to three specified size ranges 4.75-9.5 mm, 0.2-0.6 mm and 75 μm, and the leachate was analyzed to determine nine metals, aluminium, cadmium chromium, copper, iron, manganese, nickel, lead, and zinc respectively.

The concentration of heavy metal leachate from the Biofly bricks in general was similar or lower than the concentration of leachate from conventional clay brick except in the case of cadmium and iron. Hence, all leachate concentrations were found to be well within the Standard limits.

The raw materials used for making the Biofly bricks had a high concentration of heavy metals than the leachate from burnt bricks. This proves that the Biofly brick process has the potential to reduce the heavy metal leachate. This also proves that the heavy metals in the sludge and fly ash are trapped inside the brick during the encapsulation process.

It is expected that the concentration of metals in the leachate should be increased with the increased exposed surface area of the smaller particles. This was not the case, and the metals remained “locked up” even in the small particles, retention was 99.98%. This may be due to the greater ion exchange capacity of the smaller particles which prevents significant leaching of the metals.

For the iron samples, the leachate concentration behaviour is different from most of the other metals. It was clear that the variation of the iron leachate concentration varied with the different type of sludge addition. Iron invariably leached at a much greater rate than did any other metal and this may indicate that the metals are bound into the solid differently.

11.7. Gas analysis

The heavy metal emission from the biofly bricks was found to be lesser than that of the conventional clay bricks and emission values are well within the Australian standards limits.
Even though the raw materials used for making the biofly bricks had a very high concentration of heavy metals, the emission rates are comparatively low. This proves that the biofly brick process has the potential to reduce the heavy metal emission. This also proves that the heavy metals in the sludge and fly ash are “locked up” inside the brick during the solidification process, with 99.98% retention.

The fluoride emission was comparatively low in case of the biofly bricks. This indicates that by substituting the clay/shale with sewage sludge and fly ash, the fluoride emission from brick kilns can be reduced.

The pollutant emission varied with firing temperature. When bricks of the same composition were fired, the concentration of pollutants in the stack gas increased with increasing temperature.

The gaseous pollutants emission from Port Kembla biofly bricks was higher than that of the conventional clay bricks, however Shellharbour biofly bricks produced lesser emissions than the clay bricks. This certainly indicates the effect of the type of sludge, which varied between the industrial type of sludge of Port Kembla to domestic sludge of Shellharbour.

These research findings suggest that sewage sludge with heavy metals, can satisfactorily be incorporated within commercial brick manufacturing operations. the contained metals were believed to be physico-chemically locked inside the vitrified brick, possibly due to a silicate-based entrapment mechanism.

11.8. Energy and cost savings

Preliminary analysis of the theoretical fuel availability indicate that depending on the biofly mix composition, energy savings between 32-54% can be achieved. This was verified in the laboratory for two biofly mixes. It was shown that approximately 44% energy saving can be achieved for biofly mix with 55-65% waste replacement. This is primarily attributed to the energy content in the sludge, the minimal energy required to heat fly ash which is a pre-fired material and as well as the overall reduction in the clay content in the biofly mix.
Biofly bricks can be produced at low cost due to a number reasons. Since the kiln throughput is doubled in comparison to a commercial bricks, the production rate can be significantly increased in a given time. Moreover the biofly bricks are lighter than conventional bricks and hence costs associated with transport, material handling and storage can be reduced.

11.9. Environmental benefit

The fly ash and sewage sludge are essentially two waste products which will be reused and utilised efficiently. The waste products will become an asset instead of a liability, which will have significant benefits for the society in terms of waste reuse and preservation of the environment by minimising potential pollution problems, without any new environmental costs, with an additional benefit in preserving the clay/shale resource.

Compared with other methods of disposal/reuse options of fly ash and sewage sludge, the environmental consequences are significantly minimised by solidifying the waste products.

Biofly brick is a beneficial product with no damage to the environment. The use of sludge and fly ash by this way transferring unattractive wastes to an attractive product.

11.10. Health issues and safety

Guidelines for the use of the materials with brick making have been prepared. It is felt that basic sanitary and health precautions need to be followed by all the workers in accordance with clearly established guidelines.

The results of mutagenicity and animal studies in the published literature demonstrate that fly ash has low biological activity. Clinical studies have not revealed any pathological chest lesions which can be attributed to exposure to fly ash. There is no evidence to support any change in the exposure limit value of 10 mg/m$^3$ of total dust.

Odours associated with the biofly brick processing can be reduced or eliminated with various techniques. To control odours during drying of biofly bricks absorption technique was used. The odorous gas is brought into contact with a liquid absorbent
(NaOH solution) whereby the odour-producing substances are removed through dissolution and chemical reactions.

Hydrocarbon odours have also been recognised during firing of biofly brick between 0 and 430°C. Both the height of the exhaust stack and the weather conditions will then influence the efficiency of odour removal through firing. If this odour persists, one may need to use additional scrubber for the stack gas.

### 11.11. Recommendations for future research

- The processes for manufacture of full scale biofly bricks in pilot scale have been investigated and envisaged to be similar to the conventional brick. It is envisaged that a factory trial run is needed to finalize the detailed process of manufacture of full size brick in the factory at a commercial scale.

- Further studies should be conducted to determine the structural/leachability/gas analysis using different types of fly ash with the same types of sludge and clay/shale used in this study. This study will show the effect of different types of fly ash on the characteristics of the biofly bricks.

- Greater understanding on the pollutant entrapment mechanism within the bricks is needed to control the pollutant leachate/emission from the bricks. This can be done using thin sectioning and differential thermal analysis.

- Biofly process uses high temperature and determination of leachate/emission rates of other pollutants such as dioxins, furans and heavy metals like cobalt, mercury, arsenic and selenium are important.

- The volatalisation mechanisms of different heavy metals from the solidified brick under different temperatures need further research.

- Biofly process can produce odour during storage of material, drying and firing stages. Although these odours can be controlled with different types of scrubber systems, simple, cheap and innovative techniques need to be found. In this context, addition of fly ash with sludge before storage need to be investigated further.


• It has been shown clearly that the biofly bricks can be produced with superior strength than ordinary bricks. The mechanisms which causes this increased strength have not been dealt with successfully. A comprehensive study relating to phase changes and microstructure of the composite materials need to be undertaken.

• The current firing curves have been established on a batch to batch basis using Port-O-Kiln in the laboratory. Hence for this using continuous tunnel kilns, optimum factory, firing curve need to be developed.

• The colour of all the successful biofly bricks are orange. One possible reason may be due to the effect of adding the sludge and fly ash to the clay, as well as firing in an oxidation atmosphere. Firing in reduction atmosphere need to be undertaken to evaluate the effect on colour.

• Although the hot and cold water absorption values of biofly bricks are higher than clay/shale bricks, they are infact comparable to average values obtained from other waste bricks in South Africa. Hence, a technique to minimise biofly bricks water absorption values need to be developed, may be by using additives.
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