Chemical studies on the flocculation of argillaceous slurries

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CHEMICAL STUDIES

ON THE FLOCCULATION

OF ARGILLACEOUS SLURRIES

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An investigation of the problems encountered with the flocculation and dewatering of coal washery tailings was carried out. This investigation encompassed a study of the ion exchange rates and properties of coal tailings with respect to the Ca$^{2+}$ ion. It was found that ion exchange was very rapid in normal tailings although different behaviour was encountered when clay derived from the decomposition of igneous dykes was mixed with the tailings.

The optimum flocculation conditions for tailings, "dyke" clay and a tailings and "dyke" clay mixture were determined. The use of the Ca$^{2+}$ ion (derived from CaCl$_2$·2H$_2$O) together with a 20% anionic polyacrylamide flocculant produced optimum flocculation in terms of settling rate, filtration rate and turbidity. This reagent combination was found to be superior to a combination of aluminium sulphate and polyacrylamide at present used in the washery with the added benefit that the Ca$^{2+}$ ion can be partially recycled.

A new analytical technique based on the reaction of nitrous acid with amides was developed. This technique was then applied to the analysis of the degree of hydrolysis of polyacrylamides and the distribution of polyacrylamide between the solution and the clay surface. By suitable modifications to pH and temperature this analytical method was applied to the analysis of compounds containing primary and/or secondary amino groups.

The analytical method enabled the investigation of the mechanism of flocculation in the presence of a metal ion. This investigation was carried out on pure samples of the clay minerals kaolinite and montmorillonite.
It was found that optimum flocculation of clays occurs when half the surface of the clay particle was covered with flocculant and optimum flocculation occurs only in the presence of a minimum quantity of metal ion. The complexation of divalent metal ions by polyacrylamide flocculants was investigated utilising ion selective electrode potentiometry and it was found that this complexation occurred before flocculation took place.

The final aspect of this project was a full scale plant trial at a coal washery to show that CaCl$_2$.2H$_2$O could be used as an aid to flocculation and to determine the amount recycled in actual washery operation.
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INTRODUCTION
GEOLOGY OF COAL SEAMS IN THE ILLAWARRA REGION

The Illawarra Region of New South Wales is one of Australia's major coal producing areas. The coal seams exploited in this region yield coal that is used locally in the manufacture of steel and for electricity generation. However the vast majority of the coal mined is exported to Japan. The low sulphur content of the coal and its excellent coking properties make it very suitable for steel manufacture (Edwards and Robinson 1971).

The coal is found in a sequence of rocks called the Illawarra Coal Measures. The Illawarra Coal Measures stretch from Coalcliff in the north, where they outcrop at sea level, to Kiama in the south. The western boundary is the Burragorang Valley where further mines are situated while the eastern boundary is the Pacific Ocean (Figure 1). These coal measures are of Permian Age and lie conformably on the Shoalhaven Group and are overlain by the Triassic Age Narrabeen Group. The coal measures contain nine coal seams, all of which are mined to various extents throughout the area (Wilson 1969).

The South Bulli Washery processes coal from the Bulli and Balgownie Seams. The Bulli Seam, which varies from 1-4 metres in thickness, is the uppermost formation in the Illawarra Coal Measures. Commercially it is the most important of the coal seams and it has been extensively exploited since it contains good coking coal with a consistent ash content of between 9 and 12%. The Balgownie Seam is lower in the stratigraphic sequence than the Bulli Seam and it is about 1.5 metres thick. It usually consists of unbanded clean coal and contains about 15% ash (Menzies 1974).
DISTRIBUTION OF THE ILLAWARRA COAL MEASURES

FIGURE 1
The principal rocks of the Illawarra Coal Measures are sandstone, shale, tuff, coal and associated sediments. Sandstone is the dominant rock and contains 20% quartz and 50% rock fragments. The cementing materials are carbonates and kaolinite. The rock fragments consist mainly of claystone and quartzite. The shales are carbonaceous and are generally associated with the coal seams. Each coal seam has its own individual characteristics. Wilson (1969) found that seams consist either of coal or carbonaceous shale or an interbedded mixture of both. It may have a clean homogeneous section from its roof to its floor or it may consist of well defined coal plies separated by shale bands. Igneous dykes occasionally run through the coal seams and these are usually dolerite or olivine basalt. The dyke is seldom in its original state, being generally decomposed to a whitish clay.
GENERAL PLAN OF A COAL WASHERY

The coal washery process can be broken into three main sections:

1. Primary Separation,
2. Secondary Separation,

The run-of-mine coal is reduced in size (to below ~30 mm) by primary crushers, and after mixing with water is fed into a set of scalping screens (A in Figure 2). Large coal passes over these screens and is further processed in a dense medium cyclone plant (B), the overflow of which realises a fuel coal (26% ash) used for electricity generation.

The material passing through the scalping screens is then pumped, via desliming screens (C), into the flotation cells (D), where fine coal (less than 0.5 mm) is separated from the mineral matter by addition of frothing agents (usually 4-methyl-2-pentanol). The fine coal is removed in the form of a froth concentrate which is fed into thickening cyclones (E).
The overflow (O/F) of these cyclones is rethickened in a coal thickener where flocculants are added and the fine coal settles to the bottom of the thickener. The underflow (U/F) of the thickener is then fed together with the underflow of the thickening cyclones to the disc filter (C) resulting in coking grade coal (less than 14% ash).

The refuse, called tailings, that remains behind in the flotation cells is fed via a launder into a tailings thickener (H) where flocculant is added. The flocculated tailings are then pumped to a tailings dam (J) where the tailings settle out and the supernatant water is then recirculated back into the washery. Although the design of a coal washery is a function of the location and type of coal mined, this general description is typical of washeries found along the Illawarra Coal Measures (Ellis et al. 1973).

**RECIRCULATION OF WATER IN COAL WASHERIES.**

Coal washeries, because of the large tonnages of material treated and the high moisture content of the washed coal, must inevitably be large consumers of water, but their water consumption can be greatly reduced if the tailings effluent can be sufficiently clarified to be recycled. The recycling of water that is possible by closing the tailings circuit of a washery enables the consumption of water to be reduced from 2-3m$^3$ per tonne of raw coal to 0.1-0.2m$^3$ (Bakels 1963). The only limitations on the recycling of washery water are the maintenance of appropriate water quality for the washing, flotation and flocculation stages of the circuit. The total salinity must be kept within reasonable limits to avoid serious corrosion.

The influence of a number of water quality parameters on the coal washery process has been examined by previous workers (Bakels 1963, Meerman 1954).
TABLE 1
Permissable Concentrations (mg/l) of Various Ions in Water Used for Coal Washing

<table>
<thead>
<tr>
<th>pH</th>
<th>Cl&lt;sup&gt;-&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</th>
<th>Temporary Hardness (CaO)</th>
<th>Permanent Hardness (CaO)</th>
<th>Suspended Matter and Fines</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-8.5</td>
<td>1000-2000</td>
<td>800-1000</td>
<td>140-160</td>
<td>800-1500</td>
<td>less than 200</td>
</tr>
</tbody>
</table>

The limiting concentrations for these parameters are shown in Table 1. It has been shown that optimum flotation of fine coal occurs at near neutral pH (Zimmerman 1948) as higher and lower pH's reduced the hydrophobic character of the coal particles by the adsorption of hydroxyl and hydronium ions respectively, with consequent reduction in the recovery of fine coal. The level of suspended solids must be kept as low as possible because a concentration of colloidal clay material in the flotation slurry exceeding 0.5% will cause clogging of the filtered coal with a consequent rise in ash content.

There is thus a need to effectively maintain water quality throughout the washery and as the majority of recyclable water comes from the tailings circuit it is in this area that effective treatment of the water must occur. Ellis et al. (1974) have shown that the ionic strength of the water increases as it passes through the washery. This is due primarily to dissolution of soluble salts and minerals mined along with the coal during the washery process.

The present practice in the washery studied is to use a combination of reagents to dewater the tailings. Aluminium sulphate \([\text{Al}_2(\text{SO}_4)_3\cdot16\text{H}_2\text{O}]\) (filter-alum) is added to the tailings immediately followed by a solution of partially hydrolysed polyacrylamide flocculant (Magnafloc 155). The flocculated tailings are then concentrated in a tailings thickener where the clarified water overflows while the tailings are
pumped from the bottom as a 40% suspension to a series of tailings dams. The water percolates through the coarse refuse walls of the dams and then proceeds through a series of filtration dams to a holding pond. It is pumped from here back to the washery where it is mixed with water from other sources to be used throughout the washery.

The washery utilises a variety of sources for its water supply; namely the town supply, a natural spring in the area and mine drainage. The use of any particular source depends on availability though the washery in the main utilises a mixture from all three sources. The mine drainage is slightly alkaline and contains only a minor concentration of sulphate due to the low concentration of sulphur in the coal (Clark and Swaine 1962) and low sulphide mineralisation. This makes it quite suitable for washery use. Table 2 contains a typical chemical composition of the feed water used in the washery.

TABLE 2
Concentration of Common Ions (mg/l) in Washery Water

<table>
<thead>
<tr>
<th>pH Range</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2-8.5</td>
<td>200-300</td>
<td>1-8</td>
<td>2-6</td>
<td>5-2</td>
<td>200-500</td>
<td>20-80</td>
</tr>
</tbody>
</table>

A major problem encountered in the washery and the tailings circuit occurs when the coal seams are intruded by the remains of igneous dykes. These dykes are decomposed to a whitish clay and when this clay is mined along with the coal it causes difficulties in the washery. This "dyke" clay forms rather intractable clay slimes that tend to choke the flotation cells. The present solution to this problem is to shut the washery down and bleed the clay-rich water to a tailings dam where part of the clay settles out. However, a significant proportion must be discharged into a nearby creek.
The present combination of flocculant reagents is ineffective when this clay is present.

The present procedure when the "dyke" clay is encountered can contravene the "Clean Waters Act" and is costly due to long "down-times" in the plant, therefore there is a necessity to solve this problem and find a suitable combination of reagents that will enable effective flocculation.

This study therefore looks at the flocculation problems encountered at the South Bulli Coal Washery with a view to improving the flocculation of coal tailings and thus enabling a more efficient recirculation of water with consequent economies in washery operation.
Clay minerals are primarily crystalline aluminium or magnesium silicates with stacked-layer structures (Grim 1968). There are two types of layers in clay minerals namely the octahedral layer and the tetrahedral layer. The octahedral (O) layer consists of two layers of oxygen atoms (or hydroxyl groups) in a hexagonal close packed arrangement with aluminium or magnesium atoms respectively in the octahedral sites. The aluminium octahedra are packed so that they share edges and two opposite faces of each octahedra are in continuous parallel planes. When the oxygen atoms are completely replaced by hydroxyl groups the smallest repetitive unit has the composition and structure of the mineral gibbsite and consequently the octahedral layer is frequently referred to as the gibbsite layer (Pask 1957).

The tetrahedral (T) layer consists of silicon atoms each surrounded by four oxygen atoms in a tetrahedral arrangement; these tetrahedra are connected in a hexagonal pattern in a continuous two-dimensional array (van Olphen 1963).

KAOLINITE

Kaolinite is composed of a single silica tetrahedral sheet and a single gibbsite octahedral sheet combined in a unit so that the corners of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer. All the tips of the silica tetrahedra point in the same direction and toward the centre of the unit made by the silica and octahedral sheets. In the layer common to the octahedral and tetrahedral groups, two-thirds of the oxygen atoms are shared by the silicon and aluminium where they become O instead of OH (Brindley and Robinson 1946).
<table>
<thead>
<tr>
<th>STRUCTURE</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Two-Layer Clays</strong></td>
<td>Little isomorphous substitution, small</td>
</tr>
<tr>
<td></td>
<td>cation exchange capacity</td>
</tr>
<tr>
<td></td>
<td>nonexpanding</td>
</tr>
<tr>
<td>T</td>
<td>e.g. Kaolinite</td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Three-Layer Clays</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Expanding (Montmorillonites)</td>
<td>Substitution of a small amount of Al for Si in T-sheet and of Mg, Fe, Cr, Zn, Li for Al or Mg in 0-sheet. Large cation exchange capacity ( (M^{m+} = Na^+, K^+, Ca^{2+},...) ) Swell in water or polar organic compounds.</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Nonexpanding (Illites)</td>
<td>About ( \frac{1}{4} ) Si in T-sheet replaced by Al, similar 0-sheet substitutions. Small cation exchange capacity. ( (M^{m+} = K^+) )</td>
</tr>
</tbody>
</table>

FIGURE 3
**MONTMORILLONITE**

This clay mineral is composed of units made up of two silica tetrahedral sheets with a central octahedral sheet. All the tips of the tetrahedra point in the same direction and towards the centre of the unit. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. Between each three-layered unit water molecules can enter enabling the mineral to swell in one direction and hence montmorillonite is deemed an expanding clay mineral. There are usually exchangeable cations between these units which serve to compensate the charge on the layers (Grim 1968).

**ILLITES**

The basic structural unit is composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedral in each silica sheet point towards the centre of the unit and are combined with the octahedral sheet in a single layer with suitable replacement of OH by O. The unit is the same as that for montmorillonite except that some of the silicon atoms are always replaced by aluminium atoms and the resultant charge deficiency is balanced by potassium ions. There is seldom water between the units hence illite has a non-expanding lattice (Grim 1968).
CATION EXCHANGE IN CLAY MINERALS

Ion exchange is the reversible process by which cations and anions are interchangeable between mineral surfaces and solutions in contact with the minerals (Carroll 1959). Brindley and MacEwan (1953) summarised the structural causes of cation exchange in clay minerals. They found four structural features which caused cation exchange and these were:

1. Unsatisfied valencies produced by 'broken bonds' at surfaces and edges of particles.
2. Unbalanced charges caused by isomorphous substitution of cations, e.g. $\text{Al}^{3+}$ substituted for $\text{Si}^{4+}$.
3. Dissociation of structural $\text{OH}^{-}$ radicals, the $\text{H}^{+}$ from which may be replaced by metallic cations.
4. Accessibility of structural cations other than $\text{H}^{+}$ which become exchangeable under certain conditions, e.g. at low pH, $\text{Al}^{3+}$ ions move from the octahedral units to the exchange positions.

CATION EXCHANGE CAPACITY

The ability of a clay to undergo cation exchange is measured by its cation exchange capacity (C.E.C.). This is generally expressed as millequivalents/100 grams of clay and is measured at a fixed pH (usually 7). Kaolinite has a low C.E.C. (1-10 meq./100g) and the principal cause of cation exchange is 'broken bonds', though some isomorphous substitution can occur (Swartzen-Allen and Matijevic 1974). Montmorillonite and illite have higher C.E.C.'s of 30-120 and 10-40 meq./100g respectively (Grim 1968). In these two clay minerals isomorphous substitution is responsible for the higher exchange capacities.
Al$^{3+}$ can substitute for Si$^{4+}$ within the silica tetrahedra in illite, while in montmorillonite Mg$^{2+}$ can substitute for Al$^{3+}$ in the octahedral layer (van Olphen 1963).

**CLAY MINERAL SUSPENSIONS**

Electro-kinetic studies of aqueous clay suspensions indicate that at all pH values above 2 or 3 the clay particles carry a net negative charge which is compensated by the presence of positive counterions. The origins of this charge on the clay lattice are the same as those of the cation exchange properties namely; isomorphous substitution, lattice imperfections, broken bonds at the edges of particles and exposed structural hydroxyls (Swartzen-Allen and Matijevic 1974).

In clays which swell in the presence of water the counterions are held on the external surfaces of the aggregates and between the unit layers, whereas in non-swelling clays the counterions are adsorbed onto the external surfaces. In aqueous suspensions some of these cations may remain in a closely held Stern layer; others diffuse away from the surface and form a diffuse double layer. Provided that they are not fixed (irreversibly adsorbed) by engaging in strong specific bonding with the clay or by being trapped between unit layers that collapsed irreversibly the counterions can undergo ion exchange with other cations present in the system (Parks 1975, Wayman 1967).

The influence of cation hydration, ionic size, charge and polarizability have been studied in regard to the strength of bonding forces with clays. These studies have shown that there is a relative order in which ions bind with clay surfaces. This order is Li$^+$ < Na$^+$ < K$^+$ < NH$_4^+$ < Rb$^+$ < Cs$^+$ < H$^+$ < Mg$^{2+}$ < Ca$^{2+}$ < Cs$^+$ (Shainberg and Kemper 1965, 1966). Studies comparing the exchange of mono-, di- and trivalent cations on clay surfaces have shown in principle a
preference for cations of higher charge (Bolt 1955, Clark and Turner 1966). This trend is not always followed when a strongly held monovalent ion is compared with a relatively weakly held divalent ion, e.g. $\text{NH}_4^+$ and $\text{H}^+$ (Hodgson 1960, Riley and Arnold 1969).

A knowledge of the exchange properties of clay minerals is essential in a study of the water treatment processes in a coal washery. Earlier work has shown that the Ca$^{2+}$ ion is effective in facilitating flocculation of coal tailings (Ellis et al. 1974). To enable a more thorough evaluation of the use of Ca$^{2+}$ as a reagent in the tailings circuit of the coal washery a study of the exchange properties of the tailings was undertaken.
CHEMICAL AND MINERALOGICAL ANALYSIS OF TAILINGS AND DYKE MATERIAL

The chemical, mineral and particle size analyses of a "typical" sample of washery tailings are given in Tables 3 to 5. The predominant minerals are fine coal, kaolinite, illite and quartz together with carbonates such as calcite and siderite. These minerals are fairly typical of those found in coal tailings (Mitchell 1968). The absence of sulphide minerals such as pyrite and marcasite \( (\text{FeS}_2) \) is rather fortunate because the presence of these minerals generally leads to the problem of "acid mine drainage" (U.S. Dept. of Interior, 1968). The actual pH of the tailings suspension is 7.5-8.5 and the presence of carbonates and clay minerals will mean the tailings will have a significant buffering capacity particularly to addition of acid. (Krauskopf 1967).

The clay minerals are the result of the breakdown of shale and sandstone whilst the quartz is derived from the breakdown of sandstone. The kaolinite and illite might be expected to be responsible for most of the cation exchange capacity of the tailings as the amount of quartz is small and quartz is reported to have a low cation exchange capacity (Carroll 1959). Low grade brown coals have been observed to have ion exchange capacities (Clark and Swaine 1962) but in the case of Bulli and Balgownie Seam Coals, ion exchange properties would be unexpected due to the coal being high-rank bituminous, near anthracite in quality. Parks (1975) has examined the surface properties of non-silicate minerals with respect to ionic adsorption and from his results it could be concluded that the effect of the other minerals in tailings on ion exchange would be fairly minimal.

The dyke material as shown in Tables 6 and 7 is predominantly a mixed-layer clay while there are smaller amounts of siderite and
<table>
<thead>
<tr>
<th>Particle Size (microns)</th>
<th>% (by weight)</th>
<th>% Carbon</th>
<th>% Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 420</td>
<td>14.8</td>
<td>56.7</td>
<td>14.9</td>
</tr>
<tr>
<td>211-420</td>
<td>13.3</td>
<td>17.5</td>
<td>57.1</td>
</tr>
<tr>
<td>150-211</td>
<td>7.4</td>
<td>12.2</td>
<td>61.2</td>
</tr>
<tr>
<td>75-150</td>
<td>12.2</td>
<td>14.2</td>
<td>58.3</td>
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<td>60-75</td>
<td>3.3</td>
<td>5.1</td>
<td>76.1</td>
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<tr>
<td>45-60</td>
<td>1.8</td>
<td>5.2</td>
<td>77.2</td>
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<td>30-45</td>
<td>3.5</td>
<td>10.3</td>
<td>64.2</td>
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<tr>
<td>20-30</td>
<td>5.2</td>
<td>10.3</td>
<td>65.1</td>
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<tr>
<td>10-20</td>
<td>4.8</td>
<td>27.1</td>
<td>47.8</td>
</tr>
<tr>
<td>2-10</td>
<td>17.2</td>
<td>28.8</td>
<td>48.1</td>
</tr>
<tr>
<td>&lt; 2</td>
<td>17.0</td>
<td>23.2</td>
<td>51.2</td>
</tr>
</tbody>
</table>
**TABLE 4**

Mineral Analysis of Tailings*†

<table>
<thead>
<tr>
<th>Size Range (microns)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 50</td>
<td>Quartz 30%, Calcite 30%, Siderite 25%, Magnetite 10%, Kaolinite 5%</td>
</tr>
<tr>
<td>20-10</td>
<td>Kaolinite 30%, Illite 15%, Quartz 30%, Calcite 5%, Siderite 25%, Magnetite 5%</td>
</tr>
<tr>
<td>10-2</td>
<td>Kaolinite 50%, Illite 10%, Quartz 30%, Calcite 5%, Dolomite 2%, Goethite 3%</td>
</tr>
<tr>
<td>&lt; 2</td>
<td>Kaolinite 45%, Illite 25%, Quartz 15%, Goethite 5%, Gorceixite 5%, Ilmenite 2%, Others 3%</td>
</tr>
</tbody>
</table>

* As carbon is amorphous to X-Rays the actual coal content cannot be measured so the mineral analysis is normalized to 100% excluding carbon.

† XRD analyses by Supervise-Sheen laboratories, Sydney.

Quartz (SiO₂), Calcite (CaCO₃), Siderite (FeCO₃), Magnetite (FeO·Fe₂O₃), Dolomite (CaCO₃·MgCO₃), Goethite (Fe₂O₃·H₂O), Gorceixite (BaAl₃(OH)₇P₂O₇), Ilmenite (FeO·TiO₂).

Cation Exchange Capacity of Tailings: 4-12 meq./100g
<table>
<thead>
<tr>
<th>Size</th>
<th>%SiO₂</th>
<th>%Al₂O₃</th>
<th>%Fe₂O₃</th>
<th>%CaO</th>
<th>%MgO</th>
<th>%Na₂O</th>
<th>%K₂O</th>
<th>%TiO₂</th>
<th>%Mn₃O₄</th>
</tr>
</thead>
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<tr>
<td>420</td>
<td>57.3</td>
<td>23.6</td>
<td>11.8</td>
<td>2.86</td>
<td>.38</td>
<td>.59</td>
<td>.36</td>
<td>1.01</td>
<td>.08</td>
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<tr>
<td>211-420</td>
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<td>15.0</td>
<td>14.0</td>
<td>4.45</td>
<td>.18</td>
<td>.76</td>
<td>.39</td>
<td>1.26</td>
<td>.13</td>
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<tr>
<td>150-211</td>
<td>60.8</td>
<td>18.7</td>
<td>14.0</td>
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<td>.09</td>
<td>.48</td>
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<td>14.7</td>
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<td>60-75</td>
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<td>22.9</td>
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<td>.48</td>
<td>.98</td>
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<td>8.14</td>
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<td>.96</td>
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<td>20-30</td>
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<td>.95</td>
<td>4.20</td>
<td>2.40</td>
<td>.21</td>
<td>.05</td>
</tr>
</tbody>
</table>
CHARACTERISTICS OF DYKE CLAY

TABLE 6

Particle Size Distribution of Dyke Clay

<table>
<thead>
<tr>
<th>Size (microns)</th>
<th>% (by weight)</th>
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</thead>
<tbody>
<tr>
<td>&gt; 420</td>
<td>2.1</td>
</tr>
<tr>
<td>211-420</td>
<td>1.8</td>
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<tr>
<td>150-211</td>
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<td>75-150</td>
<td>1.5</td>
</tr>
<tr>
<td>60-75</td>
<td>1.1</td>
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<tr>
<td>45-60</td>
<td>1.0</td>
</tr>
<tr>
<td>30-45</td>
<td>1.4'</td>
</tr>
<tr>
<td>20-30</td>
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<tr>
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<td>2-10</td>
<td>20.2</td>
</tr>
<tr>
<td>&lt; 2</td>
<td>51.2</td>
</tr>
</tbody>
</table>

TABLE 7

Mineral Analysis of Dyke Clay

<table>
<thead>
<tr>
<th>Size (microns)</th>
<th>Mixed-layer clay</th>
<th>Kaolinite</th>
<th>Quartz</th>
<th>Anatase</th>
<th>Siderite</th>
<th>Goyazite</th>
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</thead>
<tbody>
<tr>
<td>50-30</td>
<td>20%</td>
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<td>30%</td>
<td>5%</td>
<td>25%</td>
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<tr>
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<td>25%</td>
<td>10%</td>
<td>30%</td>
<td>10%</td>
<td>25%</td>
<td>10%</td>
</tr>
<tr>
<td>10-2</td>
<td>75%</td>
<td>10%</td>
<td>15%</td>
<td>5%</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>&lt; 2</td>
<td>85%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
<td>5%</td>
</tr>
</tbody>
</table>

The mixed-layer clay is 90% illite, 10% montmorillonite.

Cation Exchange Capacity of Dyke Clay: 30-35 meq./100g
kaolinite present. This clay is an illite-montmorillonite mixture (90%-10%) and it would be expected that the properties of this clay mixture would greatly influence the behaviour of the dyke material in aqueous suspension. The dyke material by virtue of its particle size distribution (51% < 2μ) and high cation exchange capacity will behave differently to tailings in the washery circuit. Washery personnel report the formation of "intractable slimes" that do not respond to the present type of flocculation treatment. It was therefore desirable to examine the properties of this material in suspension in order to determine the reasons for its behaviour in the washery circuit.
ION EXCHANGE IN
CLAY MINERALS
The study of the rate of cation exchange equilibria is of great importance in assessing the behaviour of Ca\(^{2+}\) ions in the washery circuit. The Ca\(^{2+}\) ion will undergo ion exchange with the clay minerals present in the tailings and the level of Ca\(^{2+}\) at any time in the washery water will depend on the rate and amount of exchange that has taken place. The influence of such factors as ionic strength, type of cation substitution on the clay and tailings composition is of importance in determining the behaviour of Ca\(^{2+}\) in the washery water. It was therefore necessary to conduct a laboratory study of the exchange behaviour of Ca\(^{2+}\) with coal tailings in order to obtain an appreciation of the applicability of using CaCl\(_2\) as an aid to flocculation in the coal washery.

**THEORY OF CATION EXCHANGE**

Numerous attempts have been made to develop a theory of cation exchange that would permit the quantitative expression of exchange data by an equation. Equations based on several considerations have been suggested by various workers. Wiegner and Jenny (1927) derived empirical equations from the use of Freundlich's adsorption equation. Thermodynamic arguments involving some approximations have led to various mass-action equations by workers such as Kerr (1928) and Vanselow (1932). Erickson derived an equation based on the Gouy theory of the electric double layer for the mono-divalent cation exchange equilibrium. This equation was criticised by Bolt (1955) and Helmy (1964) who derived their own equations for the exchange involving monovalent and divalent exchange. These equations however, tend to be only applicable to ideal conditions and are generally restricted to certain types of pure clay.
It has been found by Gaines and Thomas (1954) and Faucher and Thomas (1954) that ion exchange equilibria cannot be described even roughly by a mass law expression in terms of stoichiometric concentrations. Their work studied the equilibria of cesium-potassium exchange with montmorillonite and found that the predictability of exchange behaviour depended on the ionic concentrations of Cs\(^+\) and K\(^+\). The results obtained also showed that the concentrations of ions on the clay played an important part in the behavioural prediction of cations undergoing exchange. The data suggested that Cs\(^+\) in Cs\(^+\)-rich clay and K\(^+\) in K\(^+\)-rich clay behave in nearly ideal fashion but when present in smaller concentrations non-ideal behaviour is observed.

Wiklander (1964) used the concept of selectivity coefficients to describe the equilibria for the interchange of ions with clay minerals. The Na\(^+\)-Ca\(^{2+}\) exchange on a clay mineral can be written as

\[
2(\text{Na}^+\text{-clay}) + \text{Ca}^{2+} = \text{(Ca}^{2+}\text{-clay} \_2) + 2\text{Na}^+
\]

A selectivity coefficient can be then defined as

\[
Q(\text{Na-clay Ca-clay}) = \frac{X_{\text{Ca-clay}}[\text{Na}^+]^2}{X^2_{\text{Na-clay}}[\text{Ca}^{2+}]}
\]

where X represents the equivalent fraction of the counter-ion on the exchanger

\[
X_{\text{Ca-clay}} = \frac{2[[\text{Ca}^{2+}\text{-clay}]}{(2[\text{Ca}^{2+}\text{-clay}] + [\text{Na}^+\text{-clay}])}
\]

These selectivity coefficients may be used to describe in a semi-quantitative way, equilibria for the exchange of cations, but these coefficients are neither constants nor are they thermodynamically well defined. The activities of the ions within the lattice structure of the clay are not known and vary depending on the composition of the clay exchanger phase and thus the coefficients tend to deviate from
constancy (Stumm and Morgan 1970). Wiklander (1964) determined the distribution coefficients of $\text{Ca}^{2+}$ and $\text{K}^+$ for kaolinite, illite, and montmorillonite at various concentrations of the ions. He showed that there is a concentration dependence on the selectivity of ions and that there is a marked difference between the selectivities of the three clays. An interesting approach to the determination of cation exchange constants has been made by Hanshaw (1964) who compacted clay samples as membrane electrodes and derived ion exchange constants from the theory of the membrane response of glass electrodes. Thus although selectivity coefficients are not thermodynamically valid they do provide a useful comparison of the behaviour of cations towards clay minerals.

These theoretical approaches to the description of cation exchange however, are of little value when describing a complex mineral assemblage such as coal tailings. The composition and concentration of tailings is not constant and may vary greatly at any given time depending on the seam that is being mined and there are even great variations in mineral composition in any one seam. Therefore the studies of the rates of exchange of cations with the tailings and the exchange behaviour must be approached rather empirically.

**RATES OF CATION EXCHANGE IN CLAY MINERALS**

The earlier studies of rates of cation exchange were by Gedroiz (1919) and Hissink (1924) who found that cation exchange in soils occurs relatively rapidly within one to three minutes. A possible reason for the limited number of studies of rates of cation exchange on clays in the past may have been the lack of equipment to measure reaction times of less than a few minutes. It was found that exchange reactions on sand and gravel-size material occurred at slow measureable rates. As a result various investigators such as Barshad (1954), Mortland (1958) and
Walker (1963) emphasized rates of exchange studies on sand and gravel-size materials. Completion times for exchange in such experiments were measured in terms of minutes, hours and days.

Grim (1968) found that the rate of cation exchange varies with the clay mineral, the nature and concentration of the cations and the nature and concentration of the anions. In general he found that exchange reactions for kaolinite are most rapid being almost instantaneous. The exchange is slower with montmorillonite (1-50 minutes) whilst illite requires an even longer time, perhaps hours or days to reach completion. Exchange in kaolinite takes place on the edges of the particles and thus can occur rapidly whereas in montmorillonite penetration of the ions takes more time. In the case of illite a part of the exchange is between basal flakes firmly held together and this is likely to be slow, resulting in a longer time to complete the reaction.

Boorland and Reitemeier (1950) conducted exchange measurements by use of the radioactive Ca$^{45}$ isotope. They found that equilibration of Ca$^{2+}$ between the solution and solid fractions of aqueous systems of kaolinite, illite and montmorillonite is complete within an hour. Their technique did not permit the study of slower reaction times. Their work also showed that the exchangeable Ca$^{2+}$ of calcium saturated clays is in kinetic equilibrium with soluble Ca$^{2+}$. A novel approach to measure cation exchange rates was developed by Brown (1964) who found that by dipping glass slides containing a thin layer of Ca-saturated montmorillonite into various salt solutions he could control the length of time the displacing cation was in contact with the clay mineral. The amount of Ca$^{2+}$ released into the exchange solution after dipping the slide for a known time interval was considered a measure of the exchange rate.
The use of ion selective electrodes to measure cation exchange rates was pioneered by Kennedy and Brown (1964) who used a sodium selective electrode to measure Mg-Na exchange. They demonstrated that under the conditions of their experiment 90% of the Mg-Na exchange on kaolinite, illite and montmorillonite occurred within two seconds. Malcolm and Kennedy (1969) used both potassium and sodium electrodes to measure cation-exchange rates for kaolinite, illite and montmorillonite. They found that Ca-K, Mg-K, Ca-Na, and Mg-Na exchange rates were rapid for all clay types with 75% of the exchange occurring within three seconds.

The use of ion selective electrodes in measuring cation activities in a suspension phase has been questioned by several workers (van Olphen 1963, Peech et al. 1953). They argue that the liquid junction potential of the reference electrode leads to errors in measurement. Since individual ionic activities are generally measured with cells having liquid junctions it is essential that data obtained by electrode methods is comparable with that obtained by other methods. Various workers (McLean and Synder 1969a, 1969b; Marshall 1964) have shown that hydrolysis, conductimetric, osmotic pressure and Donnan equilibration techniques all yield data which are strikingly similar to electrode measured cationic activities.

RATES OF CATION EXCHANGE IN COAL TAILINGS

In the present study of cation exchange rates two experimental techniques were used. The first technique consisted of removing aliquots from a clay/cation suspension at various intervals at a fixed temperature. These aliquots were filtered immediately through a membrane filter and the filtrate analyzed using atomic absorption spectrometry.
The other technique utilized ion selective electrode potentiometry. The cation selective electrode was placed in the clay-cation suspension and connected to a digital ion-activity meter and chart recorder. The first technique was found to be limited to time intervals of one to two minutes while the second technique was directly dependant on the response time of the particular electrode and the chart recorder. In practice this was found to be about ten to twenty seconds.

The initial measurements were conducted on an "artificial" suspension of ethanol/ethanediol washed coal tailings in distilled water. A 1% suspension of the tailings was used as this closely approximates the average concentration of flotation cell underflow. The tailings contain in a "typical" sample the following exchangeable cations.

**TABLE 8**

<table>
<thead>
<tr>
<th>Cation</th>
<th>Exchangeable Cations in Coal Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>4-7 meq./100g</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.2-0.3 meq./100g</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.3-0.8 meq./100g</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.2-0.4 meq./100g</td>
</tr>
</tbody>
</table>

It can been from the table that when Ca²⁺ is added to the suspension of tailings the resultant cation exchange is predominantly that between Ca²⁺ and Na⁺. Calcium chloride (CaCl₂·2H₂O) was used as a source of Ca²⁺ ions due to the fact that it is available in commercial quantities and also the majority of the Ca²⁺ ions derived from calcium chloride are uncomplexed in distilled water suspensions. The initial concentration of Ca²⁺ was kept between 40 and 80 mg/l as earlier work had shown that this level of Ca²⁺ would be commercially competitive with the levels of "alum" used in the washery (Ellis et al. 1974).

Figure 4 shows the behaviour of a 1% tailings suspension dosed with 70 mg/l of Ca²⁺.
Figure 4

Ion Exchange Pattern of an 'Artificial' Tailings Suspension with CaCl₂

Ca²⁺ (A.A.S.)

Ca²⁺ (Electrode)

Na⁺ (A.A.S.)

Na⁺ (Electrode)

Mg²⁺

K⁺

TIME (min)
The results obtained using atomic absorption and electrode techniques are very similar with the electrode results showing a marginally lower figure for Ca$^{2+}$ due to the fact that the electrode measures only "free" Ca$^{2+}$ activity while the A.A.S. measures total calcium concentration.

The drop in the concentration is due primarily to ion exchange rather than absorption as shown by the corresponding rise in Na$^{+}$ concentration. This shows a Ca$^{2+}$ decrease to Na$^{+}$ increase ratio of almost 2:1 which is indicative of ion exchange rather than simple ion absorption. This is the expected result as at the pH of the suspension (6.8-7.5) and at this ionic strength the Ca$^{2+}$ ion would be the predominating species. The bulk of the ion exchange takes place in less than 20 seconds and all ion exchange is complete within an hour. The majority of the ion exchange would be due to kaolinite which should exchange quickly while the smaller amount of illite should undergo exchange more slowly.

The ion exchange rate of the coarser tailings fraction was also determined with the size fraction between 20 and 2μ being examined. Figure 5 shows the results obtained. The small amount of ion exchange that takes place does so much more slowly than in the composite tailings sample where the ion exchange is primarily due to the <2μ size fraction. The ion exchange takes about 30 minutes to complete so the likely explanation for the pattern observed in the complete tailings sample after the initial 30 seconds is most likely due to the slow exchange in the illite and the larger size fractions.

The rate of the Ca$^{2+}$-Na$^{+}$ exchange was determined using varying concentrations of Ca$^{2+}$ from 20 mg/l to 120 mg/l. The results in Figure 6 show that the rate is independent of concentration over the range studied.
Ion Exchange Pattern of a 1% Suspension of Artificial Tailings (20-2 micron fraction)

FIGURE 5

Ion Exchange Pattern of a 1% Suspension of Artificial Tailings at varying Ca²⁺ Levels

FIGURE 6
The rate of the \( \text{Ca}^{2+}-\text{Na}^+ \) exchange was then determined on a representative sample taken directly from the washery. The ionic strength of the authentic washery sample is much higher as shown in Table 2 and thus it would be expected from the results reported by Wiklander (1964) and Gaines (1954) that the equilibria would be shifted from that of the tailings in distilled water. However, the sample behaves in a very similar manner to the "artificial" suspension with the majority of the exchange being complete within 20 seconds and the remaining exchange taking place within an hour. Figure 7 shows the results of the exchange at \( \text{Ca}^{2+} \) concentrations of 70 mg/l and 40 mg/l with a representative sample taken directly from the washery. A large number of samples were taken from the washery over a period of twelve months and their behaviour with the addition of \( \text{Ca}^{2+} \) determined. It was found that there was very little difference in the observed rate of ion exchange in any sample. The residual concentrations of \( \text{Ca}^{2+} \) and \( \text{Na}^+ \) were found to be in a range that varied ± 8 mg/l and 90 mg/l respectively. This large variation in \( \text{Na}^+ \) concentration was due to the variation in source water for the washery and the prevailing winds at the time.

Ellis et al. (1973) have shown the chloride and sodium ion concentrations in water supplies for South Coast washeries vary depending on the prevailing wind. They found that winds from the east tend to bring salt-laden spray onto the escarpment and thus increases the salinity of the washery water supply.

The results in Figure 7 mean that the ion exchange that will take place in the washery will be virtually complete (85%) in a few seconds. It also means that the majority of ion exchange will be complete by the time the polyacrylamide flocculant is added.
FIGURE 7

ION EXCHANGE PATTERN OF A WASHERY TAILINGS SUSPENSION (1.3%)
In the washery circuit the polyacrylamide is added several seconds after the "alum" and if CaCl$_2$ is substituted for "alum" it would be added at the same location by virtue of the plant design. Later results will show that flocculation by polyacrylamide takes about 20-30 seconds to complete which means that the majority of ion exchange will be complete before flocculation occurs.

There should be around 40% of the Ca$^{2+}$ added recycled back around the plant even with a low dose of CaCl$_2$. This is shown by the residual concentration of Ca$^{2+}$ after 40 mg/l of Ca$^{2+}$ was added. This concentration was found to remain unchanged even if the suspension of tailings was agitated for over 48 hours. Therefore it has been shown at least on a laboratory scale that enough Ca$^{2+}$ will remain in solution after ion exchange has taken place to make recycling of Ca$^{2+}$ in the washery circuit a distinct possibility.

**RATES OF CATION EXCHANGE IN "DYKE CLAY"

The dyke clay as mentioned before is predominantly a mixed-layer illite-montmorillonite clay. From its mineralogical composition it would be expected that the exchange behaviour of the "dyke" material towards the addition of Ca$^{2+}$ will be different to that observed with the tailings. Table 9 shows the exchangeable cations that could be extracted from the "dyke" material with ammonium chloride in aqueous ethanol according to the method of Tucker (1974).

**TABLE 9**

<table>
<thead>
<tr>
<th>Exchangeable Cations in &quot;Dyke&quot; Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$ 20-25 meq/100g</td>
</tr>
<tr>
<td>K$^+$ 0.5-2.5 meq/100g</td>
</tr>
</tbody>
</table>
This shows that the exchange when Ca$^{2+}$ ions are added will be primarily between Na$^+$ and Ca$^{2+}$. Figure 8 shows the rate of cation exchange when a 1% suspension of the "dyke" clay is treated with calcium ions. Over half the total exchange occurs in the first twenty seconds with the remaining exchange taking around an hour to reach completion. This rather slow exchange behaviour is consistent with the reported rate of cation exchange of illites (Grim 1968). The "dyke" also exchanges almost twice the amount of Ca$^{2+}$ that the tailings does. This larger amount of Ca$^{2+}$ consumption by the "dyke" would necessitate the addition of more CaCl$_2$ to the washery circuit when "dyke" was encountered by the washery.

The "dyke" was changed to a pure sodium-substituted clay so as to ascertain the effect of the Mg$^{2+}$, K$^+$ and Ca$^{2+}$ ions on the exchange sites and to see if their behaviour effects the overall exchange rate.

Figure 9 shows the exchange behaviour of sodium-substituted "dyke" clay. This was prepared according to the method of Swartzen-Allen and Matijevic (1975). This sample of sodium-substituted "dyke" shows a similar ion exchange pattern to the "normal" "dyke" except that more sodium is exchanged instead of the Mg$^{2+}$ and K$^+$ in the "normal dyke".

An unusual phenomenon is observed when the "dyke" material, both the "normal" and the sodium-substituted, is heated about 110°C and then undergoes ion exchange. Figure 10 shows the pattern of the ion exchange behaviour of dehydrated sodium-substituted dyke clay with Ca$^{2+}$ ions. The initial exchange takes place rapidly within twenty seconds but then the Ca$^{2+}$ concentration increases for about 5-8 minutes and then decreases slowly until about 60 minutes has elapsed when the ion exchange appears to cease. The behaviour of the Na$^+$ ions mirrors this behaviour indicating that it is an ion exchange phenomenon.
Ion Exchange Pattern of a 1% Suspension of Na-Substituted Dehydrated 'Dyke'

**FIGURE 10**

Ion Exchange Pattern of a Mixture of Tailings 'T' and 'Dyke' 'D' (99% 'D' & 1% 'T')

**FIGURE 11**
This type of behaviour does not appear to have been reported in the literature though it would appear that this observation is an artefact induced by heating the "dyke" above 110°C.

Hoffman and Kleman (1950) have shown that when a Li-montmorillonite is heated above 110°C then lithium ions migrate into octahedral sites, neutralising the charge on the clay lattice hence reducing the cation exchange capacity. Greene-Kelly (1955) agreed that such migrations could take place but found that it is only possible if the preponderance of charge on the silicate layer is due to octahedral substitutions. It would therefore seem that the heating of the dyke material would produce a loss of the interlayer water in the montmorillonite fraction and this would cause the unusual exchange behaviour. Low (1962) concluded that the most important fact governing the exchangeable cation movement in the pores of a clay-water system is the structure of the adsorbed interlayer water. It seems that two types of ion exchange could be proceeding in the "dyke" clay; those on the edge of the clay particles and those in the inter-layer spaces. The edge type ion exchange would be fairly rapid as reported by Grim (1968) while the inter-layer exchange would proceed more slowly and the observed ion exchange pattern occurs as a result of the interaction of these two forms of exchange. The migration of the Ca\(^{2+}\) ions in the inter-layer spaces must produce a shift in the ion exchange equilibria with the result being that the Ca\(^{2+}\) ions initially exchanged on the edges of the particles are back exchanged with the Na\(^+\) ions produced from the exchange in the inter-layer spaces.

Washery personnel report that when "dyke" material is encountered in the washery it usually accounts for 10–20% of the total tailings composition so the ion exchange behaviour of this type of mixture was investigated.
Ion Exchange Pattern of a Washery Tailings and 'Dyke' Suspension

**FIGURE 12**

- **Na⁺**
- **Ca²⁺**

**METAL ION (mg l⁻¹)**

**TIME (min)**
Figure 11 shows the $\text{Na}^+\text{-Ca}^{2+}$ exchange pattern of a 1% tailings suspension of which 10% of the tailings is "dyke" clay, in distilled water. The exchange is slower and greater in amount than in the tailings by itself. Figure 12 shows the exchange behaviour of "dyke" mixed with a representative washery sample. The effect of the "dyke" is similar to that shown in the "artificial" suspension in that the $\text{Na}^+\text{-Ca}^{2+}$ exchange is slower and greater in amount.

The results obtained on the ion exchange properties of "dyke" show that when "dyke" is encountered in the washery circuit it will cause a decrease in the concentration of $\text{Ca}^{2+}$. This shows that it will be important to monitor the concentration of $\text{Ca}^{2+}$ in the washery water and add the appropriate concentrations when dyke is encountered in the washery. It can be seen however that the occurrence of "dyke" in the washery does not present an insurmountable problem to the recirculation of $\text{Ca}^{2+}$ in the washery water and shows that the use of $\text{CaCl}_2$ as an aid to flocculation of tailings produced by South Coast washeries is feasible.
LABORATORY STUDIES
OF FLOCCULATION
LABORATORY STUDIES OF FLOCCULATION

STABILITY OF COLLOIDS

Colloidal particles can acquire an electrostatic charge in at least three different ways.

(I) The surface may contain ionogenic groups which dissociate in a suitably polar medium,

\[ \text{e.g. } -\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+ \text{ (Polystyrene Latex)} \]
\[ -\text{SiOH} \rightarrow -\text{SiO}^- + \text{H}^+ \text{ (Silica Surface)} \]

(II) The preferential adsorption of ions of one sign over another. The classic example of this is the AgBr sols which are either positively or negatively charged according to whether Ag\(^+\) or Br\(^-\) is in excess. For this reason Ag\(^+\) and Br\(^-\) are referred to as potential determining ions (Napper 1973).

(III) Defects in a crystal lattice may confer charge. An example of this is montmorillonite where substitution of Al\(^{3+}\) by Mg\(^{2+}\) at lattice sites results in a net negative charge on the particles (Van Olphen 1963). This would be the most likely source of surface charge on the minerals in coal tailings, though it is possible that the silica present could acquire charge as in (I).

Once the surface charge has been developed the ions in the bathing medium are either attracted or repelled by the surface. The simplest possibility would be the formation of an ordered layer of counterions just balancing the charge on the surface. Such a possibility is not thermodynamically possible and thermal energy tends to randomise the spatial positions of the neutralising counterions thus forming a diffuse double layer.
This situation is further complicated by the fact that many ions do not behave as indifferent electrolytes, which exhibit non-specific behaviour and remain solely in the diffuse double layer. Ions are often specifically adsorbed at the solid/liquid interface and influence the behaviour of the potential determining ions. However, colloid stability is determined primarily by the outer regions of the diffuse double layer which is only influenced indirectly by specific adsorption (Napper 1973).

For particle aggregation to be possible there must also be an attractive force whose magnitude and range are comparable with those of the double-layer repulsion. The general van der Waals forces appear to satisfy this requirement. The van der Waals forces that are of primary importance in colloid stability are London Dispersion forces (Crees 1972; Napper 1973).

D.L.V.O. Theory

The most successful theory for the explanation of colloidal stability was independently derived by Derjaguin and Landau (1941) and Verwey and Overbeek (1968), now known as the D.L.V.O. Theory. Gouy (1910) and Chapman (1913) had earlier shown that there is a decay potential as the double layer distance from the surface increases. The thickness of the double layer ($1/K$) is arbitrarily taken as the distance from the surface at which the potential falls to $(1/e)$-th ($=0.37$) of its surface value, $e$ being the base of natural logarithms. The value of $1/K$ is a useful index of the extension of the double layer into the continuous phase. Gouy and Chapman showed that

\[
\frac{1}{K}/\text{nm} = 0.305 / \sqrt{I}
\]

where

\[
I = \frac{1}{2} \sum \frac{z_1^2}{C}
\]

and is the ionic strength.
This shows that on addition of indifferent electrolyte the added counterions would cluster in the vicinity of the surface of the colloid, thus the surface potential would drop off more rapidly and the thickness of the double layer would decrease.

The DLVO theory assumes that the stability of a colloid depends on the interaction of the double layer repulsion and the van der Waals forces of attraction. The forces of attraction and repulsion are often given the symbols $V_A$ and $V_R$ and the stability of a colloidal particle can be determined by the interaction of these forces ($V_R - V_A$). Figure 13 shows the net interaction energy ($V_R - V_A$) as a function of the separating distance between particles in low and high ionic strength medium. The net repulsion between particles may be considered as an activation energy which must be overcome for aggregation to occur, its magnitude depending upon the charge of the particles and the ionic composition of the solutions. At ionic concentrations less than 10^{-3} M ionic strength there is a large energy barrier to aggregation so that very few particles have sufficient energy to overcome this barrier. Consequently the rate of aggregation is slow and the system is stable. As the electrolyte concentration is increased the energy barrier to aggregation decreases and slow aggregation occurs while at over 5 \times 10^{-2} M ionic strengths there is very little repulsion between particles and aggregation is rapid.

**Coagulation and Flocculation**

The definitions of coagulation and flocculation used in this study follow those of La Mer (1964). Coagulation refers to a process where the repulsive potential energy is reduced so that the van der Waals forces of attraction can predominate. As mentioned previously, the concentration of potential determining ions determines the charge of the
High ionic Strength

Low ionic Strength

FIGURE 13
colloid. For example, Ag\(^+\) for a positively charged AgBr solution. By adjusting the concentrations of these ions, for example, by increasing the pAg, it is possible to reduce the surface potential sufficiently to induce coagulation. It is generally not necessary to adjust the potential determining ion concentration to exactly the point of zero charge (pzc); slow coagulation can occur against a small residual potential energy barrier, for example, within 0.5 pAg units of the pzc. At the pzc there is no effective double layer, no repulsion and so coagulation is rapid (Healy 1973; Napper 1973).

The most common method of inducing coagulation and the one referred to in this work is to increase the ionic strength by adding an indifferent electrolyte. This reduces the thickness of the double layer and permits closer approach of the particles to occur in Brownian collisions. The minimum concentration of indifferent electrolyte needed to reach rapid aggregation is termed the critical coagulation concentration (C.C.C.). The empirical Hardy-Schulze rule states that the relative effectiveness of the counterions is theoretically proportional to the sixth power of the valency. Hence the relative C.C.C's of the monovalent, divalent and trivalent counterions are predicted to be 1:1/2\(^6\):1/3\(^6\) (i.e. 1.0:0.016:0.0013) respectively. Experimental observations confirm this dependence (Shaw, 1970).

Particles that have undergone coagulation settle slowly according to Stokes Law (Ives, 1974)

\[ v = \frac{g(\rho_s - \rho)d^2}{18\mu} \]

\( v \) = size
\( \rho_s \) = density of particles
\( \rho \) = density of medium
\( \mu \) = viscosity of medium
Flocculation

Flocculation refers to the aggregation of colloidal material by soluble macromolecules. These soluble macromolecules can be natural starches, alginates gums or synthetic neutral or charged polymers and polyelectrolytes. Flocculation is characteristically much more rapid than coagulation and the aggregates formed, i.e. flocs, are loose open structures (La Mer 1964). Flocculated material of high solid content obeys the following equation of settling: (La Mer and Healy 1963a; La Mer and Smellie 1956; Smellie and La Mer 1956).

\[
\frac{t}{(h - h_0)} = \alpha + \beta t \quad t = \text{time}
\]

\[
h = \text{height of subsidence line}
\]

\[
\alpha \text{ and } \beta \text{ are constants of the system}
\]

This distinction between coagulation and flocculation is not always clear cut and it is not meant to represent two exclusive classes. The action of aluminium and iron salts shows that both the phenomena of coagulation and flocculation can occur simultaneously. When a quantity of Fe(III) or Al(III) salt sufficient to exceed the solubility limit of the metal hydroxide is added to water, a series of hydrolytic reactions, proceeding from the production of simple hydroxo-complexes (e.g. Al(OH)\(^2^+\), Fe(OH)\(^3^+\)) through the formation of colloidal hydroxometal polymers to the formation of a metal hydroxide precipitate (Stumm and Morgan 1962). These hydroxometal complexes are readily adsorbed at interfaces whereas the simple aquometal ions are not so strongly adsorbed (Matijevic et al. 1961; O'Melia and Stumm 1968). This enhancement of adsorption by complex formation is caused primarily by the reduction of the solvation energy resulting from the lowering of the ionic charge (James and Healy 1972). Thus the mode of action of hydrolysable salts such as Al(III) and Fe(III) salts depends on factors such as pH and concentrations of the salt.
Polymeric Flocculants

With few exceptions polymers soluble in water are polyelectrolytes. Solubility is conferred by polar substituents such as amino or carboxyl groups, or their charged conjugate acid or base forms (Eldridge 1973). These polar or charged groups are also important in determining the adsorption behaviour of the polymer or insoluble substrates, and hence its ability to function as a flocculant. Soluble non-electrolyte polymers contain polar groups such as ether linkages or hydroxy or amide substituents. The repeating units of several polymers commonly used as flocculants are shown in Figure 14.

The flocculants used in this study are the polyacrylamide based Magnaflocs 351, 155 and 156 (Allied Colloids). Table 10 shows the characteristics of these polymers.

<table>
<thead>
<tr>
<th>Flocculant</th>
<th>Ionic Type</th>
<th>Molecular Weight(x10^6)</th>
<th>ZN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnafloc 351</td>
<td>nonionic</td>
<td>10-20</td>
<td>calc. 19.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found 19.5</td>
</tr>
<tr>
<td>Magnafloc 155</td>
<td>20% anionic</td>
<td>10-20</td>
<td>calc. 14.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found 14.8</td>
</tr>
<tr>
<td>Magnafloc 156</td>
<td>40% anionic</td>
<td>10-20</td>
<td>calc. 10.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found 10.5</td>
</tr>
</tbody>
</table>

The flocculant behaviour of a polymer depends very markedly on its molecular weight. In general, flocculating ability increases with increasing molecular weight (Eldridge 1973). Anionic flocculants usually have high molecular weights in the range 10^5 - 10^7. The polymer dimensions in solution and hence the flocculating ability of polyelectrolytes may be affected by pH, ionic strength and the nature of the ions in the water to be treated.
Repeating Units of some Polymeric Flocculants

\[ \text{CH}_2 - \text{CH} - \text{I} \]
\[ \text{COOH} \]
POLYACRYLIC ACID

\[ \text{CH}_2 - \text{CH}_2 - \text{NH} - \]
POLYETHYLENEIMINE

\[ \text{CH}_2 - \text{CH} - \text{I} \]
\[ \text{CONH}_2 \]
POLYACRYLAMIDE

\[ \text{CH}_2 - \text{CH}_2 - \text{O} - \]
POLYETHYLENE OXIDE

\[ \text{CH}_3 \text{N}^+ \text{CH}_2 \text{Cl}^- \]
\[ \text{CH}_2^- \]
CYCLIC QUATERNARY AMMONIUM COMPOUND

FIGURE 14
In general the greater the charge on the polymer the more it will be
effected by these variables. It is therefore desirable to keep these
factors as constant as possible when testing the flocculating ability
of a polymer.

Another important factor when using a polymeric flocculating agent
is the age of the solution. One disadvantage of a polyacrylamide based
flocculant is that it can lose its effectiveness on ageing in aqueous
solution. Shyluk and Stow (1969) showed that this could be correlated
with a decrease in the intrinsic viscosity of the solution and suggested
two possible causes. Firstly, degradation of the polymer could occur
through hydrolysis of weak links formed by hydrogen abstraction during
the polymerisation. Secondly, gradual disentanglement of aggregates of
polymer molecules could occur. Both effects would lead to an
effectively lower molecular weight reducing the flocculating ability
(Mukkopadyay et al. 1969; Sakaguchi and Nagase 1966).
MODE OF ACTION OF A POLYMERIC FLOCCULANT

A large polymer molecule having a high molecular weight, can be thought of as a chain of $\tau$ segments or repeating units. The chain can be partially or extensively coiled depending on the electrolytic environment. This chain of $\tau$ segments can approach the solid-liquid interface of a dispersion of a colloid in water. A number of these segments ($\beta$) can adsorb on and cover the solid surface sites. There will be $\tau - \beta$ segments per molecule extending from the surface of the solid. The fraction of surface covered by adsorbed polymer segments is given by

$$\theta = \frac{(P_o - P)N}{sS_o}$$

where

- $P_o$ = Moles of polymer added per gram of solid.
- $P$ = Moles of polymer remaining in solution after adsorption, per gram of solid.
- $P-P_o$ = Moles of polymer adsorbed per gram of solid.
- $N$ = Avogadro's number.
- $S_o$ = Surface area per gram of solid.
- $s$ = Number of adsorption sites per unit area of solid-liquid interface.

If

$$K = \frac{sS}{N}$$

then

$$P = P_o - \frac{K\theta}{\beta}$$

The fraction of adsorbed segments per molecule ($\beta/C$) is known to be small (La Mer and Healy 1963) and much less than one. The adsorbed segments per molecule are separated by loops of polymer chain that extend into solution. In this way the reaction of each adsorbed segment with a surface site is not influenced by the adsorption of other
Possible Reactions in Colloidal Flocculation

<table>
<thead>
<tr>
<th>Possible Reaction</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Adsorption (Optimum Polymer)</td>
<td><img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td>POLYMER + COLLOIDAL PARTICLE → DESTAB. PARTICLE</td>
<td></td>
</tr>
<tr>
<td>Floc Formation</td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>DESTAB. PARTICLES + FLOC</td>
<td></td>
</tr>
<tr>
<td>Secondary Adsorption (Excess Polymer)</td>
<td><img src="image3" alt="Diagram" /></td>
</tr>
<tr>
<td>STABLE PARTICLE</td>
<td></td>
</tr>
<tr>
<td>Initial Adsorption</td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
<tr>
<td>EXCESS POLYMER + COLLOIDAL PARTICLE → FLOC</td>
<td></td>
</tr>
<tr>
<td>Floc Rupture</td>
<td><img src="image5" alt="Diagram" /></td>
</tr>
<tr>
<td>FLOC + FLOC FRAGMENTS</td>
<td></td>
</tr>
<tr>
<td>Secondary Adsorption</td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
<tr>
<td>FLOC FRAGMENT + RESTAB. PARTICLE</td>
<td></td>
</tr>
</tbody>
</table>

FIGURE 15
segments with other sites. This is analogous to the adsorption-de
desorption of small molecules and can be expressed by a Langmuir type
adsorption isotherm of the form.

\[ \frac{\theta}{1 - \theta} = bP \]

where
- \( \theta \) = The fraction of surface covered by adsorbed polymer
- \( 1 - \theta \) = The fraction of uncovered surface
- \( P \) = The residual concentration of polymer
- \( b \) = The ratio of rate constants for adsorption-desorption
  reactions.

This system of colloidal particles with adsorbed polymer molecules
that exist as adsorbed and extended segments can undergo further
reaction. If a colloidal particle with adsorbed polymer is considered
as a unit floc, these unit flocs can interact by means of a bridging
mechanism to form a macro floc. This bridging theory has been developed
by Smellie and La Mer (1958) and others (Micheals 1954; Ruehrwein and
Ward 1952). The six types of reactions that can occur on addition of
polymer to a colloidal system are shown in Figure 15.

This "bridging" mechanism serves to explain the following
phenomena:

1. Efficient destabilization is often achieved with polymers having
   a charge similar to that of the colloidal particle (La Mer and
   Healy 1963b).

2. Optimum destabilization occurs when only a fraction of the avail-
   able adsorption sites on the surfaces of the colloidal particles
   are covered (La Mer and Healy 1963b).

3. Dosages of polymer which are sufficiently large to saturate the
colloidal surfaces produce a restabilized colloid, since no sites
are available for the formation of polymer bridges (O'Melia 1971).

4. Under certain conditions a system which has been destabilized and aggregated can be restabilized with extended agitation, due to the breaking of polymer-surface bonds and folding back of the extended segments on the surface of the particles (La Mer and Healy 1963b).
MEASUREMENT OF THE DEGREE OF FLOCCULATION

Settling and Sediment Volume

A flocculating system will normally subside rather than sediment and as such leaves a clear boundary line above the flocs. The initial rate of change of boundary height $h$ with time $t$ is an empirical measure of flocculation kinetics (Vincent 1974). As previously mentioned La Mer and Healy (1963b) have suggested the following equation relating $h$ to $t$.

$$\frac{t}{h_0 - h} = a + bt$$

A number of attempts have been made to relate settling rates either to the flow of the supernatant liquid through the settling bed (La Mer et al. 1957; Gaudin et al. 1959), or to the detailed floc structure (Micheals 1962).

Whereas stable dispersions tend to sediment into close-packed cakes of small volume, coagulating or flocculating systems settle with large sediment volumes. Measurements of sediment volume after some fixed time may be therefore used to compare degrees of aggregation. Results are often expressed in terms of the ratio of the final sediment height to the initial height.

Turbidity

The procedure is generally to compare the turbidity of a set of flocculating systems after some chosen time. The turbidity is the amount of light scattered at 90° to the light path after passing through the sample. Errors with this method can occur if partial sedimentation of flocs block the light beam or if air bubbles are present they can lead to high results. These errors can be overcome easily if care is taken to reproduce the conditions of flocculation exactly each
time and if the sample is placed in an ultrasonic bath for a short time prior to measurement to eliminate air bubbles.

Filtration Rate

The rate of filtration of the supernatant liquid through the settled beds is another indication of the degree of flocculation that has taken place. The filtration apparatus can either be very simple using gravity filtration or can utilise vacuum or pressure filtration. La Mer et al. (1957) introduced a method whereby the flocs themselves are used as a filter bed, supported on a filter paper or glass fibre substitute, either in a Buchner funnel or a Millipore apparatus. The filtrate is then passed through this filter bed. In general the greater the degree of flocculation the shorter the refiltration time \( Q \).

La Mer et al. (1957) derived the following relationship for \( Q \) in terms of the variables involved, based on the equations of Carmen (1938) and Kozeny (1927) for the filtration rate.

\[
Q = \frac{APgAc^2}{InKS^2}
\]

- \( P \) = The pressure drop across the filter bed
- \( g \) = The acceleration due to gravity
- \( A \) = The cross section area of the bed
- \( K \) = A constant
- \( n \) = The viscosity of the system
- \( S \) = The surface area of the bed per unit volume of bed
- \( e \) = The porosity of the bed

La Mer and Healy (1963) have developed the following equation relating \( Q \) to the initial polymer concentration \( P_o \).
\[
\frac{P^k}{(Q - Q_o)^m} = A_m + B_m P
\]

where \( A_m \) and \( B_m \) are constants.

\( Q_o \) is the filtration rate of the stable dispersion. Experimentally, it is found that \( Q \) is a maximum, at some optimum value of \( P_o \) and La Mer and Healy (1963) suggest the situation corresponds to maximum flocculation. This theory has been criticised by Slater and Kitchener (1966), Shyluk and Smith (1969) and Dollimore and Horridge (1972) who state that it is based on several erroneous assumptions. These assumptions are that the volume of the filter bed is independent of the flocculant dosage and that the floc structure is not effected by the pressure applied to the bed to assist filtration.

In this study the filtration rate was measured rather than the refiltration rate using the apparatus described by Christian et al. (1970) and Nicol et al. (1975). This apparatus was simple to construct and use, and utilised only gravity filtration. Using the apparatus the flocculated material is poured into a glass tube which has at one end the filter medium which was a disc of Whatman 90 filter paper supported on a very coarse sintered glass disc, (see experimental section). The side of the tube has a calibrated scale which enables measurement of both settling and filtration rate.
This study of the laboratory flocculation of tailings used filtration rate, settling rate and turbidity. These methods all yielded similar results with maxima and minima at the same flocculant concentrations. La Mer et al. (1963) state that refiltration rate measurements are the best means of determining the optimum flocculant concentration. Slater and Kitchener (1972) found in a comparison of several of the above techniques that all show good agreement except for refiltration rate which showed a sharp maximum whereas the other methods showed much more gradual maxima. They concluded that there is no advantage to be gained using refiltration rate and in fact the refiltration rate maxima does not correspond to the maximum flocculation of the suspension. Similar results were found in preliminary studies on coal tailings and it was found that refiltration rates were much slower to measure than any other of the parameters and were far less reproducible.

The method of agitation is very important to the reproducibility of flocculation measurements. The suspension which had previously been agitated overnight in an end-over-end shaker, was placed in a stoppered 100 ml cylinder. To this CaCl₂ or "alum" was added first and then mixed by inverting the cylinder twenty times at one inversion per second. The flocculant was always added in two increments and inverted forty times at one inversion per second after each increment. This procedure gave the optimum flocculation and it was found that less agitation gave incomplete flocculation while more agitation broke up the formed flocs due to the shearing of the flocs. The room that these measurements were performed in was kept at constant temperature so that filtration rates and settling rates would not be affected by changes in water temperature.
Flocculation Parameters vs Floc Dose with a Washery Tailings Sample. Constant Ca$^{2+}$ Dose of 40mg l$^{-1}$

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

FIGURE 16
Figure 16 shows the results of the flocculation of a washery sample at various flocculant concentrations using the three polyacrylamide flocculants. The best results were obtained using Magnafloc 155, the 20% anionic flocculant. This type of flocculant gave superior filtration rates and settling rates than the nonionic flocculant (Magnafloc 351) or the 40% anionic flocculant (Magnafloc 156). The optimum concentration of flocculant appears to be in the vicinity of 25 mg/l. These experiments were duplicated over a two year period and although the concentration and composition of the washery samples varied from time to time very similar results were obtained on each batch of samples.

These results show that the flocculation of tailings improves rapidly up to the optimum flocculation concentration and gradually deteriorates with increasing flocculant concentration. This type of phenomenon has been widely reported in the literature (Dollimore and Horridge 1972; Nicol et al. 1975) and seems to verify the finding that optimum flocculation occurs when only a fraction of the surface of the colloid is covered by polymer. The deterioration in flocculation would seem to be indicative of a high surface coverage which would confer a surface charge on the particles with resultant instability.

The effect of the calcium ion concentration on flocculation was studied by keeping the flocculant concentration constant and varying the calcium concentration. Figure 17 shows the results obtained using turbidity, settling and filtration rate as the indicators of flocculation. The results show that there is a dramatic improvement in flocculation up to around 40 mg/l. The effect of the calcium ions on the flocculation with the nonionic flocculant is much less marked than either of the anionic flocculants.
Flocculation Parameters vs Ca\(^{2+}\) Dose with a Washery Tailings Sample. Floc Conc. 25mg.l\(^{-1}\)
This would be expected purely from charge considerations as the nonionic flocculant could be adsorbed by the negatively charged tailings whereas the anionic flocculants would be repelled by the charge on the tailings. It can be seen that the greater the charge on the flocculant the higher the concentration of calcium ions needed to produce optimum flocculation. This is shown by the behaviour of the Magnafloc 156 where the flocculation improves up to a concentration of 60 mg/l of calcium ion whereas the Magnafloc 155 only improves up to 40 mg/l of calcium ion. This shows that one of the functions of the metal ion in flocculation is that of charge reduction enabling the polymeric flocculants to be adsorbed on the suspended particles.

Figure 18 shows the results of flocculation obtained using a constant dose of flocculant and varying the concentration of aluminium ions. The concentration of aluminium was maintained so the aluminium sulphate ("alum") from which they are derived was on an equal weight for weight basis with the CaCl₂. The results again show that Magnafloc 155 used in conjunction with the "alum" gives better flocculation than either of the other flocculants. The behaviour with aluminium sulphate is very similar to that obtained with CaCl₂. The flocculation improves up to a limiting concentration after which there is no change in any of the parameters.

These results show that as the price of calcium chloride and aluminium sulphate is roughly comparable ($147.00 per tonne and $142.00 per tonne respectively) there is no economic benefit to be gained by using "alum" in the washery. The added benefit of using calcium chloride as an aid to flocculation is that calcium ions would be recirculated around the plant and thus consumption of the reagent would be reduced on a period of time.
Flocculation Parameters vs $\text{Al}^{3+}$ Dose with a Washery Tailings Sample. Floc Dose 25 mg l$^{-1}$

![Graph](image-url)
Aluminium ions on the other hand, are not recirculated, being totally adsorbed on the tailings as a hydrolyzed polymer and as Al(OH)$_3$.

It is therefore shown that for the optimum flocculation of washery tailings CaCl$_2$ used in conjunction with anionic flocculants such as Magnafloc 155 are the best combination of reagents. The fact that the best results are obtained with anionic flocculants has been widely reported in the literature (Geer et al. 1959; Drexler 1956; Franke 1956; Topokov et al. 1960; Brunard et al. 1958; Mukai and Yamauchi 1962 and Chattopadhyay et al. 1960). In all these cases anionic flocculants were used alone and for charge reduction the natural ionic strength of the washery water was relied upon. Teichmann (1962) found that for the optimum flocculation aluminium sulphate or ferrous sulphate at pH less than 7 should be used in conjunction with a anionic flocculant. Reuter (1970) however found that optimum flocculation occurred at alkaline pH's and suggested the use of Ca(OH)$_2$ in conjunction with a anionic polymer. Dru (1965) made a thorough study of flocculation of coal tailings and found that polymeric flocculants performed best at neutral pH. It would thus seem that the optimum reagents for efficient flocculation of coal tailings depend on many variables and each individual type of tailings would probably require a different combination of reagents.
FLOCCULATION OF "DYKE" CLAY

Figure 19 shows the results of the flocculation of a 1% "dyke" clay suspension with the three types of flocculants. The results show as with the tailings suspension that Magnafloc 155 used in conjunction with the calcium ions flocculates the "dyke" clay better than the other reagent combinations. The optimum dose of flocculant for the "dyke" clay however, is higher than the tailings (40mg/l vs. 25mg/l). This reflects the particle size distribution of the "dyke" clay having a significantly higher percentage of colloidal material than the tailings.

It is significant also that the concentration of calcium ions necessary for maximum flocculation is higher in the dyke clay than in the tailings (Figure 20). This is indicative of the higher cation exchange capacity of the "dyke" and the particle size distribution. One factor that is evident from Figure 20 is the differentiation in behaviour of the three flocculants in the presence of varying calcium ion concentration. The nonionic flocculant is not affected by the change in calcium ion concentration to any marked extent and this observation is much more pronounced with the "dyke" clay than with the tailings. This is probably due to the fact that the flocculant being nonionic, does not require the charge screening presence of a metal ion for adsorption on the particles. On the other hand, the anionic flocculants require a high concentration of calcium before flocculation is at a maximum (around 100 mg/l). The more anionic flocculant Magnafloc 156, requires more calcium ion than does the Magnafloc 155 for optimum flocculation of the dyke reflecting the role of the metal ion in reducing the negative charge on the particles.
Flocculation Parameters vs Floc Dose with a 1/6 'Dyke'
Suspension. Ca^{2+} 40mg l^{-1}

FIGURE 19
Flocculation Parameters vs Ca\(^{2+}\) Dose with a 1\% 'Dyke' Suspension. Floc Dose 40mg l\(^{-1}\)

- Mag. 351
- Mag. 155
- Mag. 156

**FIGURE 20**
The most unusual results are however, those obtained with aluminium sulphate and the polyacrylamide flocculants used in combination (Figure 21). These results show the rather poor flocculation when compared with that obtained using calcium ions. There is an improvement in flocculation up to 15 mg/l of Al\(^{3+}\) after which all three parameters show a gradual decline in flocculation. Magnafloc 351 appears to give the best flocculation in combination with the "alum". These results show the difficulties that arise in the washery tailings circuit when "dyke" clay is encountered are due to the combination of reagents used. The present policy when "dyke" is encountered is to add more "alum" to the tailings to try and cause more efficient flocculation. The results obtained in this work show that this would aggravate the situation and cause the material to settle out more slowly.

The effect of aluminium ions and their interactions with polyacrylamide on the flocculation of clay suspensions was studied by Roberts et al. (1974). They found that at pH 5 or above with nonionic or anionic polyacrylamides efficient sedimentation was obtained with low dosages of aluminium ions (5-10mg/l) but that higher dosages of pre-added aluminium ions gave rise to lower sedimentation rates, unless a much higher concentration of polymer was added. Their results show that bonding interactions between the hydrolyzed aluminium ions and the anionic and nonionic polyacrylamides have a decisive influence on flocculation behaviour of the respective polyacrylamides towards clay suspensions. These interactions were specific and were thought to have involved opposite charge interactions between hydrolyzed metal ion polymers and polyacrylamide with hydrogen bonding playing a part in these interactions. They found that the hydrolyzed metal ion polymers act as "anchor sites" for the polyacrylamide to attach itself to the negatively charged surface of the clay.
Flocculation Parameters vs $\text{Al}^{3+}$ Dose with a 1% 'Dyke' Suspension. Floc Dose 40 mg l$^{-1}$

![Graph showing flocculation parameters vs $\text{Al}^{3+}$ dose](image-url)

- Turbidity (N.T.U.s)
- Floc Rate (ml sec$^{-1}$)
- Sedimentation Rate (cm sec$^{-1}$)

Legend:
- ▼ Mag. 351
- • Mag. 155
- ■ Mag. 156

FIGURE 21
They also found that an excess of "anchor sites" hindered flocculation and this phenomenon is most likely the cause of the poor flocculation of the "dyke" clay over the concentration range of aluminium ions tried.
FLOCCULATION OF A TAILINGS AND "DYKE" MIXTURE

The final laboratory study of flocculation was performed on a mixture of tailings and "dyke" clay with the "dyke" constituting 20% of the total suspension. Figure 22 shows the results obtained by varying the concentration of flocculants and keeping the concentration of calcium ion constant. The optimum flocculant concentration is around 35 mg/l which is between the optimum concentrations for the separate and "dyke" suspensions. The effect of the "dyke" is to increase the concentration of flocculant needed to cause maximum flocculation.

The effect of calcium ion concentration on flocculation is shown in Figure 23. The results show that for maximum flocculation to occur the concentration of calcium ion is around 80 mg/l which is higher than that required for the tailings only suspension and lower than that required for the "dyke" only suspension. This reflects the sequence of cation exchange capacities of the three types of sample. The "dyke" only suspension has the highest cation exchange capacity followed by the "dyke" tailings mixture then the tailings.

The flocculation of this suspension with varying concentrations of aluminium ions is shown in Figure 24. The results show that aluminium ions are markedly inferior to calcium ions when used in conjunction with the polyacrylamide flocculants. The presence of the "dyke" is particularly noticeable in these results and shows how the best way to minimise the effect of the "dyke" would be to add calcium chloride together with an increased concentration of flocculant.
Flocculation Parameters vs Floc Dose with a Tailings & 'Dyke' Mixture. Ca\(^{2+}\) 40mg l\(^{-1}\)

**Figure 22**

- Mag. 351
- Mag. 155
- Mag. 156
Flocculation Parameters vs Ca$^{2+}$ Dose with a Tailings & 'Dyke' Mixture. Floc Dose 35mg l$^{-1}$

FIGURE 23
Flocculation Parameters vs Al\(^{3+}\) Dose with a Tailings & 'Dyke' Mixture. Floc Dose 35mg l\(^{-1}\)

**FIGURE 24**
SUMMARY

The above results lead to the following conclusions:

1. Calcium chloride used in conjunction with hydrolyzed polyacrylamide is suitable for the effective flocculation of coal washery tailings, the best results being obtained when it was used in conjunction with the 20% hydrolyzed polyacrylamide Magnafloc 155.

2. Calcium chloride is as effective as "alum" when used in conjunction with a polymeric flocculant on a weight-for-weight basis.

3. Calcium chloride produces a markedly superior floc of "dyke" clay when used in combination with the polyacrylamide flocculants than does "alum".

4. The combination of "dyke" clay and tailings is best treated by use of calcium chloride and an anionic polyacrylamide.

5. The most effective way to treat "dyke" clay when it is encountered is to increase both calcium chloride and flocculant concentration.

6. The economics of using calcium chloride in the washery is justified by its price, its effectiveness in aiding flocculation of tailings, its ability to facilitate flocculation of "dyke" and the fact that part of its concentration could be recycled and thus with a resultant drop in reagent concentration.

7. The detailed explanation for the phenomena observed lies in the mechanism of flocculation and a study of the effect of metal ions on flocculation.
ANALYSIS OF AMIDES
AND AMINO COMPOUNDS
ANALYSIS OF AMIDES

The explanation for the previous observations on the flocculation of clay minerals using polymeric flocculants in conjunction with metal ions lies in the examination of the mechanism of flocculation. To accomplish this successfully an analytical method is required so as to examine the adsorption of polymeric flocculant on the mineral surface and determine the effects of the metal ion on this adsorption.

The earliest attempts to examine this using an analytical technique were by Linke and Booth (1960) who used a micro-Kjeldahl procedure to examine the adsorption of polyacrylamide on colloidal silica. Another attempt to obtain quantitative data on polymer adsorption was by Black et al. (1966) who used a carbon-14 labelled cationic polymer. They followed the adsorption of this polymer by measuring polymer residuals in the supernatant using liquid scintillation counting techniques. Iler (1971) developed a useful qualitative method for rapidly determining the presence or absence of flocculant in the supernatant liquid. The method is essentially a spot test using as an indicator a sol of 100-200 nm silica particles, which are visible due to an interference colour developed when they are adsorbed onto a black glass plate. The glass plate is dipped into the clear supernatant, rinsed and dried, then wetted with indicator sol, rinsed and dried. If more than 5ppm of polymer is present, a layer of silica is adsorbed and a darkened interference colour is seen in reflected light.

Schamp and Huylebroeck (1973) determined polymer concentration in the supernatant liquid by using viscosity measurements, referring to a calibration curve made with the same polymer.
Attia and Rubio (1975) devised a nephelometric method based on tannic acid for the determination of polyethyleneoxide. This method was adapted by Rubio and Kitchener (1976) for the determination of residual polyethyleneoxide after adsorption onto silica. Most of these methods however, are indirect and subject to error. The only method of those used in the literature appropriate to the present study is the micro-Kjeldahl procedure used by Linke and Booth (1960) which is time consuming and fairly non-specific. Thus a method for the analysis of amides that would be applicable to the analysis of polyacrylamide was needed.
Active-Hydrogen Methods

Hydrogen atoms attached to elements other than carbon are known as active-hydrogen atoms. Amines, alcohols, primary and secondary amides, primary and secondary sulphonamides, thiols, imides and water are representative of active-hydrogen compounds which react with alkyl magnesium halides (Grignard reagents) to form the corresponding alkane or with lithium aluminium hydride to form hydrogen.

\[
\begin{align*}
\text{RH} + \text{CH}_3\text{MgI} & \rightarrow \text{CH}_4 + \text{RMgI} \\
4\text{RH} + \text{LiAlH}_4 & \rightarrow 4\text{H}_2 + \text{LiAlR}_4
\end{align*}
\]

By measuring the volume of methane or hydrogen liberated from a known weight of sample, the number of active hydrogens present can be calculated. These active-hydrogen methods are generally accurate to about 3% and have been largely replaced by more specific and precise functional group methods (Cheronis and Ma 1964).

Paulsen and Cooke (1964) used NMR spectroscopy for the determination of active hydrogen. They determined active hydrogen in acetamide on the basis of its exchange with deuterium oxide. Jurecek (1946) reduced amides using Grignard reagent in diamyl ether and anisole and found that primary amides exhibited two active hydrogens at 85°C. Treatment of primary amides with Grignard reagent liberates two moles of methane; secondary amides yield one mole (Stone 1963).

Bromination Methods

The Hoffman rearrangement of an amide to a primary amine proceeds through the formation of an intermediate N-bromoamide. On the basis of this Post and Reynolds (1964) developed a spectrophotometric titration for primary aliphatic amides.
The amide was dissolved in water and treated with potassium bromide and calcium hypochlorite. The hypobromite ion formed during the titration converted the amide to its N-bromo derivate. Hypobromite ion in alkaline solution has an absorption maximum at 350 nm and at the end point a sharp increase in absorbance occurs due to excess hypobromite. In a later paper Post and Reynolds (1965) used an amperometric titration with similar reagents.

Scoggins and Miller (1975) used a variation of this bromination method in a spectrophotometric determination of amides. Their method is based on the oxidation of the amide functional group by bromine. Following destruction of excess bromine with sodium formate, the amide oxidation product oxidises iodide ion, which is measured as the tri-iodide-starch complex.

\[
\begin{align*}
RCNH_2 + Br_2 & \rightarrow RCNHB \quad + \quad HBr \\
Br_2 + HCO^- & \rightarrow H^+ + 2Br^- + CO_2 \\
RCNHB + HOH & \rightarrow RCNH_2 + Br^+ + OH^- \\
Br^+ + OH^- + I^- + 2H^+ & \rightarrow \frac{1}{2} I_2 + HBr + H_2O \\
I_2 + I^- + Starch & \rightarrow I_3^- - Starch \quad (blue\ complex)
\end{align*}
\]

This method was found to be suitable particularly for water soluble amides and suffered from interferences by primary and secondary amines. However, the limits of detection for the water soluble amides were around 20 mg/l.
Colorimetric Methods

The formation of hydroxamic acids by reaction of amides with hydroxylamine has been known since last century (Hoffmann 1889). The hydroxamic acids react with iron (III) salts to form iron(III)-hydroxamic acid chromophores which have a characteristic red violet colour (Feigl 1934). Primary, secondary and tertiary amides can undergo the reaction:

\[
\begin{align*}
\text{RCN} & \quad \text{NH}_2\text{OH} \\
\text{RCNHOH} & \quad \text{HN} \\
\text{RCNHOH} & \quad \text{Fe}^{3+} \\
\end{align*}
\]

where \( R_1 \) and \( R_2 \) are H or an alkyl group (Bergman 1952). The reaction rate is pH and temperature dependent (Soloways and Lipschitz 1952). This method has also been applied to the analysis of carboxylic acids by Montgomery et al. (1962), Kasai et al. (1975) and Kasai et al. (1974) via the formation of amides or esters which can then undergo the above reaction.

Reduction Methods

Amides are reduced to amines in nearly quantitative yields with lithium aluminium hydride (Nystrom and Brown 1948).

\[
\begin{align*}
2\text{RCNH}_2 & \quad \text{LiAlH}_4 \\
2\text{RCH}_2\text{NR}_2 & \quad \text{LiAlO}_2 \\
\end{align*}
\]

Siggia and Stahl (1955) demonstrated the usefulness of this reaction with primary, secondary and tertiary amides. The reduction may be carried out in ether to give the corresponding amines which are distilled from the reaction mixture and titrated with standard acid.
Alternatively the distillate may be taken up in standard acid and a back-titration carried out with standard base.

**3,5 Dinitrobenzoyl Chloride**

Mitchell and Ashby (1945) developed a method for the analysis of primary amides based on the reaction with 3,5-dinitrobenzoyl chloride in pyridine.

\[
\text{RCNH}_2 + 3,5(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CCl} \rightarrow \text{RCN} + \text{HCl} + 3,5(\text{NO}_2)_2\text{C}_6\text{H}_3\text{COH}
\]

A blank determination is carried out along with the sample. Unreacted mineral acid chloride is decomposed by adding methanol and the sample and blank are then titrated with standard sodium methoxide solution. The difference in the titration between the blank and sample is equivalent to the primary amide content. This method is applicable to primary amides of monofunctional or difunctional aliphatic and aromatic carboxylic acids.

**Titration Methods**

Perchloric acid exhibits increased acidic behaviour in the presence of acetic anhydride, which permits the titration of amides as bases (Wimer 1958). In practice the amide is dissolved in acetic anhydride and titrated with perchloric acid dissolved in acetic acid or dioxane. Glass and modified calomel or glass and silver-silver chloride electrodes are used to detect the end point (Streuli 1958).

A variation of this method was the photometric titration of amides in acetic acid as neither the potentiometric or the visual end point are sufficiently clear for good quantitative work. In the photometric method the colour change of an indicator in acetic acid is influenced by the relative concentrations of the acid and base forms of the indicator.
The absorbance change of the sample containing the very weak indicator base SudanIII is plotted as a function of perchloric acid added (Higuchi et al. 1956).

Tiwari et al. (1966) developed a titrimetric method which involves alkaline hydrolysis followed by elution through a cation exchange resin with pyridine. The resultant carboxylic acid was titrated with ethanolic sodium hydroxide under an atmosphere of nitrogen.

Gasometric Methods

Renard and Deschamps (1951) used the reduction of nitrate ion by amino groups to determine α-amino acids. Hassan and Tollan (1975) used this reaction to determine amides by gasometric analysis. Amides undergo the following reaction with nitric acid.

\[
\text{RCNH}_2 + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}
\]

The amides are hydrolysed to form an acid and ammonium nitrate, which decomposes into nitrous oxide. The liberated nitrous oxide is collected in a nitrometer over sodium hydroxide. This method is suitable for the analysis of primary amides down to a sample mass of 1-2 mg.

Most of the methods described above are unsuitable for the determination of polyacrylamide. The analysis of polyacrylamide requires a method that has a detection limit around 0.5 mg and must be applicable for the analysis of water soluble amides. The only possibilities in the above methods are the hydroxamic acid formation and the gasometric determination via N₂O. The reaction between primary amides and nitrous acid to yield nitrogen and a carboxylic acid afforded a possible gasometric procedure but the reaction suffered from the instability of nitrous acid which generally produced serious error (Cheronis and Ma 1964).
It was therefore decided to attempt to utilise and modify this reaction to overcome these difficulties.

**Reaction of Nitrous Acid with Primary Amides**

Nitrous acid reacts with an amide to form the corresponding carboxylic acid and nitrogen gas.

\[
\text{R CNH}_2 + \text{HNO}_2 \rightarrow \text{RCOOH} + \text{N}_2 + \text{H}_2\text{O}
\]

The mechanism of this reaction was investigated by Ladenheim and Bender (1960) who found that the reaction of the nitrous acid with benzamide was \(2.7 \times 10^7\) times faster than hydrolysis by either alkali or mineral acid. They found that the reactive species is the nitrosonium ion \(\text{NO}^+\) which reacts with the amide according to the following mechanism:

\[
\begin{align*}
\text{R CNH}_2 + \text{NO}^+ & \rightarrow \text{R CN-N=N=O} \quad \text{slow} \\
\text{R CN-N=N=O} & \rightarrow \text{R CN=N=NOH}^+ \quad \text{fast} \\
\text{R CN=N=NOH}^+ & \rightarrow \text{R CN=N}^+ \rightarrow \text{R CN^+} + \text{N}_2 \quad \text{fast} \\
\text{R CN^+} + \text{H}_2\text{O} & \rightarrow \text{RCO}_2\text{H}^+ \rightarrow \text{RCO}_2\text{H} + \text{H}^+ \quad \text{very fast}
\end{align*}
\]

This higher rate of reaction has been used to advantage on a preparative scale for the preparation of carboxylic acids from sterically hindered amides such as 2,4,6-trichlorobenzamide (Bouveault 1892; Sudborough 1895).

The possibilities for an analytical method are: (1) to measure the nitrogen given off or, (2) the residual concentration of nitrite. Shenton and Johnson (1972, 1973) used the reaction of nitrous acid...
with cyclamate to form cyclohexyl nitrite and nitrogen. They determined the amount of cyclamate in soft drinks by measuring the amount of cyclohexyl nitrite formed using a non-aqueous diazotization procedure. They also determined the amount of residual nitrite by its colour producing reaction with safranine. It was decided in this method to measure residual nitrite left after the reaction with the amide. The most suitable method for the analysis of nitrite was found to be the method of Shinn (1941). This method utilises the diazo-coupling reaction between nitrite, sulphanilamide and N-[[1-naphthyl]-ethylenediamine which produces a red dye. There are numerous methods available for the determination of nitrite in the literature (Garg et al. 1976; Toei and Kiyose 1977). Most of these involve variations of the reaction of the nitrite ion with an aromatic amine to yield a diazonium salt which is then coupled to another aromatic amine to form an azo-dye whose colour is then measured spectrophotometrically. The limits of detection of these methods is from 1 to 20 μg/l.

The spectrophotometric kinetic studies of Singer and Vamplew (1956) showed that nitrous acid made by adding a strong mineral acid to sodium nitrite was extremely unstable. This instability was partially controlled by completely filling and stoppering the spectrophotometric cells used in the measurements. This showed the need to use a closed system to prevent escape of the decomposition products of nitrous acid. It was found by Ladenheim and Bender (1961) that high acidity favours the formation of nitrosonium ions (NO$^+$) which are the active species for the cleavage of amides, so the reaction should be kept at acidities between 6 to 8 M. Unfortunately the high acidity also favours the disproportionation of nitrous acid into nitric acid and nitrogen oxide by the reaction: \[3\text{HONO} \rightleftharpoons \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}\]
The rate of this reaction has been shown to be increased by a high acidity in the solution leading to roughly equal concentrations of nitrosonium ions (Turney and Wright 1959).

**Experimental Procedure**

The apparatus used is shown in Figure 25. It consists of a small volume tube (2 x 5 cm) with a B24 socket at the top (D). A and B are 10 ml burettes with PTFE taps set into a B24 cone. C is a B7 socket with a key set into the side of the tube. The amide was dissolved in a sodium nitrite solution in the reaction tube. Burette A contained 16M sulphuric acid while burette B contained 10M sodium hydroxide. The reaction tube was heated for 30-40 seconds in a water bath then the burette assembly inserted into the reaction tube. Amides that were insoluble or slightly soluble in water were dissolved in 16M sulphuric acid in a PTFE cup (E) that was suspended from the key in the wall of the tube (C).

The reaction tube was then cooled in an alcohol/dry ice mixture contained in the beaker (F). The stopcock of burette A was opened and sulphuric acid was drawn in by the partial vacuum created, and allowed to run down the side of the tube into the amide-nitrite mixture that was gently stirred by a small, magnetic PTFE stirrer bar. A vigorous reaction ensured resulting in a pale blue solution of nitrous acid. The solution was then stirred at 0-4° and after 5-20 minutes depending on the amide used, the stopcock on burette B was opened in order to admit the sodium hydroxide solution. When all the alkali had been added, the contents of the tube were shaken so as to absorb all the nitrous fumes and the alkaline solution transferred to a volumetric flask.
FIGURE 25

AMIDE APPARATUS
To this flask was added citric acid to adjust the pH to 7-10 and the solution made up to the mark.

An aliquot of this solution was then taken and the residual nitrite content determined using Shinn's method (1941). The initial results showed that there was very little nitrite recovered even when a four-fold excess of nitrite was used. It was therefore necessary to test the recovery of nitrite from the solution without the addition of amide. It was found that only a small percentage (20-40%) of the added nitrite was recovered. As the apparatus was under reduced pressure throughout the reaction until the neutralization and pH adjustment steps, it was unlikely that these low figures for the recovered nitrite were caused by leakage of nitrogen oxides to the atmosphere. The apparent consumption of nitrite ion was probably caused by disproportionation of the nitrous acid into nitric acid and nitrogen oxide and oxidation of nitrogen oxide to nitrogen dioxide with air in the reaction vessel, with consequent conversion of a significant proportion of the initial nitrite into nitrate ions. Both these reactions are favoured by stirring and by the large air space relative to the volume of solution that is necessary for the safe conduct of the reaction in a sealed system.

It was therefore necessary to find a method to reduce the nitrate ion formed back to nitrite ion. Foyn (1951), Vatova (1956), and Chow and Johnstone (1962) used zinc powder for the reduction, but the reduction is sensitive to temperature, and it is necessary to centrifuge or filter each sample. The reduction was found not to be very reproducible and only 85-95% of the nitrate is reduced to nitrite (Morris and Riley 1963). Mullin and Riley (1955) used hydrazine, in the presence of cupric ion as a catalyst, to reduce nitrate to nitrite.
This method requires 24 hours to complete and is also sensitive to changes in temperature.

The use of cadmium as a reducing agent was suggested by Potzl and Reiter (1960) and has proved to have advantages in the reduction of the nitrate to nitrite. The method of Morris and Riley (1963) reproducibly reduces 91± 1% of the nitrate to nitrite when samples are percolated through a column of amalgamated cadmium filings. Grasshoff (1964) modified the method of Morris and Riley (1963) by lengthening the reducing column and treating the metal with an alkaline ammonium chloride solution to complex the oxidised Cd\(^{2+}\) ion, thus prolonging the life of the column. The procedure was further refined by Strickland and Parsons (1965) who replaced the ammonium chloride by the tetrasodium salt of EDTA, for the column conditioner. They also suggested washing the cadmium filings with nitric acid before amalgamation. This procedure appeared to pit the surface of the Cd, providing greater surface area.

Wood et al. (1967) replaced the mercury by copper and found that the percentage reduction was raised to 99-100%. The procedure recommended by Wood et al. (1967) was interposed between the pH adjustment step with citric acid and the colorimetric determination. Thus the sample was adjusted to pH 7-8 by addition of citric acid then tetrasodium EDTA added and an aliquot of the sample was then run through a reducing column containing copperized cadmium. Subsequently it was found that the reduction proceeded smoothly at pH's as high as 10.

When this procedure was adopted the recovery of nitrite was always found to be in the range 99-101% of the theoretical. This step therefore eliminated the problems reported by Cheronis and Ma (1964) caused
<table>
<thead>
<tr>
<th>Amide</th>
<th>m.p. (b.p.) (°C)</th>
<th>Sample Mass (mg)</th>
<th>N Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formamide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111°)</td>
<td>10</td>
<td>98.1-101.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28</td>
<td>98.5-100.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>38</td>
<td>98.4-101.1</td>
</tr>
<tr>
<td>Acetamide</td>
<td>82.5°</td>
<td>10</td>
<td>98.8-98.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>100.5-101.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>99.9-100.2</td>
</tr>
<tr>
<td>Propionamide</td>
<td>81.5°</td>
<td>20</td>
<td>99.3-101.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>100.3-100.7</td>
</tr>
<tr>
<td>Butyramide</td>
<td>115°</td>
<td>20-35</td>
<td>99.2-100.4</td>
</tr>
<tr>
<td>Benzamide</td>
<td>133°</td>
<td>30-50</td>
<td>98.9-100.7</td>
</tr>
<tr>
<td>Phenylacetamide</td>
<td>157°</td>
<td>40-50</td>
<td>99.5-100.7</td>
</tr>
<tr>
<td>Acrylamide</td>
<td>84°</td>
<td>20-50</td>
<td>99.3-100.6</td>
</tr>
<tr>
<td>Magnafloc 351†</td>
<td></td>
<td></td>
<td>98.6-99.7</td>
</tr>
<tr>
<td>(polyacrylamide)</td>
<td></td>
<td>25-30</td>
<td></td>
</tr>
<tr>
<td>Magnafloc 155†</td>
<td></td>
<td></td>
<td>98.9-99.4</td>
</tr>
<tr>
<td>(20% anionic polyacrylamide)</td>
<td></td>
<td>30-40</td>
<td></td>
</tr>
<tr>
<td>Magnafloc 156†</td>
<td></td>
<td></td>
<td>98.9-100.5</td>
</tr>
<tr>
<td>(40% anionic polyacrylamide)</td>
<td></td>
<td>20-43</td>
<td></td>
</tr>
</tbody>
</table>

*Reaction time 5-7 min.

† Microanalyses by the University of New South Wales Microanalytical Laboratory gave the following results:

Magnafloc 351 Found: N, 19.5. Calc. for C₃H₅ON: N, 19.7% ;

Magnafloc 155 Found: N, 14.7; Na, 6.1. Calc. for C₁₅H₂₃O₅N₂Na₂ (20% anionic) N, 14.8; Na, 6.1% ;

Magnafloc 156 Found: N, 10.8; Na, 11.5. Calc. for C₁₅H₂₁O₅N₃Na₂ (40% anionic) N, 10.5; Na, 11.5%
by the instability of nitrous acid. The reduction also eliminated any error associated with nitrate impurities in the sodium nitrite reagent.

Results

Table 11 shows the results obtained using the method on a variety of aliphatic and aromatic primary amides and the results of the analysis of polyacrylamide flocculants.

Sensitivity and Precision

The effect of mass of sample on the precision of the method was explored by carrying out five replicate determinations at each of four concentration levels. Sample masses of 50, 10, 1.0, and 0.1 mg of butyramide were taken and the relative standard deviation at these masses determined.

<table>
<thead>
<tr>
<th>Mass of amide (mg)</th>
<th>50</th>
<th>10</th>
<th>1</th>
<th>0.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Standard Deviation (%)</td>
<td>1.8</td>
<td>1.4</td>
<td>2.9</td>
<td>4.2</td>
</tr>
<tr>
<td>n = 5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The amide used was isobutyramide; samples < 10mg were prepared volumetrically from a freshly prepared aqueous solution of isobutyramide.

The absolute sensitivity is determined ultimately by the absorptivity of the red dye formed; by using 10 cm cells, nitrate concentrations as low as 14.0 g/l of nitrogen have been measured by Wood et al. (1967) with a relative standard deviation of 4%. When all the manipulative steps of the analytical procedure are taken into account, amide solutions containing 0.015 mg of nitrogen can be determined with
a relative standard deviation of 4.2%.

**Interference**

The major interfering substances are those that are reactive towards nitrous acid i.e. N-mono-substituted amides and phenols. Subsequent work has shown that amines do not interfere in the determination as they react very slowly at the pH of the reaction mixture. Inorganic ions that can reduce nitrites will interfere but minor concentrations of oxidising inorganic ions should not interfere as the nitrate ions produced would be reduced back to nitrite ions by the cadmium column. High concentrations of metal ions could interfere with the function of the EDTA, which serves to complex the Cd$^{2+}$ released by oxidation of the metallic cadmium.

The procedure is thus rapid, accurate and sensitive and can be used for direct microanalysis of solid or liquid amides or of dilute aqueous solutions of primary amides or polyamides after removal of water. The method is superior in sensitivity to other procedures that have been described and does not require a lengthy digestion step. It could be readily adapted to automated analysis as Hendriksen and Selmer-Olsen (1970) have already described automated procedures for determining nitrate and nitrite ions.
ANALYSIS OF AMINO-ACIDS AND AMINES

Following the success of the nitrous acid reaction with amides and polyamides, it was decided to examine the reaction of nitrous acid with amines and amino acids to give an hydroxyl group, with nitrogen being liberated. This is the basis of the well-known method of Van Slyke (1911) for the estimation of primary amino groups. In this method the compound containing the amino group is reacted with nitrous acid to liberate elemental nitrogen which is collected in a nitrometer. This reaction was further extended by Kainz (1953) for the determination of primary amino groups in primary aliphatic and aromatic amines, and sulphonamides. Nitrous acids also react with secondary amines and N-monosubstituted amides to give N-nitroso derivatives, but without evolution of nitrogen.

N-nitrosation

N-nitrosation is the term used to include the nitrosation of secondary amides, the deamination of primary aliphatic amines, and the diazotization of primary aromatic amines. The reactions are characterized by an initial attack of nitrous acid on the nitrogen atom of the free amine. Hughes, Ingold and Ridd (1958) and Schmid (1954) investigated the kinetics and mechanism of these reactions. The overall reaction of a primary amine with nitrous acid is

\[ \text{RNH}_2 + \text{HONO} \rightarrow \text{ROH} + \text{H}_2\text{O} + \text{N}_2 \]

Rate measurements of this reaction indicate that the reaction is second order for nitrous acid (Taylor 1928).

\[ \text{Rate} = k_1(\text{RNH}_2)(\text{HONO})^2 \]
The aromatic amines tend to parallel the aliphatic amines (Schmid 1937), the difference in product being due to the fact that the diazonium ion is stabilized by conjugation with the aromatic ring. At low acidities, where the proportions of free amine is increased the rate equation changes.

\[
\text{Rate} = k_2(HONO)^2
\]

This indicates that the nitrosating agent is dinitrogen trioxide which, at low acidities is consumed as rapidly as it is formed (Hughes, Ingold and Ridd 1958). The interpretation of the rate equations results in the following mechanism:

\[
\begin{align*}
2\text{HONO} &\rightleftharpoons \text{N}_2\text{O}_3 + \text{H}_2\text{O} \\
\text{RNH}_2 + \text{N}_2\text{O}_3 &\rightarrow \text{RNHNO} + \text{HONO} \quad \text{slow} \\
\text{RNHNO} + \text{H}^+ &\rightarrow \text{RN}_2^+ + \text{H}_2\text{O} \quad \text{rapid} \\
\text{RN}_2^+ + \text{H}_2\text{O} &\rightarrow \text{ROH} + \text{N}_2 + \text{H}^+ \quad \text{rapid}
\end{align*}
\]

This means that the optimum pH for the diazotization of amines is above pH 3 and the reaction rate declines markedly below this. At the low pH necessary for the reaction of amides with nitrous acid \((6\text{M H}_2\text{SO}_4; \text{Turney and Wright 1957})\) amines are fully protonated and are therefore unreactive. This difference in kinetics at varying \(\text{H}^+\) concentrations means that for the optimum reaction of nitrous acid with amines the pH must be kept above 3. This was achieved in this method by the use of a hydrochloric acid-sodium acetate buffer.

Secondary amines react with nitrous acid to form nitrosamines:
Nitrosamines are unaffected by alkali and hence upon neutralization with the concentrated sodium hydroxide do not decompose as is the case in concentrated acid (Vogel 1966). It was therefore found that the nitrosamines formed do not affect the subsequent determination of residual nitrite and are thus able to be determined by this method.

**Results**

Table 13 shows the results obtained using a variety of primary and secondary amines, and amino acids.

**Scope and Limitations of the Method**

The method is applicable to the analysis of primary and secondary amines and amino acids. Primary and secondary amines are not distinguished but the method could be used in conjunction with the direct spectrophotometric determination of secondary amines as their nitroso derivatives as suggested by Clark and Morgan (1956). As the optimum pH for the diazotization of amines is above 3, by appropriate pH adjustment the procedure can be used to determine amines in the presence of amides and vice versa.

The reaction is not seriously affected by steric hindrance and gives better results than the Van Slyke procedure for "anomalous" amino acids. An example of this is glycine, which when determined by the Van Slyke method does not give a quantitative result because it contains an active methylene group. This results in the formation of nitrous oxide and nitrogen through a nitrolic acid intermediate and occurs at high temperatures and high nitrite concentrations (Austin 1950, Kainz et al. 1957, Kainz et al. 1959) The present method utilises a low sample concentration and only a moderate excess of nitrous acid; the probability of the intermediate reacting with water is therefore enhanced relative to its reaction with nitrous acid.
<table>
<thead>
<tr>
<th>Amino compound*</th>
<th>Reaction time (min)</th>
<th>Sample mass (mg)</th>
<th>N Recovery † (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1° amines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-butylamine</td>
<td>40</td>
<td>1.8</td>
<td>96.7-101.6</td>
</tr>
<tr>
<td>i-butylamine</td>
<td>60</td>
<td>3.7</td>
<td>98.3-100.5</td>
</tr>
<tr>
<td>t-butylamine</td>
<td>60</td>
<td>1.7</td>
<td>97.7-99.4</td>
</tr>
<tr>
<td><strong>2° amines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>piperidine</td>
<td>60</td>
<td>2.1</td>
<td>97.7-106.5</td>
</tr>
<tr>
<td>dicyclopentylamine</td>
<td>60</td>
<td>3.2</td>
<td>98.4-100.9</td>
</tr>
<tr>
<td><strong>amino acids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glycine</td>
<td>40</td>
<td>3.0</td>
<td>99.8-101.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0</td>
<td>99.7-103.0</td>
</tr>
<tr>
<td>glycylglycine</td>
<td>50</td>
<td>4.0</td>
<td>98.8-102.0</td>
</tr>
<tr>
<td>phenylalanine</td>
<td>50</td>
<td>2.0</td>
<td>100.5-103.5</td>
</tr>
<tr>
<td>leucine</td>
<td>50</td>
<td>4.0</td>
<td>96.3-102.0</td>
</tr>
<tr>
<td>tyrosine</td>
<td>45</td>
<td>4.0</td>
<td>99.5-101.0</td>
</tr>
<tr>
<td><strong>amine-amide mixtures</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t-butylamine (+ 4mg isobutyramide)</td>
<td>60</td>
<td>1.7</td>
<td>98.8-99.4</td>
</tr>
<tr>
<td>isobutyramide (+ 1.7mg t-butylamine)</td>
<td>15</td>
<td>1.0</td>
<td>98.0-103.0</td>
</tr>
</tbody>
</table>

* amines and amino acids were diazotised at pH 3.5-4.

Amide groups were diazotised in 6M sulphuric acid.

† three replicate determinations of each amino compound.
The principal classes of interfering substances are as for the Van Slyke procedure (Kainz et al. 1957). Positive interference may be expected from isonitroso and active methylene groups and from monohalogenocarboxylic acids, phenols, sulphur compounds oxidisable by nitrous acid, indoles and oxindoles, and lactams (Cheronis and Ma 1964). Negative errors will arise for amines that are difficult to dissolve or diazotize. Shimoe (1956) reported that cupric chloride suppresses the side reactions associated with the active methylene group, while Kendrick and Hanke (1937) found that iodide ions do likewise. The use of dilute sodium nitrite in this method seems to eliminate this problem however. Phenol interference can be eliminated by adding bromine water before the diazotization as in the case of tyrosine which was determined quantitatively. Tyrosine was found by Kainz et al. (1957) to be one of the anomalous amino acids due to the phenol group present. The Van Slyke procedure has two additional sources of error that do not occur using this method. Amines which give relatively stable diazonium salts and side reactions of the intermediate diazonium salts both lead to low results due to some of the nitrogen not being liberated.

Inorganic ions which can reduce nitrite interfere, but minor concentrations of oxidising inorganic ions do not; any nitrate produced is reduced to nitrite by the cadmium column. High concentrations of metal ions could interfere with the function of the EDTA which complexes the Cd$^{2+}$ released by the oxidation of the cadmium (Wood et al. 1967).

**Sensitivity and Precision**

The precision of the method was studied by performing five replicate determinations at each of two different concentration levels with phenylalanine and t-butylamine (Table 14).
When all manipulations of the procedure are taken into account, solutions containing as little as 0.017 mg of amino nitrogen can be determined with a relative standard deviation of 2.7%. Because the method is based on comparison with absorption of a blank subjected to the entire procedure, errors associated with nitrate impurities in the nitrite reagent and uptake of nitrogen oxides from the atmosphere are minimised. The sensitivity depends on the absorptivity of the azo dye used to measure nitrite concentrations. With 10 cm cells, nitrite concentrations as low as 14μg N/l have been measured by Wood et al. (1967) with a relative standard deviation of 4%.

This procedure affords a sensitive and accurate method for determining primary and secondary amines and amino acids. The apparatus is simpler to use and construct than the Van Slyke apparatus. It avoids the chromophoric substituent effects associated with direct spectrophotometric determination of the derivatives formed with 2,4,6-trinitrobenzenesulphonic acid (Koch and Weidel 1956) or 2,4-dinitrofluorobenzene (Fields 1971). It also gives a stable colour in contrast to that given by ninhydrin (Moore et al. 1958).

Table 14

<table>
<thead>
<tr>
<th>Mass of phenylalanine (mg)</th>
<th>Mass of t-butylamine (mg)</th>
<th>Relative Standard Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.2</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

n = 5
MECHANISM OF FLOCCULATION

Note: All experimental results in the following section refer to a sample volume of 100 ml.
STUDIES ON THE MECHANISM OF FLOCCULATION

A number of investigations have been made previously in an effort to explore the mechanism of the chemical reactions occurring at the particle/polyelectrolyte interface.

Linke and Booth (1960) studied the mechanism of the flocculation of silica with polyacrylamide by using a micro-Kjeldahl nitrogen analysis. They investigated the distribution of polyacrylamide between the liquid and floc phases as a function of polymer concentration. From their analysis they found that up to a certain concentration practically all of the added polymer is adsorbed on the solid; none was left in the solution. The point beyond which the polymer was not completely adsorbed corresponded to an optimum polymer/solid ratio found by observation of the settling rates. They also found that there was no point of saturation of polymer on the solid. This phenomenon however appears to be a result of the continued agitation of the formed flocs with a consequent uncovering of silica surface.

The existence of an optimum flocculant/solid ratio indicated to Linke and Booth (1960) the presence of two competing processes when polymer is added to a suspension. The processes were:

1. adsorption of polymer on the solid and
2. the formation of polymer "bridges" between particles as suggested by Ruehrwein and Ward (1952).

The second step can only occur after the first and the extent to which (2) can occur depends on the frequency with which the particles approach closely enough to form the "bridge". Thus up to a point increasing the concentration of polymer causes more "bridges" to form but excessively high polymer doses tended to cover the exposed surfaces before the interparticulate collisions needed for "bridging" could occur.
Black, Birkner and Morgan (1966, 1968) used a $^{14}$C labelled cationic and anionic polymer to study the mechanism of flocculation of kaolin and montmorillonite. They found that there was a well-defined optimum flocculant dosage which maximised the degree of suspension destabilization. The polymer adsorption data fitted a Langmuirian model and as polymer dosage was increased the polymer-clay system passed through a zone of optimum turbidity and into a repelptized system where the clay particles become saturated with polymer molecules.

Slater and Kitchener (1966) found that in the flocculation of fluorite particles settling rates and filtration data did not show corresponding peaks where maximum flocculation occurred. The filtration and refiltration rate curves showed peaks at a lower polymer concentration than those of the settling rate. Nicol et al. (1975) found similar results for the flocculation of hematite suspensions. They reasoned that in contrast to settling and supernatant turbidity data that the filtration and refiltration maxima cannot be reconciled with the floc growth/floc breakdown theory of La Mer and Smellie (1962) because the optimum flocculant dosage occurs at a lower concentration than that required for maximum settling rates. This implied that the descending portion of the refiltration curve cannot be attributed to restabilization phenomena thus the decrease in filtration rate required a different explanation to the decrease in settling rate observed with increasing polymer concentration.

Nicol et al. (1975) explained this qualitatively by introducing a model in which increases in filtration rates are obtained by increasing floc size. These increases are counteracted by flow restrictions brought about by a process in which the flocs themselves become aggregated by a network of polymer chains resulting in a
The mechanism of polymer adsorption has been reviewed by Vincent (1974) and it has been found that the charge on the polymer has been a major influence on the flocculation of colloidal suspensions.

Non-Ionic Polymers

The major variables that are important in controlling stability behaviour using non-ionic polymers seem to be polymer concentration, molecular weight and structure, electrolyte concentration and particle concentration. Ash (1976) studied the effects of these parameters in the flocculation of a polystyrene latex using poly(ethylene oxide). He concluded that the stability of the latex passes through a minimum with increasing polymer concentration. Ash (1976) also found that the optimum polymer concentration for flocculation moves to lower values with increasing molecular weight and that the rate of flocculation at a given polymer concentration increases with molecular weight. Studies by Sakaguchi and Nagase (1966) on the subsidence rates of calcium carbonate and kaolinite suspensions with non-ionic polyacrylamide showed a sharp increase in flocculation rates with polymer molecular weight. The general trend thus seems to be for increasing efficiency of flocculation with increase in molecular weight, although the effect occurs over a narrow polymer concentration range.

In general the interactions that govern the adsorption of neutral polymers onto dispersed particles are van der Waals forces, ion-dipole forces and hydrogen bonds (Vincent 1974). When hydrogen bonding is the dominant mode of interaction strong specific effects may be observed. Griot and Kitchener (1965) found that fresh silica dispersions could be readily flocculated with polyacrylamide but the rate of flocculation decreased with increasing aging of the sols eventually decreasing to
zero after some time. This effect was also shown when the silica was treated with sodium hydroxide and sodium fluoride which catalyze the condensation of silicic acid. They therefore concluded that polyacrylamide adsorption only takes place through hydrogen bonding with free silanol groups present on the silica surface.

The results of Ash (1976) and Fleer (1969) show that the co-addition of neutral polymer, up to a certain concentration, and electrolyte favour flocculation. However, Slater and Kitchener (1966) found in the flocculation of fluorite suspensions by polyacrylamide that the refiltration rate actually decreases as the electrolyte concentration is increased. These results however, may result from the fact that the refiltration rate may not be a true indication of flocculation as discussed previously or that at the concentration of electrolyte used the polymer molecule may be more tightly coiled which would cause less efficient "bridging".

Rubio and Kitchener (1976) studied the adsorption of poly(ethylene oxide) on silica and found a distinct correlation between polymer adsorbed on the silica and flocculation. They found that good flocculation corresponds to virtually complete adsorption of the polymer; any measurable excess polymer left in solution corresponds to some degree of restabilization. They also found that optimum flocculation was generally obtained with a dosage, which was wholly adsorbed, corresponding to about 20-30% of the maximum adsorption capacity of the silica. They also found that ionic strength had a more marked effect on the flocculation than on the adsorption of the poly(ethylene oxide). This was attributed to a reduction in the long range double layer repulsion between silica particles which caused the interparticulate distance to be diminished sufficiently to allow the poly(ethylene oxide)
molecules to bridge the gap.

**Anionic Polymers**

This type of system, where the polymer has the same charge as the particle, has been studied extensively and has been the subject of a number of reviews (Crees 1972; Vincent 1974; O'Melia 1971). All these studies have shown that co-addition of electrolyte is necessary for flocculation to occur.

Mortensen (1961) conducted adsorption experiments using hydrolysed polyacrylonitrile on kaolinite. He found that it was necessary to add electrolyte to induce flocculation and adsorption. He found that exchange cations on kaolinite increased adsorption in approximately the same order as such cations reduced zeta potential, that is,

$$\text{Th}^{4+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{H}^+ > \text{NH}_4^+ > \text{K}^+ > \text{Na}^+.$$  

There was also an increase in adsorption when divalent cations particularly those of transition metals were used. He reasoned that this was due to complexation of the metal ion with the polymer which reduced the charge and size of the polymer chains hence the increased adsorption.

Black, Birkner and Morgan (1968) studied the destabilization of kaolinite and montmorillonite with anionic polyacrylamide. They found that there was a minimum dose of CaCl$_2$ required to enable the destabilization to occur. They deduced that the divalent calcium ion functioned in three different ways.

1. By compressing the thickness of the double layer of the clay particle thereby reducing interparticulate forces.

2. By reducing the repulsive forces between the anionic polymer and clay particle.
3. By reducing interactions between polymer molecules adsorbed on clay particle surfaces.

Sommerauer et al. (1968) have investigated the role played by various cations, in particular Ca\(^{2+}\) and Cu\(^{2+}\), in the flocculation of negative silver bromide sols by anionic polyelectrolytes. They concluded that the mechanism by which polymer adsorption occurs involves formation of a complex in the vicinity of the interface between the counter ions the functional groups (carboxylate) of the polyelectrolyte, the concentrations of both species being considerably enhanced near the interface. The adsorption of the counterions is much faster than the adsorption of the polyelectrolyte. The complexes formed with divalent ions lead to local sites of positive charge on the polyelectrolyte facilitating adsorption on the negative surface. Miller and Grahame (1961) showed that the presence of anions, particularly those that specifically adsorb on mercury, is necessary for the adsorption of cationic polyelectrolyte on positively charged mercury surfaces.

Nemeth and Matijevic (1968) have concluded that the anionic polyelectrolyte functions by adsorbing onto the surface of the colloid and thereby reducing the surface potential, thus making it possible for the electrolyte to be effective by double-layer compression. Sarkar and Teot (1973) studied the flocculation of polystyrene latexes by sodium polystyrene sulphonate together with multivalent cations. They suggested that the flocculant is a neutral complex of the cation/polyelectrolyte but that a minimum excess cation concentration is required before flocculation occurs. They concluded that the neutral complex was likely to be "coiled up" and hence it cannot flocculate according to the bridging mechanism. However, this configuration at the interface is unknown and as previously mentioned neutral polymers are
effective flocculants.

Kuzkin and Nebera (1966) have pointed out that the presence of electrolyte may simply act to screen the coulombic repulsion between the particle surface and the polyelectrolyte without specific effects occurring. Slater et al. (1969) showed that it was possible to "activate" the adsorption of 30% hydrolysed polyacrylamide onto freshly dispersed quartz particles by the presence of cupric ions and hence induce flocculation. However, aged quartz could not be "activated" by the cupric ions even though the cupric ions are still adsorbed at the surface. They concluded that the cupric ions only play a charge-screening role.

Lindstrom and Soremark (1976) studied the destabilization of cellulosic dispersions with sodium alginate in the presence of divalent metal ions. They proposed a mechanism that involves the adsorption of the anionic alginate polymer onto the cellulosic particle, with the divalent metal ions acting as cross-links between the polymeric chains. The specific action of the different metal ions in assisting the flocculation of the dispersion is closely associated with the ability of the alginate polymer to bind different ions.

These results all show a rather confused picture of the flocculation mechanism particularly that of the anionic flocculant in conjunction with the divalent metal ion. Therefore it was thought desirable to conduct a quantitative study of the adsorption of various types of polyacrylamide flocculants on the two clays kaolinite and montmorillonite. With the development of a simple sensitive, precise method for determining residual polyacrylamide, the mass of polymer adsorbed on the two clays was examined in relation to polymer concentration and metal ion concentration.
RESULTS AND DISCUSSION

The initial part of this study involved an examination of polymer adsorption and flocculation with kaolinite. A pure kaolinite was selected rather than a tailings mixture as the complex nature of the tailings could lead to complications in the polymer analysis. The tailings had a low cation exchange capacity (4-6 meq./100 g) and it could be assumed from this that they had a fairly low surface charge at neutral pH.

The change in flocculation characteristics of a 1% kaolinite suspension as the polymer concentration is varied is shown in Figure 26. This shows that there is a dramatic improvement in flocculation up to the optimum flocculant concentration around 25 mg/l. The three parameters of filtration rate, settling rate and turbidity of the supernatant all show good agreement as to the optimum concentration of flocculant and all show a region where the characteristics are fairly constant after which all show a worsening of flocculation. The nonionic flocculant Magnafloc 351 clearly gives a much better flocculation than the anionic flocculants Magnafloc 155 and Magnafloc 156. These two anionic flocculants show a much more marked worsening in flocculation characteristics past the optimum flocculant concentration.

The adsorption of the flocculants on the kaolinite is shown in Figure 27. In actual fact the residual polymer was determined and any polymer not in the supernatant was assumed to be adsorbed on the clay. The Magnafloc 351 was found to be almost totally adsorbed up to a concentration of 50 mg/l. Above this concentration no more polymer was adsorbed unless the flocs were vigorously agitated to expose more surface area. This concentration corresponds to approximately twice the optimum flocculant concentration.
FIGURE 26
Effect of Polymer Concentration on Flocculation
1% Kaolinite Suspension No Ca²⁺
POLYMER ADSORPTION vs POLYMER CONCENTRATION
1% Kaolinite Suspension No Ca^{2+}

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

POLYMER ADSORBED (mg)

POLYMER CONC. (mg l^{-1})
This agrees with the observations of La Mer and Healy (1963a) that for optimum flocculation half the surface sites on the suspended particles would be covered by flocculant. Rubio and Kitchener (1976) found that in the flocculation of silica by poly(ethyleneoxide) optimum flocculation corresponded to around 30% of the maximum amount of flocculant adsorbed.

The concentrations where there is excess polymer in the supernatant corresponded to poor flocculation. This phenomenon was also observed by Rubio and Kitchener (1976) who also found that the concentrations of polymer that corresponded to poor flocculation were those where there was excess polymer in the supernatant. This excess polymer must lead to restabilization of the clay suspension. The anionic polymers are not adsorbed to the same degree and hence do not flocculate the suspension to the same degree as the nonionic polymer. The region where they are not totally adsorbed occurs at a much lower concentration than the nonionic flocculant and the result of this "non-adsorption" is seen in the flocculation parameters.

Figure 28 shows the results of flocculation of kaolinite using a constant concentration of calcium ion of 60 mg/l and a varying polymer concentration. The optimum flocculant concentration appears to be around 25-30 mg/l but in the presence of calcium ion the three flocculant types give very similar results. The nonionic flocculant Magnafloc 351 gives superior results past the optimum flocculant concentration. This is because the anionic polymers are less well adsorbed at these polymer concentrations as shown in Figure 29. The presence of calcium ion however is necessary for complete adsorption of the anionic polymers at concentrations between 25 and 50 mg/l. However, it is not only polymer adsorption that is responsible for efficient
FIGURE 28

Effect of Polymer Concentration on Flocculation
1% Kaolinite Suspension Constant Ca²⁺ Conc. (60 mg l⁻¹)

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

TURBIDITY N.T.U's

F.R. ml sec⁻¹

S.R. cm sec⁻¹

POLYMER CONC. (mg l⁻¹)
Polymer Adsorption vs Polymer Concentration
1% Kaolinite Suspension Constant Ca^{2+} Conc. (60mg l^{-1})

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156
flocculation as can be seen from the results with polymer concentrations around 20-30 mg/l. When calcium ion is present then flocculation is much superior even though the amount of polymer adsorbed is the same in both cases. This leads to the conclusion that without calcium ion present low concentrations of anionic polymers can be adsorbed on localized regions of the clay but with calcium ion present adsorption is spread over more on the clay surface and hence the flocculant can form "bridges" between the clay particles. It can be seen that the calcium ion acts to screen the charge on the clay so the anionic polymers can be adsorbed over the total surface of the clay.

The effect of calcium ion concentration on the flocculation of kaolinite at constant polymer concentration is shown in Figure 30. The results show that for the nonionic flocculant initially there is a small improvement in flocculation up to a concentration of around 30 mg/l of calcium ion. The small improvement in flocculation would be due to increased polymer adsorption though this may not be caused by the charge screening effect of the calcium ion. The most likely explanation is that as the calcium ion concentration rises the long range double layer repulsion between the clay particles is reduced; the double layer thickness is then small enough to allow the polyacrylamide molecules to bridge the gap.

The anionic flocculants show a much greater improvement in flocculation with increasing calcium ion concentration. The Magnafloc 155 shows optimum flocculation around 60 mg/l calcium ion whereas the Magnafloc 156 shows optimum flocculation around 70-80 mg/l. The most likely explanation for this phenomenon lies in the charge screening effect of the calcium ion. The Magnafloc 156 being 40% anionic, would need the highest concentration of calcium ion to be adsorbed and this
Effect of Ca$^{2+}$ Concentration on Flocculation
1% Kaolinite Suspension Polymer Conc. Constant (50 mg l$^{-1}$)

**FIGURE 30**
FIGURE 31
Polymer Adsorption vs Ca$^{2+}$ Concentration
1% Kaolinite Suspension Polymer Conc. Constant (50mg l$^{-1}$)
can be seen in Figure 31 where only at calcium ion concentrations greater than 60 mg/l is it totally adsorbed.

The next step was to compare the results obtained with kaolinite with a clay having a much higher cation exchange capacity as well as a higher surface area and surface charge. For this purpose Wyoming Bentonite was chosen. This was found to be 95% sodium montmorillonite together with traces of feldspar and carbonates. This clay, as will be seen in the following results, was much more difficult to flocculate.

The initial study of the flocculation of the montmorillonite was to ascertain the effect of polymer concentrations. The results of the flocculation were too poor to place credence in them. The adsorption of the three flocculants was examined even though the suspensions of the clay were not properly flocculated. Figure 32 shows the adsorption of the polymers at different polymer concentrations. This shows that the nonionic flocculant is totally adsorbed up to a concentration of polymer around 70-80 mg/l. The anionic polymers however, are only adsorbed in small amounts with there being large concentrations of residual polymer in the supernatant. As was previously stated the flocculation was too poor to be meaningful, hence a comparison of adsorption versus flocculation was not possible.

It was thus decided to add sufficient calcium ion concentration to the suspension so as to enable the extent of flocculation to be meaningfully measured. Figure 33 shows the results of the flocculation at a constant calcium concentration of 120 mg/l with varying polymer concentration. The flocculation shows a distinct improvement up to a concentration of flocculant around 60 mg/l. The anionic flocculants Magnafloc 155 and 156 are clearly superior at all concentrations to the nonionic flocculant Magnafloc 351.
FIGURE 32

Polymer Adsorption vs Polymer Concentration
1% Montmorillonite Suspension No Ca$^{2+}$
Effect of Polymer Concentration on Flocculation
1% Montmorillonite Suspension Constant Ca$^{2+}$ Conc. (120 mg l$^{-1}$)

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

Polymer Concentration (mg l$^{-1}$)

Turbidity NTU's

F.R. ml sec$^{-1}$

Polymer Spec. Values

S.R. cm sec$^{-1}$

0 30 60 90 120 150

Polymer Conc. mg l$^{-1}$
FIGURE 34

Polymer Adsorption vs Polymer Concentration
1% Montmorillonite Suspension Constant Ca²⁺ Conc. (120mg l⁻¹)

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156
All flocculants show a similar pattern with an initial rapid improvement up to the optimum flocculant concentration followed by a "plateau" region where increasing the concentration of flocculant has little effect. This in turn is followed by a region where adding more polymer causes a distinct worsening of flocculation.

These observations were examined in conjunction with polymer adsorption on the clay. The optimum concentration of flocculant corresponds to half the maximum concentration of polymer that can be adsorbed on the clay surface. This would again seem to confirm the observations of LaMer and Healy (1963a) that optimum flocculation occurs when half the surface of the colloidal particles are covered with flocculant. The flocculation also appears to worsen when there is excess polymer in the supernatant again in agreement with the experimental evidence of Rubio and Kitchener (1976). However, one point that is very clear from these results is that although polymer adsorption is necessary for flocculation to occur, simple adsorption of the flocculant does not necessarily produce good flocculation. There appears to be some mechanism at work other than their adsorption on the clay which causes the flocculants to behave differently. The polymers appear to be bridging between the clay particles differently and the reason for this may be tied to their behaviour with calcium ions.

The effect of calcium ion concentration on flocculation is shown in Figure 35. The nonionic flocculant shows very little improvement in its flocculation on increasing calcium ion concentration whereas the anionic flocculants Magnafloc 155 and 156 show a dramatic improvement. The explanation for this would seem to be one of charge screening phenomena. The results of the polymer adsorption as shown in Figure 36 confirm this.
FIGURE 35

Effect of Ca$^{2+}$ Concentration on Flocculation
1% Montmorillonite Suspension Constant Polymer Conc. (120 mg l$^{-1}$)

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

TURBIDITY N.T.U.'S

F.R. ml sec.$^{-1}$

S.R. cms sec.$^{-1}$

Ca$^{2+}$ CONC. mg l$^{-1}$
FIGURE 36

Polymer Adsorption vs $\text{Ca}^{2+}$ Concentration
1% Montmorillonite Suspension Constant Polymer Conc. (120mg l$^{-1}$)

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156
The anionic show a marked increase in adsorption with increasing calcium ion concentration up to around 180 mg/l. The results also show that the nonionic flocculant adsorption increases with increasing calcium ion concentration but the effect is not as dramatic as with the anionic flocculants. This would be expected purely from charge considerations.

Another important factor shown in Figures 35 and 36 is that while polymer adsorption is necessary for flocculation to take place there must be other factors operating as the nonionic flocculant is more readily adsorbed than the anionic flocculants. One possible explanation of this is that postulated by Sommerauer et al. (1968) where polymer adsorption involves formation of a complex in the vicinity of the interface between the calcium ions and the functional groups of the polymer. In this case the nonionic polymer has little complex forming potential as there are no carboxyl groups present. The two anionic polymers have free carboxyl groups due to hydrolysis and these could possibly complex with the calcium ions. These complexes if formed, could lead to localised sites of positive charge on the polymer thus facilitating "bridging" between particles by the polymer. It was therefore necessary to further investigate this possibility.

SUMMARY

1. For the kaolinite suspension the nonionic flocculant was superior to the anionic flocculants in producing optimum flocculation.

2. The montmorillonite was best flocculated by the anionic polymers particularly the 20% hydrolyzed variety in the presence of a certain concentration of calcium ions.

3. For flocculation to occur polymer must be adsorbed on the clay surface;
excess polymer not adsorbed on the clay surface produces poor flocculation. Optimum flocculation corresponds to approximately half the total polymer that is possible to adsorb.

4. The presence of a certain concentration of positively charged ions is necessary for the anionic polymers to be adsorbed and hence act as flocculants.

5. Simple polymer adsorption is a prerequisite for flocculation to occur but there appears to be another mechanism at work in order to achieve maximum "bridging" between particles. This is shown with the montmorillonite suspension where the nonionic polymer is adsorbed more than the anionic polymers yet produces a much poorer flocculation.
ION EXCHANGE AND FLOCCULATION

In order to verify the fact that optimum flocculation occurred when half the surface sites on the clay were covered with polymer further experimentation was carried out. The dehydrated "dyke" clay which exhibited the unusual pattern of ion exchange, as discussed in previous sections, was examined for its ion exchange pattern in the presence of various concentrations of flocculant. When calcium ions are added to a suspension of the dehydrated "dyke" clay the pattern of exchange is as follows: the calcium ion concentration initially drops very rapidly then rises for a period of about five minutes. It then drops slowly to limiting value after an hour. In the presence of flocculant this pattern changes depending on the concentration of flocculant added. When 80 mg/l of flocculant, which corresponds to twice the optimum flocculant concentration, is added the ion exchange exhibits none of the fluctuations previously observed. The calcium ion concentration falls to the level previously observed but then remains at this concentration indefinitely. If less than 80 mg/l of flocculant is added then part of the original pattern is observed, eg. in Figure 37 40 mg/l of flocculant has been added.

The explanation for this phenomenon lies in the fact that the initial exchange of calcium ions is very rapid taking place within a few seconds whereas flocculation occurs in about 20-30 seconds. As previously postulated the initial exchange of ions would take place on the surface of the clay, whereas the slower exchange would be concerned with the internal lattice of the clay. The flocculant, on being adsorbed onto the surface of the clay, would cover the surface sites of the clay and thus prevent further migration of ions into the lattice of the clay.
FIGURE 37

Effect of Flocculant on Ion Exchange
1% "Dehydrated-Dyke Clay" Suspension

Flocculant - Magnfloc 155
- No Flocculant
- 40 mg l\(^{-1}\) Floc.
- 80 mg l\(^{-1}\) Floc.

![Graph showing the effect of flocculant on ion exchange with time.](image-url)
When twice the optimum concentration of flocculant is added to the clay all the surface sites on the clay would be covered by flocculant hence the pattern of exchange would be changed as shown in Figure 37. The previously observed pattern of exchange manifests itself if less than 80 mg/l of flocculant is added and the extent to which it does so depends on the amount of flocculant added. The concentration of calcium ions remains at a constant level no matter how long the flocculated suspension is left. It was also found that the vigorous agitation of the floc caused the ion exchange to again commence presumably because the agitation ruptures the flocs exposing the surface ion exchange sites of the clay.
THE ROLE OF THE METAL ION IN FLOCCULATION

The mechanism postulated by Sommerauer et al. (1968) proposes that flocculation by anionic polymers involves the formation of a complex between the polymer and the metal ion. This occurred at the interface where the concentration of both species was considerably enhanced. The mechanism proposed consists of four basic steps:

1. Divalent metal ions accumulate in the double layer of the suspended particles. This is a fast step and is accompanied by a compression of the double layer.

2. The approach of the partially surface active anionic polymers to the surface of the particles is thus facilitated.

3. Complex formation between the metal ion in the double layer and the functional group of the polymer results in the formation of positively charged groups that can be anchored on the particle surface.

4. The individual particles are bridged together through polymer chains as proposed by La Mer et al. (1958).

They found that polyelectrolytes such as polyacrylic acid, hydrolysed polyacrylamide and polystyrene sulphonate could complex divalent metal ions such as \( \text{Ca}^{2+} \) and \( \text{Cu}^{2+} \) to various degrees and reasoned that this must occur before flocculation can take place. Eldridge (1973) has reviewed the ion binding by polyelectrolytes and he found that the majority of ion binding occurred in polyelectrolytes containing free carboxyl groups. O'Neil et al. (1965) and Constantino et al. (1967) have shown that the binding of the alkaline earth cations to polyacrylate and polymethacrylate is virtually stoichiometric at all degrees of neutralization.
It is assumed that at high degrees of neutralization divalent counterions are chelated by neighbouring carboxylate groups (Ikegami and Imai 1962).

\[
\text{CH}_2\text{CH}^\text{+}\text{CH}_2\text{CH}^\text{+}\text{CH}_2\text{CH}^\text{+}
\]

The complexes of the transition metals with polyelectrolytes have been studied extensively (Gregor 1955, Mandel 1964). There is evidence that the binding of the transition metal ions by the polyelectrolytes is extensive. The effect on binding of the stereoregularity of the polyions is different for different counterions (O'Neil 1965), supporting the view that the bound complex involves neighbouring carboxyl groups and is therefore sensitive to the local geometry of the polyion. Yamashita et al. (1976) studied the complex formation between Cu\(^{2+}\), Cd\(^{2+}\) and poly(acrylic acid) and poly(itaconic acid). They determined the equilibrium constants of the metal-carboxylate complexes and also found that the complex involves neighbouring carboxyl groups. They employed ion selective electrodes to measure the activity of the Cu\(^{2+}\) and Cd\(^{2+}\) and found that the most stable complex was that formed between the Cu\(^{2+}\) ion and poly(itaconic acid).

The binding of the Cu\(^{2+}\) ion with poly(acrylic acid) and poly(methacrylate) was found by magnetic susceptibility measurements to involve Cu-Cu bonding showing that counterions are bound tightly to specific sites on the polyion (Leyte et al. 1967).
The general trend in the strength of binding shows that there is an increase in the binding between the metal ion and the polyelectrolytes from alkali metals, through the alkaline earths to the transition metals. From the above evidence it is obvious that to attempt the study of the metal ion in flocculation a transition metal ion will show complexing if any more readily than an alkaline earth cation such as the calcium ion.

The results reported in the literature show that it would be expected that the more hydrolyzed the polyacrylamide used as a flocculant, the better it would complex metal ions. The polyacrylamide used by Sommerauer et al. (1968) was 70% hydrolyzed and the extent of the complexing formed with metal cations such as Ca$^{2+}$ and Cu$^{2+}$ was too small to cause substantial changes in the composition of the solution. The complexes could only be detected in the presence of an interface which has the effect of producing localized concentrations of all species involved in the complexation. The anionic polyacrylamides used in this study were only 20% and 40% hydrolyzed thus it would be expected that their ability to form complexes would be small. The non-ionic polyacrylamide Magnafloc 351 does not contain any free carboxyl groups so that it is doubtful if it would form complexes with metal cations to any extent. Preliminary measurements utilising Ca$^{2+}$ and Cd$^{2+}$ ion selective electrodes indicated that there was little or no measurable amount of complexation between the polyacrylamides and these cations in the absence of an interface.

In a study of the influence of metal ions on flocculation the nature of the metal ion on the clay surface is very important if there is to be any formation of complexes in the vicinity of the interface. In recent years there have been fairly extensive studies on the
adsorption of heavy metal cations on clays and soils. Typical of these is that by Helz et al. (1975) who studied the behaviour of five heavy metal cations in an estuarine environment. They found that all these metal cations were adsorbed quantitatively on sediments. Farrah and Pickering (1976a, 1976b, 1976c) investigated the sorption of copper and zinc species on clay minerals. They found that the observed adsorption behaviour of copper species on montmorillonite could be interpreted in terms of an ion exchange model with all positively charged species competing for available exchange sites. They also found that for illite and kaolinite the controlling process appeared to be the formation of polymeric hydroxy species attached to particular sites on the clay. The pH of the solution containing the copper species controls the development of the hydroxy bridged species and ligands influence the uptake of the copper species by prevention of hydroxy species formation. Anionic complexes such as those formed by reaction with E.D.T.A. prevent sorption by the clay.

In the case of zinc species similar mechanisms were observed (Farrah and Pickering 1976c). The sorption onto kaolinite and illite appeared to be controlled by the attachment of hydroxy species to particular sites on the particle edges. The predominant mechanism operating with montmorillonite appeared to be ion exchange at negative lattice sites.

In this study Cd$^{2+}$ ion was chosen as the metal ion to investigate as it is readily complexed by a variety of ligands (Cotton and Wilkinson 1973). The chemistry of cadmium in natural waters has been the subject of two papers by Gardiner (1974a, 1974b). He found that cadmium was readily adsorbed on clays and humic acids suspended in natural waters though desorption was easily attained.
Bittel and Miller (1974) determined the selectivity coefficients of Cd\(^{2+}\) on montmorillonite and found that it could be readily displaced by Ca\(^{2+}\) suggesting that at pH values below 7.5 in the absence of complexing anions that cadmium ions exist as free Cd\(^{2+}\).

As previously stated cadmium readily forms complexes with most common anions. Cadmium nitrate, cadmium sulphate and cadmium perchlorate are the only cadmium salts thought to contain the simple ion Cd\(^{2+}\) (Mellor 1963). Sillen and Martell (1964, 1971) have accumulated a considerable amount of data on complexation of cadmium ion. This data has been used by Mangel (1971) to investigate complexation in sea water and by Hem (1972) whose findings confirm the view that cadmium is readily complexed by a variety of organic and inorganic ligands in nature. The results of Sillen and Martel (1964, 1971) show that cadmium nitrate contains the greatest proportion of the free cadmium ion even though the existence of species such as \([\text{CdNO}_3]^-\) has been reported (Davis and Plane 1968). It was unfortunate that it was not possible to use cadmium nitrate in this work as the nitrate ion could cause interference in the determination of residual polymer by the nitrous acid hydrolysis. The cadmium salt used was cadmium perchlorate because of the very weak co-ordinating ability of the perchlorate ion. It was found that at pH values below 7.0 that the vast majority of cadmium in solution was present as free Cd\(^{2+}\) and as will be seen later this was confirmed by ion exchange experiments with montmorillonite.
The Effect of the Exchangeable Cation on Polymer Adsorption

The effects of the exchangeable cation on the adsorption of flocculant was the first parameter to be examined to ascertain the role of the metal cation in flocculation. The evidence presented by Gardiner (1974a) suggested that cadmium will exist as the free Cd\(^{2+}\) ion at pH values below 7.4 in the absence of complexing species. This together with the findings of Farrah and Pickering (1976b, 1976c) and those of Gardiner (1974b) show that the most likely mode of adsorption of Cd\(^{2+}\) on montmorillonite would be one of ion exchange. This was confirmed by ion exchange rate measurements where a sodium-substituted montmorillonite suspension was reacted with a solution of cadmium perchlorate. Figure 38 shows the resultant pattern of ion exchange where there is an almost 2:1 ratio of sodium ions released to cadmium ions adsorbed which is indicative of the fact that ion exchange took place between the clay and the free cadmium ion.

As it had been established that most of the cadmium adsorbed would be situated on the ion exchange sites of the clay, a cadmium-substituted montmorillonite was prepared. The flocculation of this cadmium-substituted montmorillonite was then compared to that of a sodium-substituted montmorillonite. It was found that the cadmium-substituted clay showed better flocculation than the sodium-substituted clay even though both clays flocculated poorly in the absence of divalent metal ions. The adsorption of the three flocculant types at varying concentrations however, showed a fairly marked difference in the case of each substituted clay.

Both the sodium-substituted and cadmium-substituted clays showed a similar adsorption versus flocculant dose plot (Figure 39) with the nonionic Magnafloc 351. (See also Figure 40).
FIGURE 38

Ion Exchange Pattern of a 1% Na-Montmorillonite Suspension with Cd\(^{2+}\)

- O Na\(^{+}(1)\)
- ▼ Na\(^{+}(2)\)
- ● Cd\(^{2+}(1)\)
- ■ Cd\(^{2+}(2)\)
Polymer Adsorption vs Polymer Concentration
1% Montmorillonite Suspension (Na-Substituted)
FIGURE 40

Polymer Adsorption vs Polymer Concentration
1% Cd-Substituted Montmorillonite Suspension

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

POLYMER CONC. (mg/l)

POLYMER ADSORBED (mg)
However, with the anionic flocculants Magnafloc 155 and Magnafloc 156, the cadmium-substituted clay shows a much greater adsorption of these flocculants (at concentrations of 120 mg/l of flocculant the cadmium-substituted clay adsorbed over twice as much of the flocculants as the sodium-substituted clay). The explanation for this phenomenon appears to be the fact that the anionic polymers are capable of forming metal complexes with cadmium ions at the solid/liquid interface. This complex formation leads to localized regions of positive charge on the polymer which can then be adsorbed more readily than in their absence. These results also show that while complex formation is important in facilitating polymer adsorption and hence flocculation, it is necessary to have sufficient ionic strength present to screen the repulsive charge between the clay and polymer.
THE EFFECT OF COMPLEXING LIGANDS ON THE ROLE OF THE METAL ION IN FLOCCULATION

This part of the study involved the investigation of the effect of complexing ligands on the role of the divalent metal ion in flocculation. If the mechanism proposed by Sommerauer et al. (1968) is correct then by introducing a complexing ligand into the system that preferentially complexes the metal ion the extent of flocculation should decrease due to the fact that the metal-flocculant complexes can no longer be formed. The metal ion chosen was again the Cd\(^{2+}\) ion derived from Cd(ClO\(_4\))\(_2\). The Cd\(^{2+}\) ion readily forms complexes with most common anions (Sillen and Martell 1964) and in this work the chloride ion was chosen. Cadmium ions react with chloride ions to form the positively charged monochlorocadmate(II) ion:

\[
\text{Cd}^{2+} + \text{Cl}^- \rightleftharpoons [\text{CdCl}^+] 
\]

This reaction was found by Gardiner (1974) to be independent of pH below a pH of 7.4. The extent of the complexation was measured by use of a cadmium specific-ion electrode.

The cadmium specific-ion electrode is extremely useful in a study of complex formation since it responds only to free cadmium ion in solution and not to complexes. The response of the electrode was found to be independent of pH below a pH value of 7.5. Theoretically the potential response \(E\), of the cadmium electrode follows the relation:

\[
E = A + B \log a_{\text{Cd}^{2+}} = A + B \log f_{\text{Cd}^{2+}} + B \log [\text{Cd}^{2+}] 
\]

where \(A\) and \(B\) are constants and \(a_{\text{Cd}^{2+}}\) and \(f_{\text{Cd}^{2+}}\) are the activity and activity coefficient of the cadmium ion respectively. Plots of \(E\) against \(\log [\text{Cd}^{2+}]\) with Cd\(^{2+}\) from \(10^{-2}\) M to \(10^{-5}\) M in KNO\(_3\) from 1M to \(10^{-2}\) M were straight lines.
Effect of $\text{Cl}^-$ on Flocculation

![Graph showing the effect of Cl⁻ on flocculation with data points for Magnafloc 351, Magnafloc 155, and Magnafloc 156.](image)

Effect of $\text{Cd}^{2+}$ on Flocculation

![Graph showing the effect of Cd²⁺ on flocculation with data points for Magnafloc 351, Magnafloc 155, and Magnafloc 156.](image)
The slope was $30(\pm 1)\text{mv}$ for each 10-fold increase in concentration, which is quite close to the theoretical value of $B$ (29.6 mv).

Gardiner (1974) calculated the equilibrium constant $K$ where $$ K = \frac{[\text{CdCl}^+]^2}{[\text{Cd}^{2+}][\text{Cl}^-]} $$ for the monochlorocadmate (II) ion. He found that the value of $K$ was $48(\pm 8) \text{ litre mole}^{-1}$ using cadmium nitrate as the source of cadmium ion. In this work cadmium perchlorate was used as the source of cadmium ion and this fact together with the added complication of the clay being present lead to values of $K$ that were about half those obtained by Gardiner (1974). This is understandable because of the greater tendency of the perchlorate ion to form complexes with cadmium such as $[\text{CdClO}_4^+]$, over the nitrate ion.

The effect of this complex formation on the flocculation of the sodium-montmorillonite with the three types of polyacrylamide flocculants was then studied. The flocculation of the montmorillonite was thus conducted with a constant total cadmium concentration and varying concentrations of chloride ion which in turn varied the cadmium activity. As adding more chloride ion had the effect of increasing the ionic strength, this effect on flocculation and polymer adsorption was measured. Figure 41 shows the effect of increasing the concentration of chloride (in the form of NaCl) ion on flocculation with the three polymer types. The nonionic flocculant shows a definite improvement in flocculation with increasing chloride concentration. This would be most likely due to better "bridging" by the polymer as the clay's interparticulate repulsion would be reduced due to the charge screening effect of the increased ionic strength. The effect of increasing sodium chloride concentration is not as great with the anionic polymers and they flocculate rather poorly at all concentrations.
Residual Polymer vs Cl⁻ Conc.
Polymer Conc. Constant (120 mg l⁻¹)

- ▪ Magnafloc 351
- ■ Magnafloc 155
- ▼ Magnafloc 156

FIGURE 43
Residual Polymer vs Cd$^{2+}$ Conc. at Const. Polymer Conc. (120 mg l$^{-1}$)

FIGURE 44

- Magnafloc 351
- Magnafloc 155
- Magnafloc 156

Residual Polymer (mg)

Log (Cd$^{2+}$)
Figure 43 shows the residual polymer left in the supernatant liquid after adsorption of the flocculant at varying concentrations of sodium chloride. The adsorption results mirror the flocculation results as where the nonionic polymer improves the flocculation with increasing chloride concentration there is increased polymer adsorption. The anionic polymers show increased adsorption with the initial increase in chloride concentration but adsorption remains fairly static after this. This shows that while ionic strength is needed for adsorption of the anionic polymers it is not the only factor necessary.

When cadmium ions are present then adsorption of the anionic polymers is increased and at the same time flocculation shows a distinct improvement (Figure 42). Figure 44 shows the residual polymer increasing with decreasing cadmium activity. The decrease in cadmium activity is due to addition of sodium chloride with the resultant formation of the monochlorocadmate (II) species. Thus while the cadmium activity is decreasing the total ionic strength of the system is increasing yet anionic polymer adsorption decreases. This shows that with the anionic polymers not only is ionic strength necessary to reduce interparticulate repulsion but that the free divalent metal ion is necessary for maximum polymer adsorption and hence optimum flocculation.

The most likely explanation for this is that proposed by Sommerauer et al. (1968) where the divalent metal ion forms complexes with the anionic polyacrylamide thus leading to localized sites of positive charge and hence increased adsorption. Figure 45 shows the results obtained with the montmorillonite suspension in the presence of cadmium ions and chloride ions. The results show the expected evidence of a decrease in cadmium activity as the chloride concentration increases but there is also evidence of another phenomenon occurring.
Cd\(^{2+}\) Conc. vs Cl\(^{-}\) Conc. at Constant Polymer Conc. (120mg.l\(^{-1}\))

FIGURE 45
There is a marked difference in cadmium activity in the presence of the three polymers. The lowest activity for a given concentration of cadmium ions and chloride ions is always seen with the 40% anionic Magnafloc 156 and the highest activity is shown with the nonionic Magnafloc 351. This would seem to be evidence of complexation occurring between the divalent metal ion and the anionic polymers. The amount of complexation always follows the same order expected from the degree of anionic character in the polyacrylamide given that complexing occurs between the metal ion and the free carboxyl groups on the polymer.

This complexation was only observed in the presence of the clay suspension in agreement with those observations of Sommerauer et al. (1968) who found that complexing occurred only in the presence of an interface as here there was a greater concentration of the metal ion and the polymer. Thus the mechanism of flocculation, from the results of this work, can be summarized in the following steps:

1. Divalent metal ions ion exchange with those available on the clay surface and accumulate in the double layer of the clay. This step is very rapid occurring within a few seconds and is accompanied by a compression of the double layer.

2. This compression of the double layer allows the approach of the anionic polymers to the clay surface. It also reduces interparticulate distance so that nonionic polymers can "bridge" between particles more readily thus flocculate better.

3. Complex formation between the metal ion in the double layer and the functional group of the polymer results in the formation of positively charged groups that can be anchored to the clay surface. In the case of polyacrylamide the complex is formed between free carboxyl groups and the divalent metal ions.
The particles of clay are then "bridged" through polymer chains as proposed by La Mer et al. (1958). The formation of the complexes aids "bridging" by providing anchor sites for the polymer to commence the "bridging" from.
THE "ALUM-DYKE" ANOMALY

In a previous section the flocculation behaviour of the "dyke" clay in the presence of either "alum" and a flocculant or calcium ion and a flocculant was studied. It was found that while the "dyke" flocculated readily with calcium ions and flocculant, the flocculation behaviour in the presence of the aluminium ions was poor and did not improve with increasing concentration of the aluminium species (Figure 21). It was therefore decided to examine this poor flocculation behaviour in terms of flocculant adsorption onto the clay.

Roberts et al. (1974) proposed that the hydrolyzed aluminium ions and polyacrylamide flocculants interact on the clay surface with the interactions arising from the opposite charge of the species and from hydrogen bonding. The positively charged, hydrolyzed metal ions act as "anchor-points" to attach negatively charged polyacrylamides to the negatively charged clay surface.

A suspension of the "dyke" was prepared and flocculated with a constant concentration of 20% hydrolyzed polyacrylamide and varying concentrations of aluminium ions. The amount of polymer adsorbed at each of the aluminium ion concentrations was determined to give the results shown in Figure 46. Initially, as the concentration of aluminium added increases so does flocculant adsorption. As more alum is added polymer adsorption remains constant but flocculation becomes poorer (Figure 21). Roberts et al. (1974) suggested that up to a certain dose of aluminium ion adsorption of the polyacrylamide is enhanced but after this dose the hydrolyzed aluminium species form an excess of "anchor-points" which causes localized adsorption of the polyacrylamide and hence interparticulate "bridging" is reduced.
Effect of $\text{Al}^{3+}$ Conc. on Polymer Adsorption
1% Dyke Suspension

Polymer Adsorbed (mg)

$\text{Al}^{3+}$ Conc. (mg l$^{-1}$)

- Magnafloc 155
  
  (80 mg l$^{-1}$)

FIGURE 46
Our experimental results support this suggestion and also show that the present practice of adding more "alum" to the washery water when "dyke" is encountered should be discouraged in favour of CaCl$_2$ addition.
PLANT TRIAL
PLANT TRIAL AT THE COAL WASHERY

The last part of this work consisted of a full scale plant trial to ascertain the effect of the addition of CaCl$_2$ to the washery water. The trial lasted for eighteen hours during which time CaCl$_2$ was added to the washery water for approximately seven hours. Four sampling points were chosen to gauge the effect of CaCl$_2$ addition and these were the flotation cell, the tailings dam, the second filtration dam and the point where recycled water enters the washery circuit (Figure 2). The water samples were monitored for pH, temperature, suspended solids, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$. The solids collected were analysed for ignition loss, cation exchange capacity, extractable cations and several X-Ray diffraction analysis were carried out so as to keep a check of the constancy of tailings mineral composition.

RESULTS AND DISCUSSION

The trial commenced at 3.45 p.m. when sampling from the various locations was undertaken, with CaCl$_2$ addition beginning at approximately 4.25 p.m. and being maintained until around 11.00 p.m. The CaCl$_2$ was supplied as solid and mixed with town water in a mixing tank and then pumped via a control valve to the section of the washery between the flotation cells and the tailings thickener. The addition of the CaCl$_2$ was set so as to maintain the concentration of Ca$^{2+}$ at approximately 40 mg/l. This was tested by measuring residual Ca$^{2+}$ activity using a calcium ion-selective electrode in the tailings thickener after the point of Ca$^{2+}$ addition and comparing this to a tailings suspension (collected before Ca$^{2+}$ addition) spiked with CaCl$_2$. The overall results of the plant trial can best be examined by looking at the individual sample locations.
THE TAILINGS DAM

The calcium level rose very slowly at first due to the fact that both dilution and ion exchange with the tailings reduced the concentration. It can be seen from Figure 48 and Table 15 that approximately 40-60% of the calcium ion added was either exchanged or adsorbed by the tailings. This was in agreement with the previously described laboratory tests. The levels of Ca\(^{2+}\) in the tailings dam effluent reached a peak around 11.00 p.m. as recirculated calcium from the recycled water began entering the plant. The clarity of the supernatant improved after the addition of the CaCl\(_2\) because the flocculation of the tailings increased leading to faster settling. The Mg\(^{2+}\) and K\(^+\) levels rose marginally as the calcium was added due to ion exchange of the clay minerals with the increased concentration of calcium ions. The Na\(^+\) concentration increased gradually as the CaCl\(_2\) was added but the increase was not as great as expected and this suggested that the tailings themselves contain soluble sodium salts and that the make up water in the washery contains varying concentrations of sodium ion. The ignition loss figures on the tailings show that calcium ions do not seriously effect the operations of the flotation cells in separating the fine coal from the refuse. The suspended solids show a good correlation with increasing calcium concentrations in that as calcium levels increase so does settled solids which indicates that the flocculation of tailings improved thus increasing the amount of solids that was removed from suspension.
FLOTATION CELLS

At this sampling point the calcium levels rose slowly at first though this rise was earlier than expected. This was due to calcium entering the wash water from the overflow of the tailings thickener. It can be seen from the chloride ion levels that the calcium from the recycled water does not appear until about 8.00 p.m. The amount of solids from the flotation cells varies quite widely during the course of the trial with this being due to the nature of the washery feed at any particular time. Ignition loss figures show that calcium in the washery water and the resultant higher ionic strength arising from its addition do not seriously effect flotation efficiency.

THE FILTRATION DAM

The calcium levels at this sampling point remained fairly static for about two hours then rose steadily to a maximum value at about 11.30 p.m. The most likely reason for this slow rise would be ion exchange with the tailings in the tailings dam and the first filtration dam. As these tailings gradually had more of their exchange sites occupied with calcium ions then the free calcium ions in solution could pass through and complete the washery circuit. The concentrations of the Na\(^+\), K\(^+\) and the Mg\(^{2+}\) ions were much the same as in the tailings dam although the chloride ion concentration drops due to adsorption and anion exchange. The most important factor however was the drop in the levels of suspended solids with increasing calcium concentration indicating that flocculation improved.
The main features of the results from this sampling point are the time taken for calcium to be recycled and the increased clarity of the recycled water. The calcium took about five hours to initially complete the washery circuit though the through-put time of the water is probably less than this. The factors mentioned in the previous sampling points of exchange with the tailings would cause this slow initial through-put of calcium. The increased clarity of the water is very important for the efficient washing of coal as flotation is suppressed if the wash water contains high levels of suspended argillaceous material. One point that should be noted is the unusually high pH of the washery water at the time of the trial which would have caused some loss in the efficiency of calcium recirculation due to precipitation of calcium as calcium carbonate. This high pH was due to the use of mine water during the trial, whereas the average pH of the washery is between 7 and 8 indicating a lower carbonate content which would mean increased calcium recirculation when other sources of water are used in the washery.

SUMMARY OF FINDINGS

1. Calcium ions are recirculated around the washery in contrast to aluminium species which are totally adsorbed onto the argillaceous material.

2. The presence of calcium ion does not appear to suppress flotation of coal.

3. Calcium ions are recycled to the extent of 30-50% of the original amount added which would result in a significant saving in cost as CaCl₂ and "alum" are competitively priced ($147.00 per tonne and $142.00 per tonne).
The use of calcium chloride as an aid to flocculation increases the clarity of the effluent from a coal washery thus enabling a more efficient use of recycled water and producing a more acceptable effluent from the point of view of the environment.
Ca$^{2+}$ CONC. vs TIME DURING THE PLANT TRIAL

- Recycled Water
- Filtration Dam
- Flotation Cell
- Tailings Dam

TIME

FIGURE 47
**TABLE 15**

**Exchangeable Cations and C.E.C. Measurements**

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<th></th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>C.E.C.</th>
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These figures show that before calcium addition began that the clay content of the tailings had mainly sodium ions on the exchange sites. As calcium ions were added they exchanged with the sodium ions on the clay leading to increased sodium ion content and decreased calcium ion content of the washery water. The increase in C.E.C. of the tailings corresponds to the decrease in ignition loss of the tailings indicating a lowering of the carbon content of the tailings.
An X.R.D. analysis of the tailings was carried out during three stages of the plant trial. The three stages were:

1. before CaCl$_2$ addition
2. during CaCl$_2$ addition
3. about four hours after the addition had ceased.

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<th>2.</th>
<th>3.</th>
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<tr>
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<td>10%</td>
<td>10%</td>
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<tr>
<td>Siderite</td>
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<td>Gorceixite (BaAl$_3$(OH)$_7$P$_2$O$_7$)</td>
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<td>5-10%</td>
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<td>Haematite/Goethite</td>
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This table shows that the mineral content of the tailings did not vary to any great extent during the trial although the percentage of coal in the tailings did as indicated by the ignition loss figures in Tables 17 to 20.
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* Ignition loss of suspended solids after first drying at 100°C
† Suspended Solids
### TABLE 18

**Tailings Dam Water Analysis (mg/l)**

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<th>Time (h)</th>
<th>Sett.S. † (%)</th>
<th>pH</th>
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<th>Mg$^{2+}$</th>
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* Ignition loss of suspended solids after first drying at 100°C

† Settled Solids
## TABLE 19
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* Ignition loss of suspended solids after first drying at 100°C

† Suspended Solids
TABLE 20

**Filtration Dam Water Analysis (mg/ℓ)**

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* Ignition Loss of suspended solids after first drying at 100°C

\( ^\dagger \) Suspended Solids
CORROSION STUDIES

One of the major problems associated with coal washing operation is corrosion of plant in contact with washery water. Washery personnel expressed concern at the use of \( \text{CaCl}_2 \) in the washery circuit as it might cause increased corrosion of equipment. The majority of the washery plant is fashioned from "mild-steel" so it was decided to test this steel for corrosion in the presence of \( \text{CaCl}_2 \). The tests performed were quite simple and consisted of immersing identical pieces of steel in test solutions for certain periods of time and measuring the loss of weight during the time of immersion (Collins 1976).

The first test performed was to immerse two identical pieces of the "mild-steel" in stirred suspensions of washery effluent and add equal weight doses of either \( \text{CaCl}_2 \) or "alum" to each. The results in Table 21 show that the percentage material corroded is virtually the same in both cases, thus showing \( \text{CaCl}_2 \) added to washery water will not cause any more corrosion than "alum". To test if corrosion of the steel was due to abrasion by the suspended tailings or due to the action of the ionic content of the washery water a sample of tailings was divided into two portions and one portion filtered and a piece of steel immersed into the filtrate. Another piece of steel was immersed in the unfiltered sample and both samples stirred vigorously for several weeks and tested for weight loss. It was found that both samples had again corroded the same amount thus showing that corrosion was due to the dissolved solids content of the washery water.
TABLE 21

Corrosion Tests on Samples of Mild Steel

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RECOMMENDATIONS FOR OPTIMUM PLANT OPERATION

1. CaCl₂ should be substituted for "alum" because of:
   a) The better flocculation obtained with it particularly in the presence of "dyke" clay.
   b) Cost considerations; CaCl₂ is competitively priced compared to "alum" and as it can be partly recycled much less reagent could be used over a long period of time.
   c) CaCl₂ has the added benefit of changing the clay content of the tailings to the calcium-substituted form. The calcium substituted clay has improved permeability, effecting its ability to support plant growth and drainage (Krauskopf 1967). This is important as the majority of tailings is used as land fill.

2. A monitoring system should be installed to monitor calcium ion levels as well as conductivity of the washery water. This would ensure optimum calcium levels in the washery water and would minimise corrosion due to excessive ionic content. This monitoring system would also help to minimise variation in ionic content of the make-up water no matter what the source of this water was.

3. Pilot plant trials should be conducted on the "Dehydrum" process proposed by Yusa et al. (1975, 1976). This process involves flocculation of the tailings with calcium chloride, "alum" and polyacrylamide and then subjecting the flocculated material to a pelletization process. This process would alleviate the need for the tailings dam and the filtration dam and enable the dewatering of tailings to proceed much more rapidly.
EXPERIMENTAL
APPARATUS AND REAGENTS USED

All ultraviolet and visible absorbance measurements for colorimetric techniques were performed with either a "Cary" 17 UV-Vis-IR recording spectrophotometer or an "Optica" CF4 manual spectrophotometer.

Distilled water throughout this project was obtained through the following water purification system. City mains tap water was pre-filtered through two "AMF Cuno Aqua-Pure" (AP-10) water filters containing a 50μ and 5μ filters connected in series, before being distilled into an 80 litre reservoir by a "Labmaster" (D.H.A. Aust.) 3000W still. This distilled water was then fed through a "Zerolit" portable dual bed deionizer (Mark 8F) before final double distillation out of a "Geesthact" quartz glass still (BI-BD15) into sealed polythene containers.

The grade of all chemicals used has been given as they have been mentioned in the text; a list of the manufacturers of the various trade names follows:

"UNIVAR"  Ajax Chemicals Sydney Australia.
"UNILAB"  Ajax Chemicals Sydney Australia.
"FLUKA"  Fluka A.G. Buchs, Switzerland.
"SUPRAPUR"  E. Merck, Dalmstadt Germany.
SAMPLING PROCEDURE

All samples collected from the washery were obtained in 1 litre polythene containers. These were cleaned by first washing with phosphate free detergent (Decon-90) and then rinsed with tap water to remove detergent. They were then rinsed three times with triple distilled water and dried at room temperature. To collect each sample each bottle was rinsed three times with the water being collected before the sample was withdrawn. Stream samples were collected mid-stream and at mid-depth.
BASIC EXCHANGEABLE CATIONS

The clay or tailings sample (25 grams) was shaken in a round-bottomed flask for 30 minutes with 200 ml of a 10% ethylene glycol/ethanol mixture (Analar) (Tucker 1971). The sample was then filtered through a Whatman 42 filter and the sample washed with $5 \times 50$ ml portions of the ethylene glycol/ethanol mixture until there was no trace of Cl$^-$ in the leaching solution. The sample was then dispersed in 200 ml of 1M NH$_4$Cl (Suprapur) in 60% aqueous ethanol buffered at pH 7. The sample was shaken for two hours and then filtered through a Whatman 42 filter paper and washed with $3 \times 50$ ml portions of the NH$_4$Cl solution. The leachate was then made up to 500 ml and a 20 ml aliquot removed and pipetted into 10 ml of HCl (Aristar) and 5 ml of 2M CsCl (Suprapur) and the solution made up to 100 ml. The extracted cations were then determined using a Varian AA6D atomic absorption spectrophotometer. All instrument settings used were those recommended by the manufacturer (Varian). The Ca and Mg were determined using the nitrous oxide-acetylene flame with flame stoichiometry varying to suit the individual element. Na and K concentrations were determined using an air-acetylene flame.

Standards were prepared from B.D.H. metal standards and were made up in 10 ml of conc. HCl (Aristar) and 5 ml of 2M CsCl (Suprapur) in a NH$_4$Cl matrix to approximate that of the sample.
PREPARATION OF CATION SUBSTITUTED CLAYS

The clay was initially hand-ground in a mortar and then shaken with triple distilled water for several hours. It was then allowed to settle in a 1250 ml measuring cylinder and the finer fractions decanted off. The clay fractions were then oven dried at 110°C. The clay was cation substituted by treating the solid with a 5M solution of a salt of the cation (either as the nitrate, chloride or perchlorate). This treatment was repeated until a total equilibration time of 24 hours had been reached. The clay mixture was then either washed with a mixture of ethanediol in ethanol (10% w/v Analar) ten times until no free ions could be detected in the washing solution or dialyzed in triple distilled water. Both treatments yielded comparable results. The clay was then oven dried at 110°C for several days.

Stock suspensions of 1% w/v clay were prepared by dispersing the clay in triple distilled water for 24 hours in an end-over-end shaker.

Kaolinite was purchased from B.D.H. while the montmorillonite (Wyoming Bentonite) was supplied by Wormald Australia.
CATION EXCHANGE CAPACITY

The clay or tailings (25 grams) was shaken in a round bottomed flask for thirty minutes with 200 ml of 10% ethylene glycol in ethanol (Analar) (Tucker 1971). The suspension was then filtered with suction through a Whatman 42 filter paper and the sample washed with 5 x 50 ml portions of the ethylene glycol/ethanol mixture till no trace of Cl⁻ was detected in the leaching solution. The sample was then redispersed in 200 ml of 1M NH₄Cl (Suprapur) in 60% ethanol buffered at pH 7 with NH₃ and HCl (Aristar). The sample was then shaken for two hours and filtered and washed with the ethylene glycol/ethanol mixture until the leachate showed no trace of Cl⁻. The sample was then dispersed in a 1M mixture of KNO₃ and Ca(NO₃)₂ (Analar) (Tucker 1974). This was then filtered through a Whatman 42 filter with suction and then leached with 3 x 5 ml portions of the 1M KNO₃ and Ca(NO₃)₂ mixture. The leachate was collected and then placed in a Kjeldahl flask together with a granule of Zn and 0.25 ml of Dow anti-foam A. To this was added 10 mls of 10M NaOH and the NH₃ formed was distilled into 100 ml of a 10% boric acid solution. This solution was titrated with 0.1M HCl (Aristar) to a pH 4.5 (B.D.H. indicator) end point.
Measurement of Ion Exchange Rates by Atomic Absorption

The dry clay (12.50g) was transferred to a 1250 ml cylinder and distilled water added to the mark. This was then placed in an end-over-end shaker for 24 h to get the clay fully into suspension. A 250 ml aliquot was taken immediately and then it was transferred to a 250 ml round-bottomed flask. The flask was placed in a thermostatted water bath (25°C ± 1°C) on a water powered magnetic stirrer where the suspension was stirred at constant speed and allowed to come to thermal equilibrium. To this was added the relevant quantity of either CaCl₂ (0.1M Analar) or CdCl₂ (0.1M P.&B.) and time keeping commenced. At certain time intervals a 2 ml aliquot was withdrawn and immediately filtered through a 0.45μ membrane filter. This was then rinsed with distilled water and the filtrate transferred to a 100 ml volumetric flask containing 2 ml of CsCl (5M, Suprapur) and 10 ml of conc HCl (Aristar). The various ionic components were then determined utilising atomic absorption spectrometry.

Measurement of Ion Exchange Rates by Electrode Potentiometry

The dry clay (12.50g) was transferred to a 1250 ml cylinder and distilled water added to the mark. This was then placed in an end-over-end shaker for 24 h to get the clay fully into suspension. A 250 ml aliquot was taken and transferred to a 250 ml round-bottomed flask. The flask was placed in a thermostatted water bath (25°C ± 1°C) on a water powered magnetic stirrer where the suspension was stirred at constant and allowed to come to thermal equilibrium. An Orion (90-01) single-junction reference electrode was inserted into the suspension. These electrodes were connected to a Phillips high impedance ion activity meter (Model PW 9414) which was in turn connected to a Rikadenki (Model B 181 H) flat bed chart recorder. The relevant quantity of CaCl₂ (0.1M Analar) was added and time keeping commenced.
The chart recorder then kept a record of the ion exchange and this tracing was converted to a concentration-time plot by reference to a calibration curve.
ELEMENTAL ANALYSIS OF ASHED TAILINGS AND CLAY MINERALS

The basis of the method was a fusion technique with lithium metaborate followed by analysis using atomic absorption spectrophotometry as in the method of Boar and Ingram (1970).

Preparation of Lithium Metaborate

Stoichiometric amounts of anhydrous lithium carbonate (73.89 g) (Analar) and boric acid (122.6 g) (Univar) were intimately mixed and then placed in a porcelain dish and heated slowly for four hours in a muffle furnace at a temperature of 400°C. The fused mass was then ground to pass a 250 mesh B.S.S. sieve.

Fusion Technique

The sample (0.500 g) to be analysed (previously ground to pass a B.S.S. 250 mesh sieve) was mixed with 2 g of lithium metaborate in a platinium crucible and heated in a muffle furnace at 900°C until a clear melt was obtained. In the fractions containing magnetite 30 mg of ammonium vanadate (Univar) was added to the fusion mixture to assist in complete fluxing of the iron. The fusion melt was then cooled to ambient temperature and placed in a beaker containing 8 ml of conc. nitric acid (Aristar) in 150 ml of distilled water. The mixture was stirred with a magnetic stirrer using a P.T.F.E. slug until dissolution was complete. 2.5 g of tartaric acid (Analar) was added and the solution made up to 250 ml in a volumetric flask.

The solutions were then analysed using a Varian AA6D atomic absorption spectrophotometer according to the flow diagram shown (Figure 48). The standard for each element was prepared from B.D.H. metal standards which were then matched with appropriate concentrations of lithium metaborate, nitric and tartaric acids. Where appropriate CsCl was added as an ionisation suppressant.
Flow Diagram of A.A. Procedure

Sample
0.5g

Fuse with 2g of LiBO₂ at 900°C

Dissolve
Melt in HNO₃ + H₂O & tartaric acid

250ml volume

SiO₂
251.6 nm
N₂O - C₂H₂

Al₂O₃
309.2 nm
N₂O - C₂H₂

Fe₂O₃
248.3 nm
N₂O - C₂H₂

Mn₂O₃
279.5 nm
air - C₂H₂

1:20 dilution + CaCl

MgO
285.2 nm
N₂O - C₂H₂

CaO
422.7 nm
N₂O - C₂H₂

Na₂O
589.6 nm
air - C₂H₂

K₂O
766.5 nm
air - C₂H₂

FIGURE 48
In this manner SiO₂, Al₂O₃, Fe₂O₃, K₂O, MgO, Mn₃O₄, CaO and Na₂O were determined.

**Determination of TiO₂**

To 10 ml of the undiluted sample solution in a 50 ml volumetric flask, 5 ml of dilute sulphuric acid (25% v/v) and 5 ml of 30% hydrogen peroxide was added and then made up to the mark with distilled water. Another 10 ml aliquot of the sample was treated similarly but excluding the peroxide addition and used as a reference. The absorbance at 410 nm was measured and compared to a series of standards.
PARTICLE SIZE ANALYSIS

Samples for sieve analysis were collected in 1 litre polythene bottles and stored in these containers prior to analysis. A nest of four B.S.S. sieves were used to collect the following fractions:

+420, 420-211, 211-150, 150-75μ.

The samples were introduced into the largest sieve gradually to prevent the nest of sieves from blinding-up, and washed through the sieves with water. The whole nest of sieves was shaken in a mechanical sieve shaker for 30 minutes while the size analysis was taking place. In the case where the underflow from the sieves continued to be discoloured after 30 minutes additional shaking was necessary until the underflow was clear, indicating a satisfactory size separation. The contents of each sieve were then washed into large evaporating trays and the slurry allowed to evaporate to dryness in a nitrogen purged oven at 90-100°C. The solids obtained were then weighed.

The underflow of the nest of sieves was stored in large glass beakers in an oven at 80°C for several days and the slurry allowed to evaporate. A sub-sample of this dried slurry was then taken for analysis of the 75-10μ fraction by a "Warman Cyclosizer".

The "Cyclosizer" depends on an elutriation technique where samples are sized by allowing the samples to be dispersed in a fluid (water) and to settle against a rising fluid velocity. By varying the rising velocity fractions may be collected within a certain size range. In the "Cyclosizer" the elutriation action takes place in a hydraulic cyclone where the fluid is spinning and centrifugal forces are acting on the particles. The size fractions obtained were dried under nitrogen at 90-100°C and weighed.
The particle size analysis of the size fraction between 20-2μ was determined using a plummet balance according to the method of Hutton (1956). The clay or tailings sample after sieving was suspended overnight in an end-over-end shaker in 1250 ml sedimentation cylinders. The cylinders were then placed in a water bath thermostatted at 25°C. The suspension was left until it reached the temperature of the bath then stirred vigorously with a mechanical stirrer to fully suspend all the size fractions present. The suspension was then allowed to settle for a short time in order to allow the +20μ fraction to settle and the supernatant suspension decanted off. This supernatant was then evaporated to dryness in an oven at 100°C and then dispersed in 10% ethylene glycol in ethanol (Analar). The sample was then filtered with washing by the ethylene glycol/ethanol mixture to remove any trace of soluble salts that could cause coagulation or cementation of the particles.

A 1% suspension of the sample was then made up in a 1250 ml sedimentation cylinder and suspended overnight in the end-over-end shaker. The sample was then placed in a water bath thermostatted at 25°C and left until it reached thermal equilibrium. It was then agitated using a "puddling" technique according to the method of Marshall (1954). The percentage of each size fraction was then determined at certain time intervals according to Stokes' Law with the plummet balance. The plummet balance prior to this had been calibrated with NaCl (Analar) solutions of known density. The plummet was always used at a fixed depth to eliminate the error associated with the hydrometer technique (Marshall 1954). The overlapping size fractions where determinations were carried out using both the "Warman Cyclosizer" and the plummet balance showed good agreement (±1%).
pH - Temperature - Suspended Solids

"In situ" determination of pH was carried out by direct potentiometry using an Orion (91-02) combination glass pH electrode in conjunction with an Orion Series 400 portable pH/mv/concentration meter. Monitoring of pH during laboratory experiments was done with a Radiometer GK2351C combination glass electrode attached to a Phillips high impedance ion activity meter (Model PW 9414). When maintenance of a fixed pH was necessary the Radiometer GK2351C combination glass electrode was attached to a Radiometer TTTIC titrator attached to a Radiometer ABUIa autoburette.

Temperature measurements were in degrees Celsius and were uncorrected.

Suspended solids were deemed that weight of non-settleable particulate matter that was retained on a 0.45μ membrane filter. The pre-weighed membrane filters were stored in a desiccator until use then transferred to a Millipore filtration (vacuum) apparatus. The sample was transferred to the apparatus and the sample container rinsed with prefiltered triple distilled water. The membrane filter was then dried in an air oven at 110°C, cooled in a desiccator and then weighed. The difference in weight was assumed to be due to suspended solids.
Ca, Mg, Na, K

These were determined by atomic absorption spectrometry. An aliquot, (generally 1.0 to 2.0 ml) of the sample was taken and transferred to a 100 ml volumetric flask containing 10 ml of conc. HCl (Aristar) and 2.5 ml of CsCl (5M; Suprapur). The solution was made up to the mark with distilled water and the concentration of these ions in the sample determined by comparison with a standard calibration curve. The standards and blank (zero absorbance) contained identical concentrations of HCl and CsCl. The Na and K were determined with an air-acetylene flame whereas the Mg and Ca were determined utilising a nitrous oxide-acetylene flame.

Chloride Concentrations

The filtered sample was titrated potentiometrically with silver nitrate (Analar, 0.10M) using an Orion (94-16A) silver/silver sulphide electrode coupled with a Radiometer (K601) mercury/mercury(I) sulphate reference electrode.
Sulphate

The sample (200 ml) was filtered and then acidified with 1M HCl (Aristar) to pH 4-5 using methyl red indicator. The sample was then heated to boiling and 10 ml of 0.5M BaCl₂ solution was added slowly with stirring. The mixture was then digested for 4-5 h at 80-90°C and then filtered through a Whatman No 42 filter paper. The precipitate was then washed with warm distilled water until the washings were chloride free. The filter paper and precipitate were then dried and ignited at 800°C for 1-2 h in a silica crucible. The crucible was then cooled in a desiccator and weighed.

Preparation of Flocculants

The flocculant (0.500g) was weighed and transferred to a 500 ml volumetric flask. To this was added 5-10 ml of dry methanol (Analar) to "wet" the polymer followed by 300 ml of distilled water. This was then stirred for several hours using a P.T.F.E. magnetic stirrer bar. The solution was then made up to the mark with distilled water. The flocculants were freshly prepared every five days to prevent loss of activity due to change in polymer conformation (Shyluk and Stow 1969).
FLOCULATION PARAMETERS

Settling Rate

100 ml of the suspension was placed in a stoppered 100 ml measuring cylinder. To this was added the coagulant/flocculant combination in two equal doses. After each dose the cylinder was inverted by hand 30 times with each inversion taking approximately one second. The flocculated suspension was then transferred immediately to the apparatus shown in Figure 49. The settling rate was then taken to be the time it took the floc to pass between two fixed points on the side of the glass cylinder.

Filtration Rate.

The flocculated material was allowed to settle for 15 min and then the tap at the bottom of the apparatus was opened and 5 ml of liquid collected. This was then discarded and another 5 ml collected. The time it took to collect this second 5 ml of liquid was deemed the filtration rate.

Turbidity

After the flocculated suspension had settled for 10 min a 20 ml aliquot was removed from a fixed depth of 20 cm from the liquid surface. This was transferred to a large cuvette which was then placed in an ultra-sonic bath for 30 sec to remove air bubbles. The turbidity was then measured using a Hach Model 2100A Turbidimeter by comparison with latex standards.
FIGURE 49

FILTRATION APPARATUS
ANALYSIS OF AMINO COMPOUNDS

Compounds

Commercially available amines, amides and amino acids were checked for purity by gas chromatography-mass spectrometry. All reagents were of analytical reagent grade. Sodium nitrite was prepared by dilution of a stock solution prepared weekly by dissolving 7.5000g of sodium nitrite in 100 ml of distilled, demineralized water. Copperized cadmium was prepared as described previously from coarse Merck powder.

Equipment

Volumetric glassware was all certified Grade A. The diazotization apparatus (Fig. 50) consisted of a glass-stoppered (B24) 5 x 2 cm test tube with the extended ends of two 10 ml burettes sealed through the glass stopper; the tips of the burettes were angled away from each other. The vessel for the amine and amino acid determinations is similar to that used in the amide analysis but without the side-arm and key. Optical density was measured with a Cary 17 recording ultraviolet-visible spectrophotometer.

Procedure for analysis of amines and amino acids

An aqueous solution of the amino compound (0.5 ml; ca. 0.03 mmol), prepared by successive dilution of a 2 mg ml\(^{-1}\) stock solution in 1M HCl was placed in the reaction vessel. To this solution was added hydrochloric acid-sodium acetate buffer (1 ml; pH 3.6). The burette stopcocks were then closed and the burette assembly inserted in the reaction vessel. Sodium nitrite solution was placed in one burette (1 ml; 6 mg ml\(^{-1}\)) and a partial vacuum created by cooling the reaction vessel in dry ice and alcohol. The burette tap was opened briefly to admit the sodium nitrite solution and into the other burette was placed sodium hydroxide solution (1.5 ml; 8M).
FIGURE 50

DIAZOTIZATION APPARATUS
FOR AMINE ANALYSIS
The mixture was kept at 0-4°C for 45-60 minutes, depending on the amino compound used, and then warmed to ca. 40°C by immersion in hot water for 10-15 minutes to complete the reaction. The vessel was again cooled in ice and small portions of the sodium hydroxide solution were admitted from the second burette. When all the alkali had been admitted the contents of the vessel were shaken to absorb the acidic nitrogen oxides. The residual sodium nitrite was then washed from the first burette with dilute sodium hydroxide solution. The alkaline solution in the vessel was then transferred to a volumetric flask, and citric acid solution added (5M; 4 ml) to adjust the pH to 7-10. To this was added EDTA solution (4 ml; 0.1M) and the solution made up to the mark with distilled water.

A 50 ml aliquot of this solution was allowed to percolate slowly through a column (20 cm × 1 cm) of copperized cadmium and then washed with 3 × 50 ml portions of distilled water into a 250 ml volumetric flask. This was diluted to the mark with distilled water and a 10 ml aliquot removed to a 100 ml flask containing 2 mls each of sulphanilamide and N-[1-naphthyl]-ethylenediamine dihydrochloride. The contents of the flask were diluted to the mark and the characteristic red colour was formed within 15 minutes. The absorbance was measured at 543 nm in a 1 cm quartz cell. This absorbance was compared with that of a sodium nitrite blank worked up in exactly the same way.

Procedure for analysis of amides

The amide (approximately 10 mmol) was dissolved in the sodium nitrite solution (2.0 ml) in the reaction tube and the tube warmed in a water bath. The burette assembly was then inserted in the reaction tube; (amides that are insoluble or only slightly soluble in water were dissolved in 16M H₂SO₄ in a PTFE cup that was suspended from a key in
the wall of the container). The reaction tube was then cooled in a dry ice-alcohol mixture while 16M H2SO4 (1 ml) was introduced into one of the burettes while 8M NaOH was introduced into the other burette. The stopcock on the first burette was opened and the sulphuric acid was drawn in by the partial vacuum created by the rapid cooling. This was allowed to run down the side of the vessel into the stirred solution of amide-nitrite. A vigorous reaction ensued resulting in a pale blue solution of nitrous acid. After 5-20 minutes, depending on the amide used, the other burette was opened intermittently in order to admit small portions of sodium hydroxide solution. When all the alkali had been added, the contents of the tube were shaken so as to absorb all nitrous fumes and the alkaline solution was transferred into a 250 ml volumetric flask. Citric acid solution was added (10 ml) in order to adjust the pH to 7-10.

After addition of 4 ml of EDTA solution (0.1M) and dilution to 250 ml, a 20 ml aliquot of the solution was allowed to percolate through a column (20 x 1 cm) of copperized cadmium and washed through the column with 3 x 50 ml portions of distilled water into a 250 ml calibrated flask. The solution was made up to the mark with distilled water and the residual nitrite in a 10 ml aliquot was determined colorimetrically by its reaction with sulphanilamide and N-[1-naphthyl]-ethylenediamine dihydrochloride. After suitable dilution the absorbance at 543 nm was measured and compared with that of a blank worked up in exactly the same way, but without addition of amide.
COLORIMETRIC PROCEDURE FOR NITRITE DETERMINATION

Copper Sulphate Solution (0.08M)

20 g of CuSO₄·5H₂O (Analar) was dissolved in one litre of distilled water.

EDTA Solution (0.1M)

38g of the tetrasodium salt of ethylenediaminetetraacetic acid was dissolved in 500 ml of distilled water and diluted in one litre.

Column Wash Solution

This consisted of 1 ml of the 0.1M EDTA solution in 50 ml of 0.0015M HCl.

Sulphanilamide Solution

Five grams of sulphanilamide (A.R.) was dissolved in a solution of 50 ml of 10M HCl (Suprapur) and 300 ml of distilled water. This was made up to 500 ml in a volumetric flask with distilled water and transferred to an amber bottle in a refrigerator. This solution was found to be stable for several months.

N-[1-naphthyl]-ethylenediamine dihydrochloride

0.50 grams of the dihydrochloride (Puriss) was dissolved in distilled water and diluted to 500 ml in a volumetric flask. The solution was filtered through a Whatman 42 paper and then stored in amber bottle under refrigeration. It is stable for about a month.

Preparation of the Cadmium Columns

Coarse cadmium powder supplied by Merck was washed with 2M HCl in a separatory funnel, then washed thoroughly with distilled water. This was followed by washing with 0.3M HNO₃ to pit the cadmium powder, and then washed with distilled water.
FIGURE 51

REDUCTION COLUMN

Glass Wool

2mm. capillary column

34 cm.

25 cm.

8 mm. I.D.

12 cm.

30 mm. I.D.
The cadmium powder was then washed with 2M HCl to remove the NO$_3^-$ ion followed by another thorough wash with distilled water. The cadmium (approx. 40g) was then treated with 100 ml of the copper sulphate solution in a washing bottle as described by Wood (1967). It was well shaken and then washed with distilled water with special care taken to ensure that the copperized cadmium was not exposed to the air.

A small plug of glass wool was placed in the bottom of the glass column (Fig. 51), which was then filled with distilled water. The copperized cadmium was introduced slowly by inverting the copperizing vessel into the column reservoir and the column was tapped during the process to settle the cadmium. The copper and fine cadmium that settles on top of the column is removed by suction and a small piece of glass wool was placed on top of the cadmium to act as a filter. The cadmium column was washed with approximately 50 ml of the wash solution with the column being allowed to stand 24 hours before use.
Determination of Residual Polymer

The dry clay (12.05g) was transferred to a 1250 ml measuring cylinder and distilled water added to the mark. This was placed in an end-over-end shaker for 24 hours. An aliquot of the suspension was removed and transferred to a 100 ml measuring cylinder. To this suspension was added the coagulant/flocculant combination in two doses so that the total volume of the material was 100 ml. After each dose the cylinder was inverted 30 times as previously described. The flocculated material was then allowed to settle and centrifuged for 5 min at 1000 r.p.m. The supernatant was then transferred to a 250 ml round-bottomed flask and frozen by a mixture of dry ice and alcohol. The frozen supernatant liquid was then freeze-dried till no more liquid remained. The solid residue was then transferred to the amide apparatus and the polyacrylamide content determined by the method previously described.
Cd-ELECTRODE MEASUREMENTS

One (1) gram of the sodium clay was dispersed in 50 ml of distilled water in a 100 ml volumetric flask by placing the flask in an ultrasonic bath for five minutes. The contents of the flask were adjusted to pH 6.5 by addition of dilute perchloric acid (.01M Analar). To the flask was added the required quantity of cadmium perchlorate (.1M P.&B.) and sodium chloride (1M A.R.). Water was then added so as to make the total volume exactly 100 ml when the flocculant was added. The flocculant was then added and the flask inverted 30 times to promote flocculation. The flask was then immersed in a water bath at 25°C for 15 minutes. An aliquot was removed from the flask and the Cd activity measured with a cadmium ion selective electrode (Orion Model 94-48) in conjunction with an Orion Model 90-01 single-junction reference electrode. The Cd activity was read from a calibration curve made from a series of cadmium nitrate standards containing potassium as an ionic strength adjustor (both Cd(NO₃)₂ & KNO₃ were A.R.).

The aliquot was then returned to the flask and then the supernatant liquid in the volumetric flask transferred with washing to a 250 ml round bottomed flask. The contents of the flask were frozen by immersion in a dry ice/alcohol mixture and then the liquid removed with a freeze drier. The solid residue was then analyzed for amide content using the previously described method.
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