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Alternative Al production methods: Part 1 - a review of indirect carbothermal routes

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Abstract

The production of Al from its ores at present relies on the Bayer (alumina production) and the Hall- Heroult (Al production) process. The cost associated with alumina production and apparent disadvantages of the Hall-Heroult process have led to intensive research to find alternative routes for Al production. The direct carbothermal reduction process has been thoroughly investigated as an alternative technique. Another alternative includes the indirect carbothermal reduction route where alumina (or aluminous ores) is first reduced to intermediate Al compounds before reduced further to Al. The present study reviews and provides systematic thermodynamic analyses of alternative Al production routes. In this paper (Part 1), a comprehensive review of alternative Al production techniques focusing on the indirect carbothermal reduction routes is presented. These include carbochlorination, carbonitridation and carbosulphidation routes for the formation of intermediate Al compounds, followed by various Al extraction processes.

Alternative Al Production Methods:

Part I – A Review of Indirect Carbothermal Routes

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ABSTRACT

The production of aluminium from its ores at present relies on two processes: the Bayer process (alumina production), and the Hall-Heroult process (aluminium production). The cost associated with the alumina production and apparent disadvantages of the Hall-Heroult process have led to intensive research to find alternative routes for aluminium production. The direct carbothermal reduction process has been thoroughly investigated as an alternative technique. Other alternatives include the indirect carbothermal reduction process where alumina (or aluminous ores) is reduced to intermediate Al-compounds before further reduced to extract aluminium. The current study reviews and provides systematic thermodynamic analyses of alternative aluminium production routes. In this paper (Part I), a comprehensive review of alternative aluminium production techniques focusing on the indirect carbothermal reduction routes is presented. These include carbochlorination, carbonitridation and carbosulphidation routes for the formation of intermediate Al-compounds, followed by aluminium extraction processes.

Keywords: carbothermal reduction of alumina, carbochlorination of alumina, carbonitridation of alumina, carbosulphidation of alumina, thermal dissociation, electrolysis, disproportionation
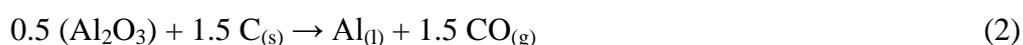
1. Introduction

Aluminium is the most abundant metallic element in the Earth's crust (about 8%) and the second most widely used metal next to steel. The production of aluminium has increased by nearly four times in the last three decades[1]. Pure aluminium cannot be found in nature because of its high affinity to oxygen. In general it is found in a variety of minerals combined with various elements such as silicon, oxygen, phosphates, fluorine, and hydroxides[2-5]. In the last century a number of methods have been developed to extract aluminium from its ores. The current commercial production method relies on two energy-intensive processes developed in the late 1800s: the Bayer process which produces pure alumina from bauxite ore, and the Hall-Heroult electrolysis process which produces aluminium metal from alumina. The cost of the Bayer process represents about 27% of the cost of aluminium production[6] and the Hall-Heroult process uses about three quarters of the total energy requirement, though these numbers vary depending on the specifics of the ores and sources of energy used.

The Bayer process is the principal industrial technique to refine bauxite to pure alumina. There has been little changes to the basic process since the first plant opened in 1893[7]. In this process, bauxite containing typically 10-30 wt% Fe_2O_3, 4-8 wt% SiO_2, and 2-5 wt% TiO_2 as major impurities[8] is dried, ground, digested in sodium hydroxide under pressure. Impurities are separated by filtration, before an alumina hydroxide is precipitated and calcined to produce commercial alumina. The relatively high purity alumina produced from the Bayer process is then transferred to the Hall-Heroult electrochemical cell for electrolysis.

The Hall-Heroult process was patented in 1886[9] and the basic process layout remains unchanged except for the form of the carbon anode[10]. There has been significant improvement in the process over last hundred years, through increasing cell size, greater automation and control, and improved control of emissions. Tarcy *et al.*[11] provides an outline of the improvements in a recent review, showing that the overall energy usage per kg of metal has decreased from typically over 30 kWh/kg Al in 1914 to below 14 kWh/kg Al by 2000.

In the Hall-Heroult process aluminium metal is extracted through electrolysis of purified Al_2O_3 dissolved in $NaF\text{-}AlF_3$ (cryolite) solution according to the following overall reactions:

$$0.5\ (Al_2O_3) + 0.75\ C_{(s)} \rightarrow Al_{(l)} + 0.75\ CO_{2(g)} \tag{1}$$

$$0.5\ (Al_2O_3) + 1.5\ C_{(s)} \rightarrow Al_{(l)} + 1.5\ CO_{(g)} \tag{2}$$

In this process, liquid aluminium is produced at the bottom of the cell and CO and CO_2 gases are evolved from the bath. The Hall-Heroult process also generates greenhouse gasses such as

CF_4 and C_2F_6 from the carbon electrode and reactions with liquid cryolite (Na_3AlF_6). Per fluorocarbons (PFCs) may also form during the so-called anode effect when the electrolyte becomes depleted in alumina[13]. In general, the process has high capital costs, low productivity compared to other metallurgical processes and consumes significant energy (from 12.9 to15 kWh/kg Al[15-17]). The production of each kg of Al consumes between 0.4 to 0.5 kg of carbon in the form of anodes and in total, aluminium production contributes to 2.5% of the world anthropogenic CO_2 equivalent emissions[14]. This value will vary from plant to plant as it depends on energy source, the details of the cell and quality of the feed materials[12].

The apparent disadvantages of the Hall-Heroult process have led to numerous researches to develop alternative routes throughout the 20th and early 21st centuries. The most important alternatives that have been envisaged include modified Hall-Heroult process utilising inert anodes, direct carbothermal reduction of alumina[18], and indirect carbothermal reduction of alumina (e.g. formation of $AlCl_3$ intermediate followed by Al extraction in the Alcoa process[18]).

In this Part 1 paper, a comprehensive review of various aluminium production methods, focusing on the indirect carbothermal reduction routes, is presented. There have been a number of major review papers on Al production routes. In 1964, Stroup[19] provided a detailed review on the carbothermal production processes of aluminium. Russell[20] provided another major review on various new technologies in 1981, including review and progress on the development of Alcoa processes. The current paper briefly reviews the recent development in direct carbothermal routes followed by systematic reviews of different indirect carbothermal reduction routes. In the Part 2 of the paper, systematic thermodynamic analyses of selected indirect carbothermal reduction routes are presented. These include evaluation of Gibbs free energy formation and equilibrium calculations of various intermediate Al-compounds formation and extraction of aluminium from these compounds.

2. Direct Carbothermal Reduction Processes

The direct carbothermal reduction of alumina to aluminium has potential for greater productivity, lower capital investment, less consumption of electric power, and lower overall greenhouse gases emission, compared to the Hall Heroult process. It is well established that direct carbothermal reduction of iron oxide, through blast furnace technology, offers far greater productivity and energy efficiency than any comparable electrolytic process. It is this desire to duplicate the merits of pyrometallurgy processing to aluminium that has driven interest in carbothermal reduction of alumina. The overall reactions for carbothermal reduction of alumina can be presented as:

$$Al_2O_{3(s)} + 3C_{(s)} = 2Al_{(s)} + 3CO_{(g)} \tag{3}$$

$$Al_2O_{3(s)} + 3CH_{4(g)} = 2Al_{(s)} + 3CO_{(g)} + 6H_{2(g)} \tag{4}$$
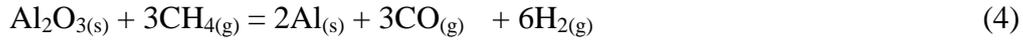
These two reactions are thermodynamically favoured above 2057°C and 1497°C, respectively[19]. Although these reactions look simple, in practice these are difficult to achieve with high Al yield. The reaction steps are not straight forward as the aluminium oxide forms intermediate and volatile sub-compounds during the process. During cooling down of the products, mixture of carbide and oxycarbide can form due to reactions between the products. The chemistry and thermodynamics of the Al-C-O system have been studied extensively [16-17, 19, 21-32].

Recent developments in carbothermic production of aluminium have evolved in the direction of a two-stage process. Cochran and Fitzgerald[33] invented a stack-type reactor in which Al_2O_3 and C was reacted in a high-temperature upper reaction zone and produced liquid mixture of Al_2O_3 and Al_4C_3 which was then transferred to a lower reaction zone for Al extraction. Alcoa and Elkem companies thoroughly investigated carbothermic production of aluminium using the stack-type reactor[34-40](ARP-Advanced Reactor Process). Alumina was carbothermally reduced in the first reaction compartment of a vessel to produce a 50% Al_2O_3-50% Al_4C_3 slag melt at approximately 2000°C. Further reaction took place between alumina and aluminium carbide in the second compartment at approximately 2200°C to produce an aluminium-carbon alloy. The reactions associated with each stage are given below:

$$3\ Al_2O_{3(s)} + 9\ C_{(s)} = (Al_4C_3.Al_2O_3)_{(l)} + 6\ CO_{(g)} \qquad T = 2000^{\circ}C \tag{5}$$

$$(Al_4C_3.Al_2O_3)_{(l)} = 6\ Al_{(l)} + 3\ CO_{(g)} \qquad T = 2200^{\circ}C \tag{6}$$
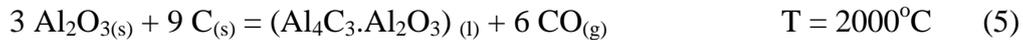
The ARP included a method for vapour recovery for recycling the aluminium and aluminium sub-oxide vapours generated. Fruehan *et al.* [38] studied the mechanism and reaction rate of $Al_2O_{(g)}$, $Al_{(g)}$ with carbon source. They found that the rate of formation of Al_4C_3 from Al_2O and Al gases in CO is controlled by diffusion of the reactant gases through the Al_4C_3 product layer. The two-zone method was also researched by Persson[41], and Dougan and Southam[42]. Dmitriev and Karasev[43] proposed an induction shaft furnace for Al_4C_3 production from alumina. Then aluminium was extracted by electrolysis in the lower zone of the furnace.

Other recent developments include the vacuum carbothermic reduction currently being developed under the ENEXAL project[44]. This process uses an electric arc furnace (EAF) with integrated shaft attachment. The EAF is the main reactor where liquid aluminium is produced and the shaft acts as condenser for the Al and Al_2O vapours. By carrying out the process under vacuum, the formation of aluminium rich vapour will be favoured over liquid aluminium. The process can also be carried out at lower temperatures, e.g. 1500°C at 10 Pa

pressure. Preliminary experimental study has been carried out using a solar furnace to demonstrate the process. At temperatures 1027 to 1727°C and pressures 350 to 1200 Pa, Al (up to 19%) along with Al_4C_3 and Al_4O_4C can be produced upon condensation[45-46]. It is unclear whether yield can be improved and whether the proposed process has potential for commercialisation.

Sayad-Yaghoubi[47] proposed a carbothermic process for the production of aluminium carbide by injection of carbon and Al_2O_3 into superheated aluminium (> 1400°C). The reaction between the injected carbon with molten aluminium followed:

$$4\ Al_{(l)} + 3\ C_{(s)} = Al_4C_{3(l)} \qquad\qquad T > 1400°C \qquad\qquad (7)$$
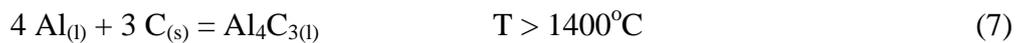
The formed Al_4C_3 attaches to Al_2O_3 and forming a mixture of Al_4C_3 - Al_2O_3. Aluminium was then extracted from this mixture in a separate zone through reaction given in Eq.6 at temperatures about 1700°C to 2000°C. This was done by maintaining a sufficiently low gas pressure in the second zone, e.g. by extracting the CO gas. Sayad-Yaghoubi[48-49] also proposed various types carbonaceous materials (such as CH_4 and other hydrocarbons) and additional reactants (such Al scrap and dross).

Despite the developments to date and significant scientific and financial investment of resources, no processes based on direct carbothermal reduction have been successfully developed to full plant scale. Direct carbothermal processes have to date suffered generally from problems with yield, associated with the formation of other compounds other than aluminium.

3. Indirect Carbothermal Reduction Processes

Researchers and industry have also directed their attention to multi-stage process, in particular indirect carbothermal reduction of alumina. These types of processes involves two or more steps where in the first step (Stage 1) alumina or aluminium ores are converted to intermediate Al-compounds. The intermediate Al-compounds are then further reduced to aluminium metal in subsequent steps (Stage 2). This is schematically shown in Figure 1.

The following sub-sections review the various indirect production processes of aluminium, focusing on the carbochlorination, carbosulphidation and carbonitridation routes for the Stage 1 followed by various Al extraction techniques in the Stage 2.
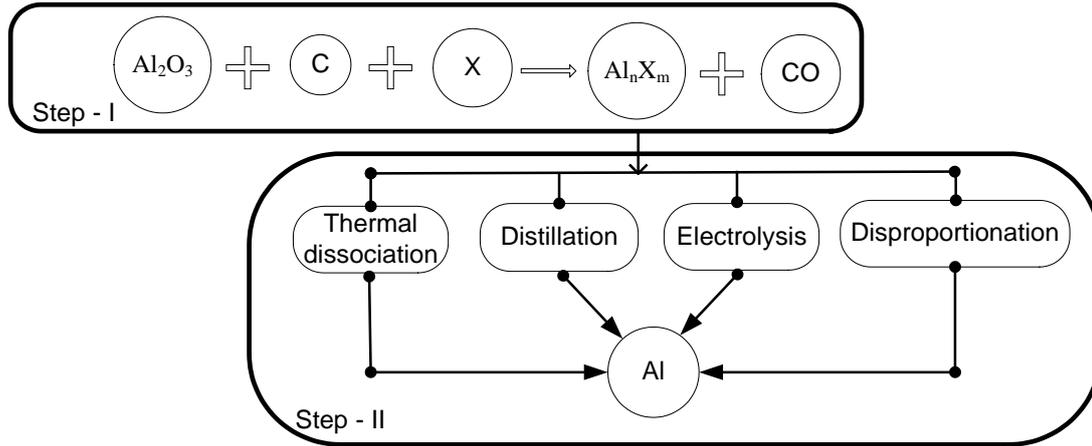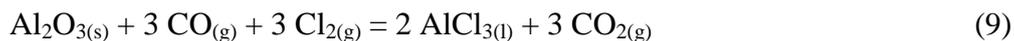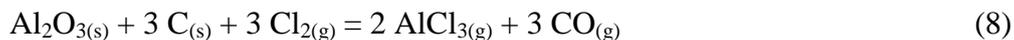
Figure 1 – A schematic diagram showing the indirect carbothermic aluminium production method from alumina.

3.1   Carbochlorination Route

This route involves the formation of aluminium chloride intermediate compounds from reactions of alumina and/or aluminous ores with carbon and chlorine sources. The production of volatile metal halides (including aluminium trichloride) from alumina has been known for many years, but most of the processes have difficulties in terms of operation and control. One of the earliest patented works in the production of aluminium trichloride was from Ferguson *et al.*[50], where they developed a continuous process using fluidised-mixture reactor. In the case of carbochlorination of alumina, the process can be represented by the reactions,

$$Al_2O_{3(s)} + 3\ C_{(s)} + 3\ Cl_{2(g)} = 2\ AlCl_{3(g)} + 3\ CO_{(g)} \tag{8}$$

$$Al_2O_{3(s)} + 3\ CO_{(g)} + 3\ Cl_{2(g)} = 2\ AlCl_{3(l)} + 3\ CO_{2(g)} \tag{9}$$

The chlorination temperature is in the range of 400 to $1000^{o}C$ depending upon the reacting agents. There have been a number of studies on the chlorination of alumina investigating the effect of various kinetic parameters (chlorination media, partial pressure of gaseous components, particle shape and size and reactor design) on the reactions in the temperature range between 427 and $1027^{o}C$[51-54]. Unless a high purity alumina source is used, other elements that are generally present such as iron, silicon, and titanium are also chlorinated and must be separated from the aluminium trichloride. Yuan *et al.*[55] carried out study of carbochlorination of alumina in vacuum and reported that $AlCl_{(g)}$ is formed at temperatures 1430 to $1580^{o}C$ at pressures 40 to 150 Pa.

Grob and Richarz[56] attempted to chlorinate alumina in kaolinitic clay in Cl_2 and CO gas mixtures. They found that the reactivity of alumina in the raw material increases when the material is first pretreated using ammonium sulphate $(NH_4)_2SO_{4(g)}$ or sulphur trioxide $SO_{3(g)}$. At temperatures below $727^{o}C$, the chlorination rates were found to be comparable to those
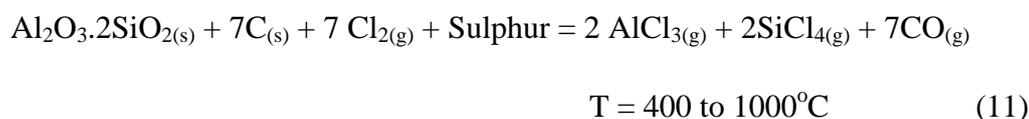
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reported for using pure gamma alumina as starting material. However above 727°C, $SiCl_4$ formed and interacted with alumina, leading to a decrease in the rate of aluminium chlorination.

Huapin et al.[57] produced aluminium trichloride from alumina through reaction with carbon and chlorine in alkali metal halides and alkaline earth metal halides molten salt baths ($AlCl_3$-NaCl-LiCl) between 400 and 950°C. Becker et al.[58] used a mixture of high purity activated carbon and alumina heated in bubbling chlorine between 500 and 775°C and was able to obtain 100% conversion to $AlCl_3$ vapour.

In 1971 Toth[59] patented a two-stage process for aluminium production where in the 1st stage, alumina was reacted with manganese chloride in the presence of carbon at temperatures 900 to 1300°C producing aluminium trichloride and manganese, through the reaction:

$$Al_2O_{3(s)} + 3\ MnCl_{2(l)} + 3\ C_{(s)} = 3\ Mn_{(l)} + 2\ AlCl_{3(g)} + 3\ CO_{(g)} \qquad (10)$$
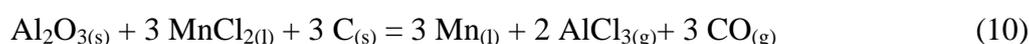
Wyndham et al.[60] and Lippman et al.[61] (of Toth Al Corporation) used alumina based ores as the source for aluminium. In the case of alumina-silica ores, the reaction was carried out in the presence of sulphur to improve the halogenation. Sulphur acted as a catalyst and the process could be carried out a temperature as low as 400°C through this reaction:

$$Al_2O_3.2SiO_{2(s)} + 7C_{(s)} + 7\ Cl_{2(g)} + Sulphur = 2\ AlCl_{3(g)} + 2SiCl_{4(g)} + 7CO_{(g)}$$

$$T = 400\ to\ 1000°C \qquad (11)$$

There are other processes for aluminium trichloride production, including various aluminium extraction techniques from the chloride. **Table 1** summarises selected processes and technological development associated with the chloride route (both the Stage 1 and 2).

3.2   Extraction of Aluminium from Aluminium Trichloride

The common routes for extracting aluminium from its chlorides are through disproportionation and electrolysis reactions. Other routes include distillation and direct reduction with other metals.

Disproportionation of Aluminium Halides (including Chlorides)

Willmore[62] (Alcoa) discovered that AlF_3 and several other fluorine compounds selectively distil aluminium at 900-1300°C. Klemm and Voss[63] indicated that this occurs because of a formation of a monovalent compound (in this case AlF) at a temperature around 1200°C. This compound was then disproportionated at a lower temperature of around 800°C according to the following reaction:

$$3 \text{ AlF}_{(l)} = 2 \text{ Al}_{(s)} + \text{AlF}_{3(s)} \tag{12}$$

In this process the aluminium condensed as a fine powder, mixed with solid AlF₃. Therefore further process using molten-flux was necessary to separate and agglomerate the aluminium. It was then found that the above reaction also occurs with other aluminium halides. The halide formation has been the basis of aluminium production and refining process using various aluminium halides and other sub-compounds. Belyayev and Firsanova[64] conducted a survey on various aluminium sub-compounds and concluded that subfluoride and subchloride provided the most potential for practical refining processes.

Gross[65-66] in 1944 proposed a process using AlCl₃ where AlCl₃ vapour was passed through a bed of impure crushed aluminium alloy above 1000°C and aluminium was extracted and condensed by disproportionation at 700°C according to the reaction:

$$3 \text{ AlCl}_{(g)} = 2 \text{ Al}_{(l)} + \text{AlCl}_{3(g)} \tag{13}$$

The reformed AlCl₃ was not condensed and was recirculated through the reaction furnace. As only aluminium was condensed, further separation process from the AlCl₃ was not necessary.

In the 60's, Alcan developed an alternative process for production of aluminium which involved carbothermal reduction of aluminous ores followed by monochloride purification[20]. This work was stopped due to problems associated handling of chlorides which included stress-corrosion cracking and inefficiency in separating manganese impurities. In the 70's Othmer[67-68] proposed a separation of aluminium from aluminous ores (bauxite, clays, feldspar) through carbochlorination (to form AlCl₃) followed by disproportionation or halogenation in a flash condenser. One of the recent works associated with carbochlorination of alumina followed by disproportionation was from Yuan *et al.*[55]. They carried out the carbochlorination in vacuum and observed AlCl₍g₎ at temperatures between 1430°C and 1580°C and pressures from 40 to 150 Pa. The AlCl₍g₎ was then disproportionate into Al and AlCl₃₍g₎ below 660°C. They were able to obtain Al metal with average purity of 95.32 wt%.

Electrolysis of Aluminium Trichloride

It has been claimed that aluminium chloride electrolysis method is attractive both from an economic and technical point of view[69]. Ishikawa and Ichikawa[70] argued that the potential advantages of aluminium chloride salt electrolysis process include:

(1) chloride salts are much less corrosive than fluoride salts which results a longer cell life;

(2) the electrolysis process requires a closed system which limit the emission of gasses;

(3) chloride salts have higher conductivities compared to the fluoride salts resulting lower energy consumption, higher power and current efficiencies;

(4) the electrolysis process has a very broad operational range of aluminium concentration which results in no "anode effect";

(5) it is possible to design an electrolytic process cell with bipolar electrodes which results in a much more compact cell with increased production potential per unit volume.

In the 70's, Alcoa developed alternative processes to produce aluminium which focused in three major directions: (1) direct carbothermal reduction of alumina and (2) indirect carbothermal reduction of aluminous ores that involved carbochlorination, monchloride purification and (3) electrolysis of aluminium chloride[20]. The general schematic of the process routes is shown in **Figure 2**.
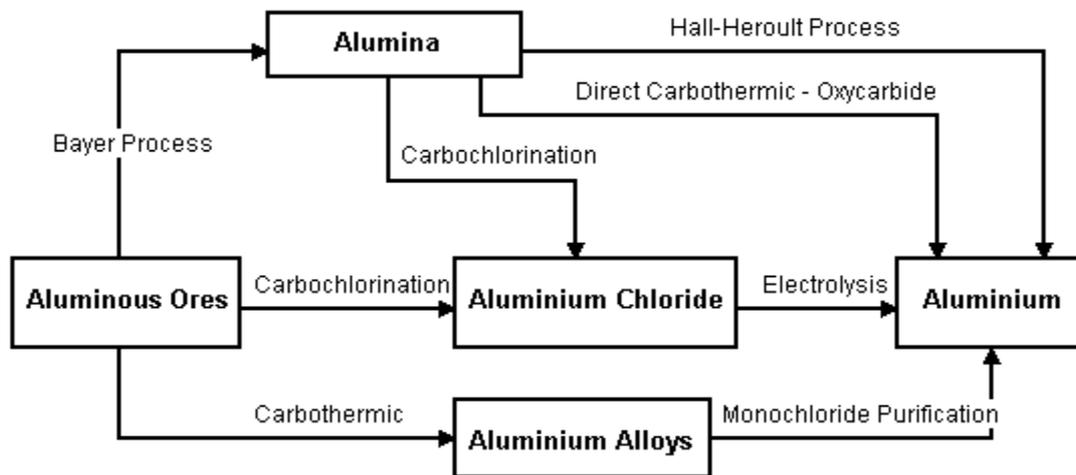

Figure 2 – A schematic diagram showing the process routes considered by Alcoa [20].

Russell *et al.*[18] from Alcoa developed an aluminium chloride electrolysis process using NaCl-LiCl (50:50 wt%) electrolyte at temperatures from 660 to 730°C. They suggested operation with 1 to 15 wt% concentration of $AlCl_3$ in the bath. The anode-cathode distance in the process was approximately 25mm. They were able to improve the current efficiency (up to 80%) and avoid the formation of sludge from the impurities using these proposed operating conditions. Dell *et al.*[71], improved the process by developing a new design with bipolar electrodes. This allowed the process to operate with a lower anode-cathode distance (less than 19mm). Alcoa developed the aluminium trichloride electrolysis route in the 1970s to a commercial level but halted operations in the 1980s, because of difficulties associated with production and handling of pure aluminium trichloride[72].

Ishikawa and Ichikawa[70] from Nippon Light Metal electrolysed $AlCl_3$ in a molten $AlCl_3$-LiCl-NaCl salt bath at 700^oC. Additions of LiCl, $CaCl_2$ or $MgCl_2$ salts to the bath improved the electrical conductivity and the current efficiency. They were able to obtain 90 to 100% current efficiency. Cohen *et al.*[73] from Pechiney proposed a continuous process through carbochlorination of alumina to form $AlCl_3$ followed by electrolysis in $AlCl_3$-alkali/alkali-earth metal halides electrolyte. One of the recent works on the electrolysis of $AlCl_3$ was from Sharma[74] where aluminium was produced through electrolysis in a chloride-fluoride salt bath at 750^oC. The electrolytes used include Na_3AlF_6-NaCl-NaF, Li_3AlF_6-LiCl-LiF, and K_3AlF_6-KCl-KF.

Wilkening[75], produced aluminium through electrolysis where the bath consists of alkali halides and/or alkali earth halides. A mixture of aluminium oxide and carbon was used as a feed material. Different arrangements of the electrolytic cell were also proposed in the work. Tomaswick[76] from Alcoa electrolysed Al_2O_3 directly in a bath containing $AlCl_3$ and an alkali metal chloride (NaCl, LiCl, KCl, $MgCl_2$, $CaCl_2$, $BeCl_2$, $BaCl_2$). The process was carried at 300^oC and aluminium was extracted as a solid metal at the cathode in a frozen layer of the alkali metal chloride.

Other Al Extraction Methods from Aluminium Trichloride

There are other methods used to extract aluminium from $AlCl_3$. One example is through direct reduction using another metal (e.g. manganese). Toth[59] patented a two-stage process where in the 1st stage, alumina was reacted with manganese chloride in the presence of carbon producing aluminium trichloride and manganese, as given in reaction in Eq. (10). The aluminium was extracted by reacting $AlCl_3$ with manganese in the 2nd stage at a temperature sufficient to reduce $AlCl_3$ to Al, according to the following reaction:

$$3 \, Mn_{(l)} + 2 \, AlCl_{3(g)} = 2 \, Al_{(l)} + 3 \, MnCl_{2(l)} \qquad T = 900 \text{ to } 1300^oC \qquad (14)$$
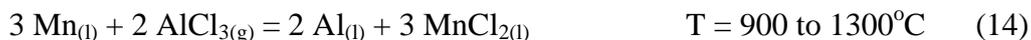
The flowsheet of the process is shown in **Figure 3**. Terry *et al.*[77] modified the process and carried out the reaction at lower temperatures (180 to 600^oC) and higher pressures (0.1 to 3.04 MPa) using solid manganese to form solid aluminium directly according to the reaction:
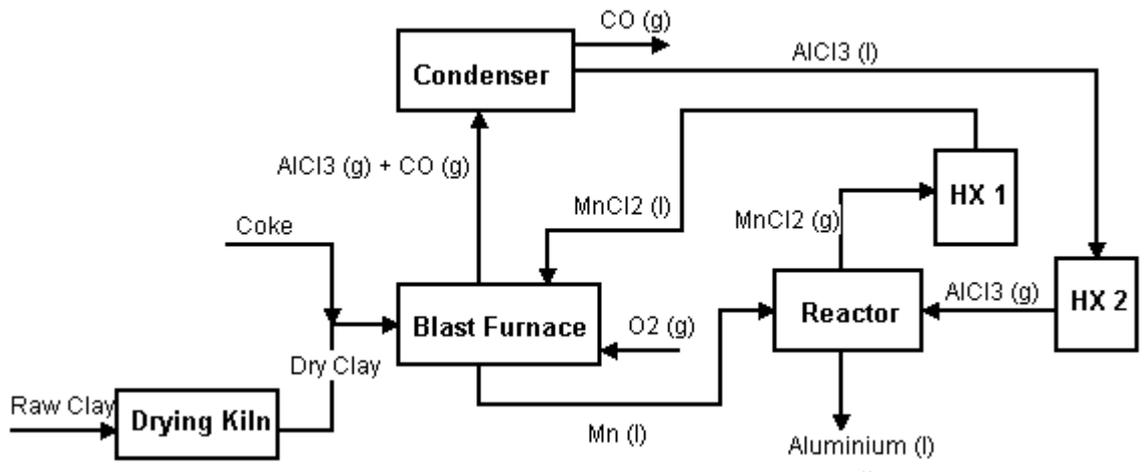
$$3 \, Mn_{(s)} + 2 \, AlCl_{3(g,l)} = 2 \, Al_{(s)} + 3 \, MnCl_{2(s,soln)} \qquad (15)$$
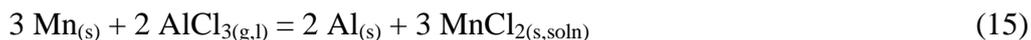
Figure 3 – A flowsheet of Toth process [59].

Table 1: Summary of previous major works/patents in the Chloride Route (*[p] refers to patent; 1st stage refers to production of intermediate Al chlorides; 2nd stage refers to extraction of Al from the chlorides)

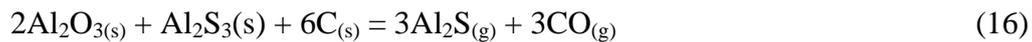| Year	Author	Reactions and Parameters	Process Information
2002	Tomaswick [76 p] (Alcoa)	$AlCl_3$ molten bath with NaCl, LiCl, KCl, $MgCl_2$, $CaCl_2$, $BeCl_2$, $BaCl_2$. T = 300°C preferably (150-200°C). Conc. of alkali metal chloride = 10-50 mol%, Voltage < 2.0 volts. Current density > $0.2A/in^2$.	Electrolysis of Al_2O_3 in a low temperature bath containing $AlCl_3$ and an alkali metal chloride. The bath is at 300°C and solid aluminium is produced at the cathode in the frozen layer of the alkali metal chloride. (**2nd Stage**)
2000	Sharma [74 p]	$AlCl_3 + 3NaF = AlF_3 + 3NaCl$ $3NaCl = 3 Na + 1.5Cl_2$ ⎫ $AlCl_3 = Al + 1.5Cl_2$ $AlCl_3 + 3LiF = AlF_3 + 3LiCl$ $3LiCl = 3Li + 1.5Cl_2$ ⎫ $AlCl_3 = Al + 1.5Cl_2$ $AlF_3 + 3Li = 3LiF + Al$ $AlCl_3 + 3KF = AlF_3 + 3KCl$ ⎫ $3KCl = 3K + 1.5 Cl_2$ ⎫ $AlCl_3 = Al + 1.5Cl_2$ $AlFl_3 + 3K = 3KF + Al$ Electrolytes: Na_3AlF_6-NaCl-NaF; Li_3AlF_6-LiCl-LiF; K_3AlF_6-KCl-KF; Temperature: 750°C	Electrolytic production of aluminium metal from aluminium trichloride using chloride-fluoride salts bath. Aluminium fluoride is separated from the bath and electrolytically reduced to metallic aluminium. (**2nd Stage**)
1990	Wilkening [75 p] (VAW Vereinigte Aluminium-Werke AG)	Electrolyte melt: > 50% consist of NaCl-KCl, 10-40% at least of cryolite, alkali fluorides and alkaline earth fluorides; $AlCl_3$ 3-5%. T = 680-850°C	Production of aluminium from alumina through electrolysis where the bath consists of alkali halides and/or alkali earth halides. Alumina is charged as briquette with carbon which also acts as anode. Bipolar electrodes designs are also used. (**2nd Stage**)
1986	Cohen et al. [73 p] (Pechiney)	$Al_2O_{3(s)} + 3Cl_{2(g)} + 3C_{(s)} = 2AlCl_{3(g)} + 3CO_{(g)}$ T = 660-800°C; Chlorinating gas: Cl_2, CCl_4, C_2Cl_6, phosgene Electrolysis: Conc. of $AlCl_3$ in bath = 10-40 mol% T = 450-900°C	Al production method through carbochlorination of alumina, followed by electrolysis of aluminium trichloride in a molten salt bath containing at least one alkali/alkali earth metal halides. Flowsheet of a continuous process. (**1st & 2nd Stage**)
1986	Rao et al. [8p] (Washington Res. Foundation)	Example for MgF_2 catalyst: $MgF_{2(s)} = MgF_{2(g)}$ $3Al_2O_{3(s)} + 2MgF_{2(g)} + 9CO_{(g)} + 9Cl_{2(g)} = 2MgAl_3F_2Cl_{9(g)} + 9CO_{2(g)}$ $MgAl_3F_2Cl_{9(g)} = MgF_{2(g)} + 3 AlCl_{3(g)}$	The use of catalysts for carbochlorination of Al_2O_3 at 750-950°C. These include: alkali fluorides, alkaline earth fluorides, alkaline earth carbonates, alkaline earth chlorides, alkaline earth bromides, alkaline earth oxides, and their mixtures. (**1st Stage**)
1981	Sinha [78 p] (CSIRO Australia)	Dehydration T = 300-400°C Chlorination T = 400-500°C $2AlCl_3.6H_2O_{(s)} + 12CO_{(g)} + 12 Cl_{2(g)} = 2 AlCl_{3(g)} + 2 CO_{2(g)} + 24 HCl_{(g)}$ Gas Mixture: 40-50%v Cl_2, 30-50%CO, 5-15%CO_2, 5-15%H_2	Development of a process to produce anhydrous aluminium chloride from aluminium chloride hexahydrate. The process involved dehydration and chlorination in a fluidized bed reactor. (**1st Stage**)

1981	Mueller *et al.* [79 p] (Swiss Al Ltd.)	Dilution Agents: quartz, corundum, MgO Size: comparable to starting materials, amount 10-90wt%. Gas flow rates: 2-30cm/sec Conversion: 58-65%	Improved carbochlorination process of aluminous ores in a fluidized bed reactor by the addition of an inert solid dilution agent to the bed. (**1st Stage**)
1981	Loutfy *et al.* [80 p] (Dept of Energy of USA)	$Al_2O_3.Fe_2O_{3(s)} + 6Cl_{2(g)} + 6C_{(s)} = 2AlCl_{3(g)} + 2FeCl_{3(g)} + 6CO_{(g)}$; T = 900-1200 K $Al_2S_{3(s)} + 2FeCl_{3(g)} = Fe_2S_{3(s)} + 2AlCl_{3(g)}$; T = 800K Yield: 99.8%.	Production of aluminium trichloride from aluminous material contains iron, titanium and silicon compound reacting with carbon and a chlorine-containing gas. Produced chloride gases are cooled down to 400 K or lower to condense the aluminium chloride and iron chloride gases then heated to 800K and passed into intimate contact with aluminium sulphide to precipitate solid iron sulphide. (**1st Stage**)
1979	Ishikawa *et al.* [70 p] (Nippon Light Metal Co Ltd)	Electrolyte Bath: $CaCl_2/MgCl_2$(15-70wt%)-(83-15wt%)NaCl; with conc. $AlCl_3$ = 2-15wt%; T = 680-780°C; Current Density: 0.5-2.0 A/cm^2 Current Efficiency: 90-100%	Production of aluminium by electrolysis of fused aluminium chloride together with an alkali metal halide. (**2nd Stage**)
1978	Harvey *et al.* [81 p] (Westinghouse Electric Corp.)	$Al_2O_3.SiO_{2(s)} + 5C + 5Cl_2 = 2AlCl_{3(g)} + SiCl_{4(g)} + 5CO_{(g)}$ $2AlCl_{3(g)} + 3Mn_{(l)} = 3MnCl_{2(g)} + 2Al_{(l)}$ $SiCl_{4(g)} + 2H_{2(g)} = Si_{(l)} + 4HCl_{(g)}$ $MnCl_{2(g)} + O_{2(g)} = Mn_2O_{3(s)} + Cl_{2(g)}$ $Si_{(l)} + Mn_2O_{3(s)} = SiO_{2(s)} + Mn_{(l)}$ T = 1227-1727°C	Production of Al through chlorination of chemically bonded Al_2O_3 and SiO_2 to produce $AlCl_3$ and $SiCl_4$. $AlCl_3$ is then reacted with Mn to produce elemental Al and $MnCl_2$. Oxidizing $MnCl_2$ produces MnO. Reducing $SiCl_4$ by hydrogen to yield silicon which can be used to reduce MnO producing Mn which is recycled to the previous step to reduce $AlCl_3$. (**1st & 2nd Stage**)
1978	Becker *et al.* [58 p] (Alcoa)	$Al_2O_{3(s)} + 3Cl_{2(g)} + 3C_{(s)} = 2AlCl_{3(g)} + 3CO_{(g)}$ Cl_2 Flow Rate: 0.95-3L/min Chlorine to $AlCl_3$: 100%; T = 500-775°C	Production of aluminium chloride by using high purity activated carbon and alumina and bubbling chlorine gas. Aluminium chloride was remove in vapour from and condensed. (**1st Stage**)
1978	Lippman *et al.* [61 p] (Toth Al Corp.)	Bauxite/Clay$_{(s)}$ + $Cl_{2(g)}$ + $C_{(s)}$ = $AlCl_{3(g)}$ + $FeCl_{3(g)}$ + $SiCl_{4(g)}$ + $TiCl_{4(g)}$ + $CO_{(g)}$ + $CO_{2(g)}$; T = 750-850°C Vaporization of $AlCl_3$-$FeCl_3$ mixture, followed by separation of $AlCl_3$ by distillation.	Process for the production of pure aluminium chloride and alumina from aluminous ores through carbochlorination followed by chlorides separation and purification. (**1st Stage**)
1978	Wyndham et al [60 p] (Toth Al Corp.)	$Al_2O_3.2SiO_{2(s)} + 7C_{(s)} + 7 Cl_{2(g)}$ + Sulphur = 2 $AlCl_{3(g)}$ + $2SiCl_{4(g)} + 7CO_{(g)}$ T = 400-1000°C (~700°C)	Improved halogenation of aluminous ores by sulphur treatment; allowing low temperature processing. Sulphur acts as catalyst but no detailed mechanisms were presented. (**1st Stage**)
1978	Pope [82 p] (Alcoa)	N/A	Development of a fluidised bed reactor for chlorination of alumina with multilayer lining. (**1st Stage**)
1977	Holliday *et al.* [83 p] (Comalco Ltd)	$Fe_2O_{3(s)\ (in\ bauxite)} + 3 SO_{2(g)} + 7 CO_{(g)} = Fe_2S_{3(s)} + CO_{2(g)}$ $Fe_2S_{3(s)\ (in\ bauxite)} + Cl_{2(g)} = FeCl_{3(g)}$ + purified bauxite T = 430-750°C Purified bauxite + $Cl_{2(g)}$ → $AlCl_{3(g)}$ (with low Fe content) T = 650-750°C	Removal of iron from bauxite by reaction with SO_2/CO gas mixtures followed by chlorination. (**1st Stage**)
1977	Haupin *et al.* [57 p]	$Al_2O_{3(s)} + 3Cl_{2(g)} + 3C_{(s)} = 2AlCl_{3(g)} + 3CO_{(g)}$	Production of aluminium chloride by reaction of aluminium oxide, carbon and

|			
	(Alcoa)	Molten bath: $AlCl_3$-NaCl-LiCl Cl_2 conversion to $AlCl_3$: 99%; T = 400-950°C	chlorine in an alkali metal halides and alkaline earth metal halides molten salt bath. Aluminium chloride was separated by vaporization. **(1st Stage)**
1975	Terry *et al.* [77 p] (Toth Al Corp.)	$3Mn_{(s)} + 2AlCl_{3(g,l)} = 3MnCl_{2(s,soln)} + 2Al_{(s)}$ Pressure range: 15-450 psi. Temperature: 180-600°C; Time: ~2hrs $AlCl_3$ Flow Rate: 0.75-3.20 g/hr	A method of producing aluminium wherein aluminium chloride in liquid phase reacted with manganese in solid phase. The manganese reduces aluminium chloride and forms essentially elemental aluminium and manganese chloride. **(2nd Stage)**
1975	Dell *et al.* [71 p] (Alcoa)	$AlCl_{3(l)} = Al_{(l)} + 1.5Cl_{2(g)}$ Electrolyte: 50-75% NaCl and 25-50%$LiCl_2$ Conc. $AlCl_3$: 1.5-10wt%; T = 660-730°C	Design and development of electrolytic cell with intermediate bipolar electrodes. This allows the flow of bath melt and settling of Al metal. Anode-cathode distance/spacing of less than ¾ inch. **(2nd Stage)**
1975	Othmer [68 p]	$3 AlCl_{(g)} = 2 Al_{(l)} + AlCl_{3(g)}$ $2 AlCl_{3(g)} + 6 S_{(l)} = 2 Al_{(l)} + 3 S_2Cl_2(g)$ T = 600-1000°C Other reactions above 1500°C: $Al_2O_{3(s)} + S_2Cl_{2(g)} + 3C_{(s)} = 2 AlCl_{(g)} + 2 S_{(l)} + 3 CO_{(g)}$ $2 Al_2O_{3(s)} + 2 S_2Cl_{2(g)} + O_{2(s)} = 4 AlCl_{(g)} + 4 SO_{2(g)}$	Extraction of aluminium from aluminium trihalide by halogenation and/or disproportionation in a flash condenser. **(2nd Stage)**
1974	Othmer [67 p]	$Cl_{2(g)} + Al_2O_{3(s)} + 3C_{(s)} = 2AlCl_{(g)} + 3CO_{(g)}$ $SiCl_{4(g)} + 2Al_2O_{3(s)} + 4C_{(s)} = 4AlCl_{(g)} + 4CO_{(g)} + SiO_{2(s)}$ $AlCl_{3(g)} + Al_2O_{3(s)} + 3C_{(s)} = 3AlCl_{(g)} + 3CO_{(g)}$ T = 1000-1200°C Removal of Fe impurities: $2AlCl_{2(g)} + Fe_2O_{3(s)} = 2FeCl_{3(g)} + Al_2O_{3(s)}$ Disproportionation T = 700°C $3AlCl_{(g)} = 2Al_{(l)} + AlCl_{3(g)}$	Separation of Aluminium from aluminous ores (bauxites, clays, feldspar, etc) through the formation of volatile tri-halide, followed by disproportionation of tri-halide to metallic aluminium. **(1st and 2nd Stage)**
1973	Russell *et al.* [18 p] (Alcoa)	$AlCl_{3(l)} = Al_{(l)} + 1.5Cl_{2(g)}$;T = 660-730°C Electrolyte: NaCl-$LiCl_2$ (50:50 wt) Conc. $AlCl_3$ in bath 1-15wt%; oxide impurities<0.25wt% ACD: 1inch, Current density: 10A, Voltage: < 5V, Current Efficiency: 80%	Production of aluminium by continuous electrolysis of aluminium trichloride. Increase of current efficiency of the process (avoiding the formation of sludge) using proposed operating conditions **(2nd Stage)**
1971	Toth [59 p] (Applied Al Research Corp.)	$Al_2O_{3(s)} + 3MnCl_{2(l)} + 3C_{(s)} = 3Mn_{(l)} + 2AlCl_{3(g)} + 3CO_{(g)}$ $3Mn_{(l)} + 2AlCl_{3(g)} = 2Al_{(l)} + 3MnCl_{2(l)}$ T = 900-1300°C	Production of aluminium by a two-steps process comprising the reaction of alumina with manganese chloride in the presence of carbon to form aluminium trichloride and manganese and the subsequent reaction of aluminium trichloride with manganese at a temperature sufficient to reduce aluminium trichloride to aluminium. **(1st and 2nd Stage)**
1948	Ferguson *et al.* [50p] (Standard Oil Development Co)	$Al_2O_{3(s)} + 3C_{(s)} + 3Cl_{2(g)} = 2AlCl_{3(g)} + 3CO_{(g)}$ T = 649-816°C	Production of Al-chloride and Al-bromides. Development of a continuous process using a "fluidised mixture" type reactor **(1st Stage)**
1939	Willmore [62 p] (Alcoa)	$3 AlF_{(l)} = 2 Al_{(s)} + AlF_{3(s)}$ T = 900°C-1000°C	Disproportionation of Al-halides, including Al-chlorides **(2nd Stage)**

3.3 Carbosulphidation Route

Another alternative aluminium production method that has received a less attention is through the formation of aluminium sulphides (Al_2S_3 and AlS), as intermediate compounds. One of the first patented works on the carbothermic production of Al_2S_3 was by Haglund[84]. Haglund produced a mixture of Al_2O_3 and Al_2S_3 from the reaction between Al_2O_3-containing ores, carbon as reduction agent, and sulphur sources in the form of FeS and ZnS. FeS was added in the form of a lump (mixed with uncalcined bauxite) where it was sink through the formed slag into the liquid iron alloy underlying the slag. Aluminium sulphide was formed as part of the reaction products, while aluminium was contained in the iron alloy.

In 1958, Weiss[85] proposed a method for producing aluminium from a mixture of aluminous ores and Al_2S_3 reacted with carbon at temperatures above 1000^oC at pressures below atmospheric pressure. The reaction resulted in vapors of aluminium subsulphide (such as Al_2S) which upon cooling disproportionated into aluminium sulphide (Al_2S_3) and aluminium precipitate. The reactions are given below;

$$2Al_2O_{3(s)} + Al_2S_3(s) + 6C_{(s)} = 3Al_2S_{(g)} + 3CO_{(g)} \qquad (16)$$
$$3Al_2S_{(g)} = Al_2S_{3(g)} + 4Al_{(s)} \qquad (17)$$

Weiss proposed the process to be carried out at 1000-1200^oC at pressure below 5 mmHg. The process could be carried out at higher pressures if the temperature of the process is increased, e.g. at temperature above 2000^oC, the process can be carried out at atmospheric pressure.

Loutfy *et al.*[86] studied the thermodynamics of the carbosulphidation of alumina and patented an aluminium production process in 1981[87]. Aluminous ores were reacted with carbon and sulphur containing gas at temperatures 1027 to 1227 ^{o}C to obtain molten aluminium sulphide (Al_2S_3) and CO gas according to the following reaction:

$$Al_2O_{3(s)} + 3C_{(s)} + 1.5S_{2(g)} = Al_2S_{3(l)} + 3CO_{(g)} \qquad (18)$$
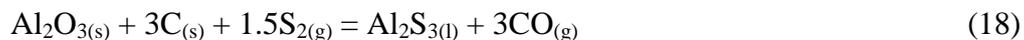
The Al_2S_3 was further heated at temperatures 1327 to 1627^oC to produce aluminium monosulphide (AlS) and sulphur. Then AlS was cooled to a temperature 927 to 1097^oC where it disproportionated to molten aluminium sulphide (Al_2S_3) and aluminium metal following the reactions:

$$Al_2S_{3(l)} = 2AlS_{(l)} + S_{(g)} \qquad (19)$$

$$3AlS_{(l)} = Al_2S_{3(l)} + Al_{(l)} \qquad (20)$$

The $Al_2S_3(l)$ produced from the reaction in Eq. 20 was then electrolysed to extract the aluminium. The flowsheet of the process is shown in **Figure 4**.
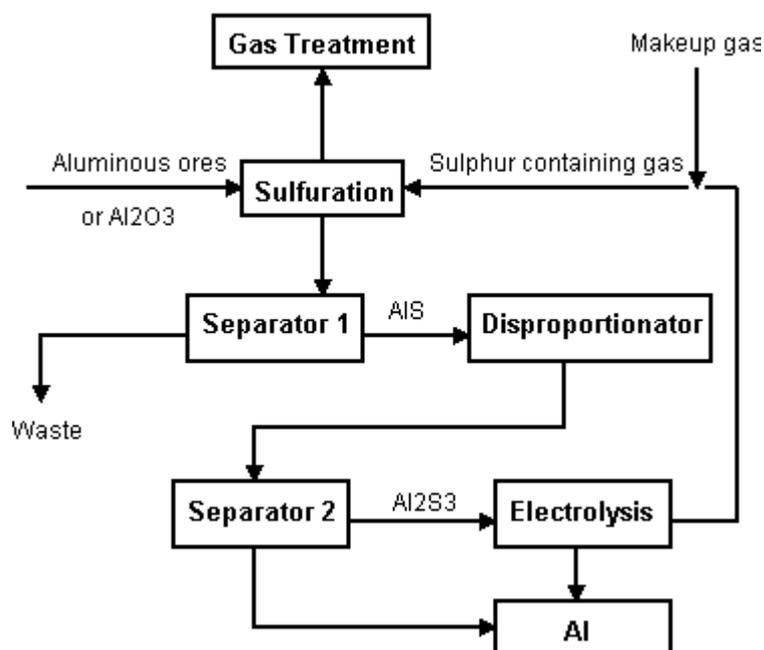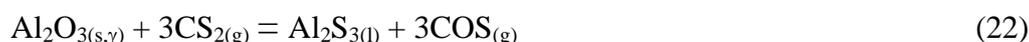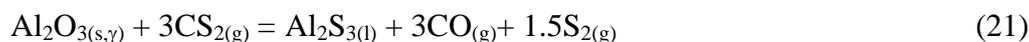
Figure 4 - A flowsheet of aluminium production through carbosulphidation followed by combination of disproportionation and electrolysis proposed by Loutfy *et al.*[87]

Sportel and Verstraten[88] (of Corus Aluminium GmbH) produced Al_2S_3 from γ-Al_2O_3 using CS_2 gas at $850^{\circ}C$ according to the following reactions:

$$Al_2O_{3(s,\gamma)} + 3CS_{2(g)} = Al_2S_{3(l)} + 3CO_{(g)} + 1.5S_{2(g)} \tag{21}$$

$$Al_2O_{3(s,\gamma)} + 3CS_{2(g)} = Al_2S_{3(l)} + 3COS_{(g)} \tag{22}$$

The carbon disulphide was produced by reacting methane with sulphur gas through the following reactions:

$$CH_{4(g)} + 2S_{2(g)} = CS_{2(g)} + 2H_2S_{(g)} \tag{23}$$

$$3H_2S_{(g)} + 1.5O_{2(g)} = 3S_{(g)} + 2H_2O_{(g)} \tag{24}$$

The process is preferably performed in the range 750 to $1100^{\circ}C$ and 5×10^5 to 35×10^5 Pa. Typically a temperature of $850^{\circ}C$ and 30×10^5 Pa is applied if solid Al_2S_3 is required[88]. This temperature was proposed to avoid transformation of γ-Al_2O_3 to α-Al_2O_3. It was shown that the reaction rate between γ-Al_2O_3 and $CS_{2(g)}$ is higher compared to reaction rate between α-Al_2O_3 and $CS_{2(g)}$. It was proposed that the resulting Al_2S_3 is then electrolysed to extract the aluminium. This route (carbosulphidation followed by electrolysis) is the basis of the Corus - Compact Aluminium Production Process (CAPP). The proposed flowsheet for this process is shown in **Figure 5**.
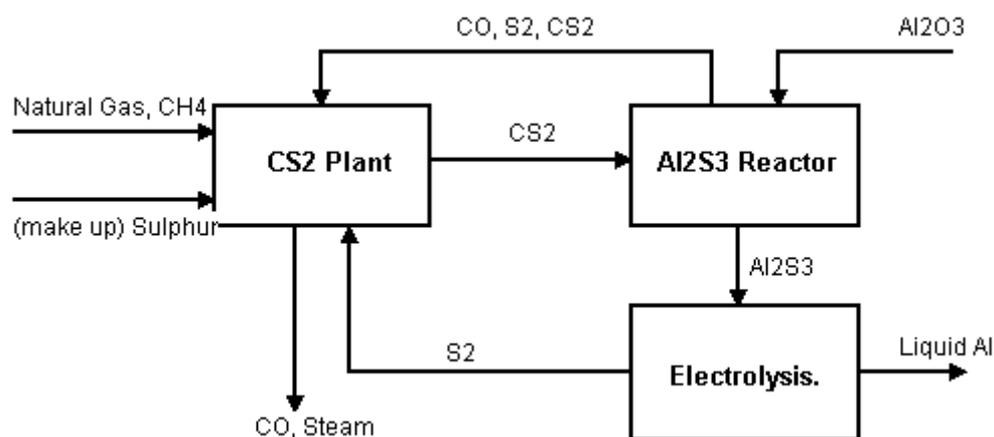
Figure 5 - A flowsheet of compact aluminium production process (CAPP^{TM})[88]

Xiao *et al.*[89], studied the kinetics of the sulphidation of alumina with CS_2 gas at ambient pressure. They suggested that the optimum temperature for sulphidation of γ-Al_2O_3 is around 850°C. In the experimental conditions studied, they reported that the particle size of γ-Al_2O_3 had no effect on the reaction rate. A maximum conversion ratio of about 40% after 5 hours of reaction at the conditions studied was achieved.

Li *et al.*[90] investigated the possibility of direct formation of aluminium monosulphide (AlS) by reacting alumina-carbon mixture with FeS according to the following reaction:

$$Al_2O_{3(s)} + 3C_{(s)} + 2\ FeS_{(s)} = 2AlS_{(g)} + 3CO_{(g)} + 2Fe_{(s)} \qquad (25)$$

They suggested the above reaction can be carried out at temperatures as low as 407-597°C at pressure range of 15 to 300 Pa.

Previous major works on the production of aluminium from alumina (or aluminous ores) through carbosulphidation reactions followed by various aluminium extraction process (Stage 1 and 2) are summarised in **Table 2**.

3.4   Extraction of Aluminium from Aluminium Sulphides

The literature review on the production of aluminium through carbosulphidation route revealed that the methods proposed to extract aluminium from its sulphides are disproportionation and electrolysis.

Disproportionation of Aluminium Sub-Sulphides

The basis of aluminium extraction by dispropotionation is through dissociation of aluminium sub-sulphides to aluminium sulphide (Al_3S_2) and aluminium upon cooling (e.g. at temperature below the disproportionation temperature of associated sub-sulphides). Weiss[85] suggested the disproportionation of $Al_2S_{(g)}$ sub-sulphide as per reaction given in Eq. (17) at pressure 5 mmHg and temperature of 1200°C. Loutfy *et al.*[86] proposed an extraction of liquid

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aluminium through disproportionation of $AlS_{(l)}$ sub-sulphide at temperature between 927 and 1097°C following reaction in Eq. (20). Loutfy et al.[86] did not provide information on the pressure for the process. Thermodynamic analysis carried out by Rhamdhani et al.[91] showed that the reaction in Eq. (20) does not occur at ambient pressure. Although mentioned in a number of patents[85-86], there is a limited published work on the details of thermodynamics and kinetics of the disproportionation reactions of aluminium sub-sulphides. Further studies on the thermodynamics and kinetics of aluminium sub-sulphide disproportionation are needed for optimisation of the process.
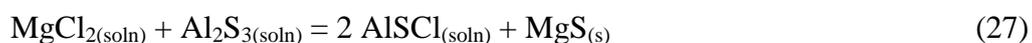
Electrolysis of Aluminium Sulphide

The extraction of aluminium metal by electrolysis of aluminium sulphide in molten salts is attractive from the viewpoint of energy utilization. By improving the cell design and electrolyte composition, the theoretical energy consumption can be reduced to 8.41 kWh/kg Al which is considerably lower than the value of 14 kWh/kg Al in the current Hall-Heroult process[92]. Aluminium sulphide ($Al_2S_{3(s)}$) has a lower theoretical decomposition potential, compared to $Al_2O_{3(s)}$ and $AlCl_{3(l)}$[93]. $Al_2S_{3(s)}$ can be electrolytically decomposed in a molten cryolite between 727 and 927°C[87] to produce molten Al and sulphur gas that can be recycled for CS_2 production.

The early works on the electrolysis of Al_2S_3 in a mixture of cryolite with NaCl were from German and Russian scientists (in 1930's and early 1940's). In these studies, a maximum current efficiency of 55% was reported[94-96]. The overall reaction for electrolysis of Al_2S_3 in molten electrolyte follows:

$$Al_2S_{3(soln)} = 2Al_{(l)} + 1.5S_{2(g)} \qquad (26)$$

In the early 1980's, Minh et al.[93,97] electrolysed Al_2S_3 to extract aluminium in an electrolytic bath containing alkali metal chloride and alkaline earth metal chlorides ($MgCl_2$-NaCl-KCl and $MgCl_2$-NaCl-KCl-$AlCl_3$). They carried out the process at 750°C and found out that the limiting current density for the process was at the graphite anode. Within the current density range investigated (0.2-1.2 A/cm^2), current efficiencies of 75 to 85% were claimed. Minh et al.[98] further patented the work in 1984. In this work it was suggested that the process be carried between 700 to 800°C, with the concentration of $MgCl_2$ in the electrolyte between 20 and 70 mol% with a balance of NaCl, KCl and $AlCl_3$. The solubility of the Al_2S_3 was about 3 wt% at 750°C, but could be enhanced by the presence of $MgCl_2$ and $AlCl_3$ according to the following reactions:

$$MgCl_{2(soln)} + Al_2S_{3(soln)} = 2\ AlSCl_{(soln)} + MgS_{(s)} \qquad (27)$$

$$AlCl_{3(soln)} + Al_2S_{3(soln)} = 2\ AlSCl_{(soln)} \qquad (28)$$

In the 2000's, Corus developed a process for Al extraction through electrolysis of Al_2S_3, as part of development of the CAPP process. Lans *et al.*[99-100] electrolysed Al_2S_3 and obtained aluminium melt and sulphur gases at the anode according to reaction given in Eq.(26). A molten electrolyte of $MgCl_2$-NaCl-KCl (50:30:20 mol %) was used and cryolite (~10 wt%) was added to enhance the solubility of Al_2S_3 and increase the activities of Al and S in the melt. This resulted in an increase in the current density up to three times. This work was the basis of the Corus patent (Van Der Plas[101]) in 2004. Further studies were carried out by Xiao *et al.*[92] to investigate in detail the mechanism of the process. It was concluded that the electrolytic process was governed by its ohmic drop. The production of sulphur bubbles at the anode was suggested to significantly affect the ohmic drop. Addition of cryolite changed the characteristic of the sulphur bubbles layer thus decreasing the ohmic drop. Increased Al_2S_3 solubility due to the cryolite addition resulted in a higher limiting current density. It was reported that a current efficiency of 62% can be achieved.

In 2006, Corus[102] developed a continuous production process of aluminium from alumina. In the first stage, alumina was dissolved in a molten salt and a sulphur containing gas (in particular CS_2) was fed through the melt; this resulted in partial conversion of alumina to aluminium sulphide. Aluminium was then separated from aluminium sulphide in a multi-pole electrolysis cell. The process was carried out at temperatures 800-900°C, at pressures above $3x10^5$ Pa in a KCl-NaCl-(10wt%) cryolite mixture.

Table 2: Summary of previous major works/patents in the Sulphide Route (*[p] refers to patent; 1st stage refers to production of intermediate Al sulphides; 2nd stage refers to extraction of Al from the sulphides)

Year	Author	Reactions and Process Parameters	Process Details
2007	Xiao et al. [92]	$Al_2S_3 = 2Al + 1.5S_{2(g)}$ Electrolytes: $MgCl_2$-NaCl-KCl Temperature: 700^oC. Yield: 42%, Current Efficiency: 62% Energy Required: 13.4 kWh/kg	The electrochemical behaviour of Al_2S_3 in molten salt on a laboratory scale. Temperature and cryolite addition have a positive effect on the current density. **(2nd Stage)**
2006	Van Der Plas et al. [102 p] (Corus Aluminium)	Temp: $800-900^oC$ Pressure: $\geq 3 \times 10^5$ Pa Salt mixture: KCl-NaCl-10 %wt. Cryolite Sulphidation gas: mainly CS_2	Continuous production of aluminium from alumina including a first step of converting alumina into aluminium sulphide (Al_2S_3) and a second step of separation of aluminium from aluminium sulphide in a separating reactor. In the first step, alumina is dissolved in a molten salt. Sulfur containing gas is fed through the melt. It is proposed that Al extraction is carried through electrolysis in multi-pole cell **(1st & 2nd Stage)**
2004	Xiao et al. [89]	$CH_{4(g)} + 2S_{2(g)} = CS_{2(g)} + 2H_2S_{(g)}$ $Al_2O_{3(\gamma)} + 3CS_{2(g)} = Al_2S_3 + 3CO_{(g)} + 1.5\ S_{2(g)}$ $Al_2S_3 = 2Al + 1.5S_{2(g)}$ Sulphidation T $= 850^oC$. Yield: 40%	Investigation of sulphidation kinetics of Al_2O_3 with CS_2 gas. The alumina with a higher specific surface area results in a higher sulphidation ratio. The particle size of γ-Al_2O_3 has no effect on the reaction ratio. **(1st & 2nd Stage)**
2004	Van Der Plas [101p] (Corus Technology BV)	Cathode: $Al^{3+} + 3e^- = Al$ Anode: $2S^{2-} = S_{2(g)} + 4e^-$ Overall: $Al_2S_3 = 2Al + 1.5S_{2(g)}$ Electrolytes: $MgCl_2$-NaCl-KCl T $= 700-800^oC$. Current Efficiency: 80%	Production of aluminium by electrolysis of Al_2S_3 in multipolar cell, using a molten chloride salt bath. The sulphur gas was collected and recycled to produce CS_2 which was used in the sulphidation step. $MgCl_2$ is added to the bath to increase solubility of Al_2O_3. Cryolite may also be added. **(2nd Stage)**
2003	Sportel et al. [88 p] (Corus Aluminium)	$3H_2S + 1.5O_2 = 3S + 3H_2O$ $CH_4 + 2S_2 = CS_2 + 2H_2S$ (T $= 550-650^oC$) $2Al_2O_3 + 6CS_2 = 2Al_2S_3 + 6CO + 3S_2$ $Al_2O_3 + 3CS_2 = Al_2S_3 + 3COS$ T $= 750-1000^oC$. P $= 1 \times 10^5$ to 40×10^5 Pa	Production of primary aluminium from alumina comprising the step of converting alumina into aluminium sulphide (Al_2S_3) and subsequently aluminium is separated from aluminium sulphide. γ-alumina is preferred for the reaction due to better kinetics. Three reactors were proposed: (1) for manufacturing CS_2, (2) for manufacturing Al_2S_3 from Al_2O_3 and CS_2, and (3) electrolysis cell for Al extraction **(1st Stage)**
1984	Minh et al. [98 p] (Dept of Energy of USA)	$MgCl_{2(soln)} + Al_2S_{3(s)} = 2AlSCl_{(soln)} + MgS_{(s)}$ Temperature: $700-800^oC$, Voltage < 2-3 V Conc. Al_2S_3 in bath 2-10 mol% Electrolytes: $MgCl_2$(20-70mol%)-NaCl-KCl $MgCl_2$-NaCl-KCl-$AlCl_3$(1-10mol%) Current Efficiency: 75-85%	Production of aluminium through electrolysis of Al_2S_3 utilizing an electrolytic bath containing alkali metal chloride and/or alkaline earth metal chloride to provide improved operating characteristics of the process. **(2nd Stage)**
1981	Loutfy et al. [87p] (Dept of Energy of USA)	$Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO$; T $= 1027-1227^oC$ $Al_2S_3 = 2AlS + S$; T $= 1327-1627^oC$ $3AlS = Al_2S_3 + Al$; T $= 927-1097^oC$	Aluminium ore is reacted with carbon and sulphur containing gas at elevated temperatures forming molten aluminium sulphide which is decomposed to aluminium sub-sulphide (AlS). Then aluminium monosulphide is cooled to below its disproportionation temperature to produce aluminium metal. Blended aluminous ores

			and coke were used. (**1st & 2nd Stage**) Note: Current thermodynamic analyses indicate that the proposed reactions of the 2nd stage of the process do not occur at the conditions specified.
1958	Weiss [85 p] (Vereinigte Aluminium-Werke AG)	$2Al_2O_{3(s)} + Al_2S_3(s) + 6C_{(s)} = 3Al_2S_{(g)} + 3CO_{(g)}$ $3Al_2S_{(g)} = Al_2S_{3(g)} + 4Al_{(s)}$ $T = 1000\text{-}1200^oC$ at $P < 5mmHg$ $T > 2000^oC$ at $P = 0.1MPa$	Production of aluminium from aluminous ores by reactions of a mixture of aluminous ores, Al_2S_3 and carbon. The reaction produce vapours of aluminium sub-sulphide which upon cooling produce aluminium sulphide and aluminium precipitate. (**1st Stage and 2nd Stage**)
1931	Haglund [84 p]	N/A	Production of mixture of Al_2O_3 and Al_2S_3 by reaction between Al_2O_3–containing materials, reduction agents (carbon) and sulphur sources (FeS, ZnS). (**1st Stage**)

3.5 Carbonitridation Route

Selvaduray and Sheet[103] and Haussonne[104] provided a review on various methods for the synthesis of aluminium nitride. In general the methods can be classified into: carbonitridation reactions, direct nitridation, floating nitridation, CVD (chemical vapour deposition), vapour phase reactions, and reactions utilising organometallic precursors[103]. Only the carbonitridation route will be described in this paper, as it is the route most relevant to industrial scale production of metal.

Carbonitridation of alumina and aluminous ores is a well-known process. It follows an overall reaction of:

$$Al_2O_{3(s)} + 3C_{(s)} + N_{2(g)} = 2AlN_{(s)} + 3CO_{(g)} \tag{29}$$
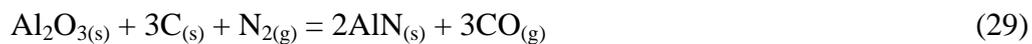
Rather than for aluminium production, the original aim of the process was to produce aluminium nitride or to purify alumina from its ores. In the later case, for example in the Serpek[105] process, a mixture of bauxite and coke is heated in an electric furnace in the presence of nitrogen to produce aluminium nitride. Aluminium nitride can then be hydrolysed through reaction with water to form pure alumina and ammonia. The reaction can be carried out even at ambient temperature[106-107] but at slow reaction rates[108].

Considerable disagreement exists in the literatures concerning the detailed reaction steps for nitride formation. Hirai $et\ al.$ [109] synthesized $AlN_{(s)}$ from $Al_2O_{3(s)}$ and graphite at temperatures between 1500^oC and 1700^oC. They observed a small quantity of aluminium oxynitride, AlON, when alumina graphite mixture was heated at 1700^oC[109]. Their results indicated that the reaction rate was not affected by the grain size of graphite, pellet diameter and flow rate of N_2; and they suggested that the diffusion of the reactant gas through the $AlN_{(s)}$ layer (formed around $Al_2O_{3(s)}$) was the rate determining step. Lefort and Billy[110] argued that the rate determining step suggested by Hirai $et\ al.$ was unlikely as the apparent activation energy (~530 kJ/mol) was beyond what would be expected from a limiting gaseous diffusion. Lefort and Billy suggested that the rate limiting process was the combustion of carbon and suggested the following reaction steps:

$$Al_2O_{3(s)} = 2Al_{(g)} + 1.5O_{2(g)} \tag{30}$$

$$3C_{(s)} + 1.5O_2 = 3CO_{(g)} \text{ (rate limiting step)} \tag{31}$$

$$2Al_{(g)} + N_{2(g)} = 2AlN_{(s)} \tag{32}$$

The dissociation of alumina was suggested to be controlled by the very low partial pressure of oxygen in contact with carbon, and followed by fast nitridation of the aluminium vapor formed. Lefort and Billy recommended temperatures from 1550^oC to 1600^oC for the process.

Chen and Lin[111], studied a carbonitridation of alumina at temperatures from 1375°C to 1552°C and developed a kinetic model for the process. A mixed mechanism was proposed comprising reaction between $Al_2O_{3(s)}$ and $C_{(s)}$ to form $Al_2O_{(g)}$ and $CO_{(g)}$, followed by surface reaction between $Al_2O_{(g)}$ and $N_{2(g)}$ to form $AlN_{(s)}$[111-112]. They suggested that the formation of $Al_2O_{(g)}$ is the rate limiting step according to:

$$Al_2O_{3(s)} + 2C_{(s)} = Al_2O_{(g)} + 2CO_{(g)} \tag{33}$$

Aluminium monocyanide, $AlCN_{(s)}$, can also form as described by Perieres and Bollack (Pechiney)[113] according to

$$AlN_{(s)} + C_{(s)} = AlCN_{(g)} \tag{34}$$

A preferred temperature of 1700°C was recommended for nitride preparation as the formation of $AlCN_{(g)}$ increases above 1700°C, which explains the apparent decrease in nitride formation and the presence of aluminium carbide in the condensates[113]. Aluminium monocyanide vapour can react with aluminium vapour forming solid encrustations of carbide and nitride.

Ide et al.[114] produced $AlN_{(s)}$ through carbonitridation of alumina at temperatures 1350°C-1450°C using $CaF_{2(s)}$ as catalyst. They reported that nitridation rate tended to increase with decreasing particle size of alumina and was affected by the history of the alumina used in the reaction. They observed the formation of intermediate compounds $CaO^.6Al_2O_3$ (CA$_6$) and $CaO^.2Al_2O_3$ (CA$_2$) and suggested that the process proceeded through the nitridation of the intermediate compounds from liquid phase system CaF_2-CA$_6$-CA$_2$. Molisani and Yoshimura[115] investigated the effect of various additives (0.5-3 wt% of CaF_2, Y_2O_3, Li_2CO_3 and $SrCO_3$) on the carbonitridation of alumina at 1300-1400°C. The addition of these additives (and their mixture combinations) was reported to reduce the synthesis temperature by a maximum of 200°C. They attributed this to the formation of aluminate phases that easy to vaporize at lower temperature.

Bartnitskaya et al.[116] studied the carbonitridation reaction at temperatures from 1800 to 1900°C in a static condition (closed system) under nitrogen atmosphere of 0.2 to 0.3 MPa. They obtained isometric AlN particles of 2 to 6 μm as opposed to fibrous type particles usually obtained in reaction carried out in a stream of nitrogen gas. They suggested that in the case of reaction at a high nitrogen pressure, alumina dissociation is suppressed which exludes the possibility of reaction in the gas phase, hence the formation of isometric particles. Chowdhury et al.[117] synthesized nano size $AlN_{(s)}$ by nitridation of C-Al_2O_3 composite particles at 1500-1600°C in an over pressure (0.4 MPa) flowing nitrogen gas. A mixture of fibrous and spherical particles was obtained.

Joo and Jung[118] investigated the effect of CO content in the N_2-CO gas mixture for carbonitridation reaction from 1000 to 1600°C. They used Al-hydroxosuccinate as precursor for the reaction. The carbonitridation reaction was found to be retarded with increasing content of CO in the mixed gas. They observed conversion sequence from ρ-Al_2O_3 to γ-Al_2O_3 to $AlN_{(s)}$ (or to δ-Al_2O_3) depending on the CO content in the gas mixture. Qin et al.[119] prepared C-Al_2O_3 composite particles from $Al(NO_3)_3 \cdot 9H_2O$, $CO(NH_2)_2$, and $C_6H_{12}O_6 \cdot H_2O$ and carried out the nitridation at 1000-1600°C in a flowing nitrogen gas. They reported a conversion to γ-Al_2O_3 followed by direct conversion to $AlN_{(s)}$ upon nitridation. Complete conversion was observed at 1400°C.

Galvez et al.[108] produced $AlN_{(s)}$ using concentrated thermal radiation through reduction of Al_2O_3 using activated C (and CH_4) in a flowing nitrogen. The radiative fluxes used were equivalent to solar concentration exceeding 4500 kW/m^2 and the reaction was carried out at 1827-2027°C. In the case of carbothermal-nitridation reaction (reaction given in Eq.28), the experimental data were fitted into a solid-solid reactions model with an apparent activation energy of 360 kJ/mol. In the case of reduction using CH_4 (methanothermal reduction), the overall reaction follows:

$$Al_2O_{3(s)} + 3CH_{4(g)} + N_{2(g)} = 2AlN_{(s)} + 6H_{2(g)} + 3CO_{(g)} \qquad (35)$$
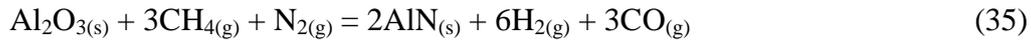
In this case, a low conversion (~10%) was observed. It was suggested that the diffusion is hindered by a carbon layer produced from the decomposition of CH_4. The kinetics, however, may be enhanced by doping the alumina with metallic particles (such as Ni and Fe). Best results were obtained when Ni is used, where it acts as nucleation site for carbon filament growth.

Galvez et al.[120] also investigated the carbothermal reduction of alumina in nitrogen atmosphere at temperatures between 1500 and 1700°C. The kinetics were described as solid-solid reactions and fitted to Jander and Ginstling-Brounshtein models with activation energies of 815 and 757 kJ/mol, respectively. They also evaluated various types of carbon sources and reported that the reaction rates vary for different carbons (listed in decreasing order of reaction rates: petcoke, activated carbon, wood charcoal, and carbon black)[121].

Baik et al.[122] and Kuang et al.[123] produced aluminium nitride through carbonitridation using sucrose precursors. Zhang and Gao[124] produced nanocrystalline aluminium nitride from δ-Al_2O_3 nanoparticles in flowing ammonia. They reported that the nanocrystalline δ-Al_2O_3 was converted into $AlN_{(s)}$ completely at temperatures 1350 to 1400°C within 5 hours in a single-step synthesis process. Xi et al.[125] synthesized $AlN_{(s)}$ by carbothermal reduction using a mechanically activated Al_2O_3. They showed that carbonitridation can be carried out at

temperature as low as 1100°C and completed thoroughly at 1250°C when milled Al$_2$O$_3$ (for 20 hours) was used.

There are two primary methods to prepare AlN powders in an industrial scale[103]: (1) direct nitridation of Al with N$_2$ (2Al + N$_2$ = 2AlN), and (2) carbothermal reduction of Al$_2$O$_3$ with carbon black (or other carbonaceous sources) in the presence of N$_{2(g)}$ at 1500-2000°C (reaction in Eq. 29). The former is beyond the scope of this paper. In terms of technological developments, a number of aluminium nitride production processes by carbonitridation in nitrogen or mixed gas atmosphere have been patented. A summary of these studies are presented in Table 3.

One of the first patents in the carbonitridation of alumina was from Shoeld[126] in 1918 where he carried out the reaction at 1800-2000°C. In the 1960's, Pechiney[113, 127-128] patented various carbonitridation processes. Perieres and Bollack[113] produced AlN powder to 99% by roasting the produced AlN$_{(s)}$ from carbonitridation reaction in an oxygen-free atmosphere at 700-800°C to burn off the excess carbon. Clair[127] developed a vertical-shaft counter-current reactor for continuous production of aluminium nitride, while Paris and Perieres[128] used a mixed environment of nitrogen and hydrocarbon gas for carbonitridation of alumina at 1200-1700°C. The hydrocarbon gas was cracked to elemental carbon in a highly reactive state in uniform distribution throughout the aluminium oxide particle.

Kuramoto et al.[129] produced AlN powder from alumina and carbon by firing the mixture at 1400-1700°C in nitrogen (or ammonia) gas atmosphere followed by heating at 600-900°C to improve the purity to 94%. Bolt[130] patented a method to produce aluminium nitride films (and fibres) using precursors containing alumina and carbon.

In the 1990's, a number of AlN$_{(s)}$ production processes were patented by various companies. Nakano et al.[131] patented a process using very fine source materials (<5μm). Dunn et al.[132] increased the purity of AlN$_{(s)}$ produced by carbonitridation by applying mechanical agitation. Most of the impurities remain in the outer zone of the pellet and a significant amount of the surface portion is removed to improve the purity of the final aluminium nitride product. Dorn et al.[133] produced AlN$_{(s)}$ through calcinations of aluminium hydroxide-carbon mixtures at temperatures from 400 to 1000°C followed by nitridation from 1400 to 1700°C. Ravenel et al.[134-135] patented a process for continuous production of aluminium nitride from 1350 to 2000°C using a moving bed reactor. Kotaka et al.[136] patented a process to produce AlN$_{(s)}$ from γ-Al$_2$O$_3$ using mixtures of ammonia and hydrocarbons from 1200 to 1700°C and claimed to obtain purity of 99%.

3.6 Extraction of Aluminium from Aluminium Nitride

One of the ways to extract aluminum from aluminum nitride is through thermal dissociation. The thermal dissociation of aluminium nitride occurs at a temperature above $2400^{\circ}C$ at 0.1MPa according to reaction:

$$AlN_{(s)} = Al_{(g)} + 0.5N_{2(g)} \tag{36}$$

The temperature of the dissociation can be reduced by operating the process at lower pressures or in a vacuum condition. Thermodynamic calculations[91] showed that the dissociation temperature can be reduced to around $1700^{\circ}C$ if the pressure is reduced to 0.1kPa.

The theoretical decomposition voltage of aluminium nitride to aluminium and nitrogen is 0.75V at $700^{\circ}C$. This is a lower decomposition voltage than that of $AlCl_{3(l)}$, $Al_2S_{3(s)}$ and $Al_2O_{3(s)}$ at the same temperature. From the thermodynamic point of view, electrolysis has a good potential to be used for extracting aluminum from aluminium nitride. One of the major challenges is to find the appropriate electrolytes that can dissolve the very stable $AlN_{(s)}$. Bonomi et al.[137] carried out a limited study on the solubility and the electrolysis of AlN in molten salt (Li_3N-LiCl) bath at 660-$700^{\circ}C$. The current efficiency for this system was 83% with a cathodic current density of about $1.5A/cm^2$. No further results indicating the successful of the process have been presented. Goto et al.[138] used the salt system of LiCl-KCl-Li_3N to deposit AlN film onto Al substrate. **Figure 6** shows the E-pN^{3-} diagram for the Al-N system in a LiCl-KCl eutectic melt at $450^{\circ}C$ showing the region where Al solid is stable. Yan[139] conducted a direct electrochemical reduction of AlN cathode in a $CaCl_2$-NaCl melt at 1133K and observed a pure Al droplet. The yield however was low, i.e. 3-5%.
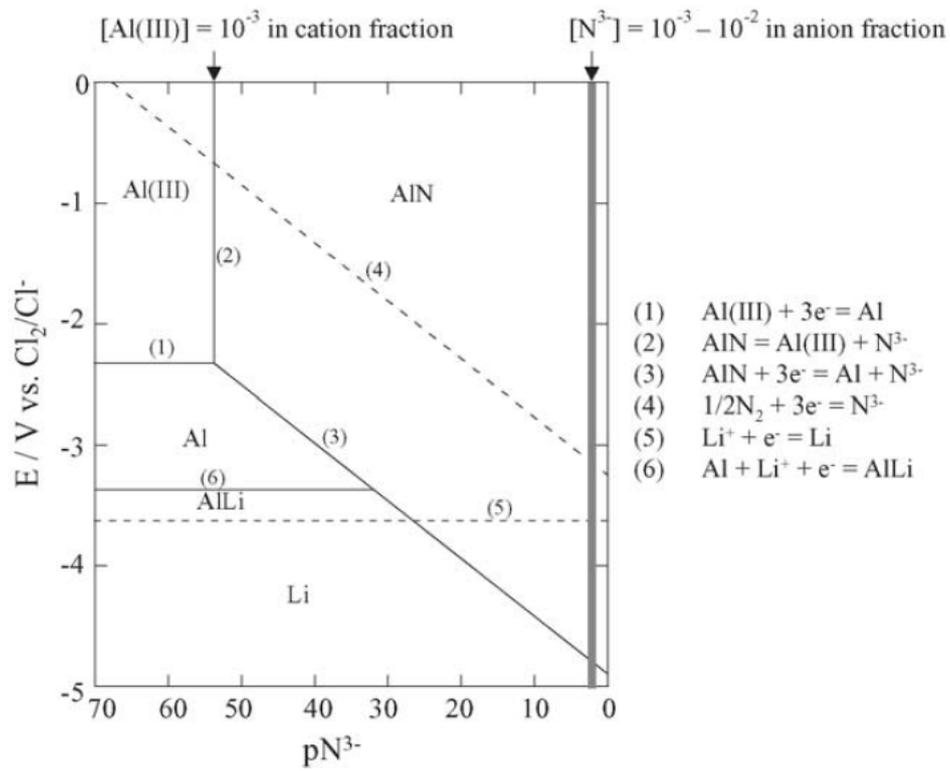
Figure 6 - A potential-pN^{3-} diagram for Al-N system of a LiCl-KCl eutectic melt in the presence of 10^{-3} cation fraction of Al^{3+} at 450°C[138].

Table 3: Summary of previous major works/patents in the Nitride Route (*p – patent)

Year	Author	Reactions and Parameters	Process Details
2008	Joo and Jung [118]	$Al_2O_3 + 3C + N_2 = 2AlN + CO$ Temperature: 800-1600°C	The carbothermal reduction and nitridation (CRN) of alumina to aluminium nitride was investigated in a gas environment consisting of N_2 and CO. The CRN reaction of alumina is slowing with increasing content of CO in the mixed gas.
1998	Kotaka et al. [136 p] (Toshiba Ceramics Co.)	Calcination of γ-Al_2O_3: 300-1100°C Nitridation Temperature: 1200-1700°C Gas: Mixtures of NH_3 and hydrocarbons Purity: 99%	A method of manufacturing aluminium nitride by calcining γ-Al_2O_3 in ammonia and hydrocarbon gas to obtain aluminium nitride having both carbon content and an oxygen content of 1wt% of less.
1997	Ravenel et al. [135 p] (ELF Atochem SA)	$Al_2O_3 + 3C + N_2 = 2AlN + CO$ Temperature: 1450-1500°C. Time: 12 hrs Residual carbon, < 700 ppm Oxygen Content < 1.1%. Flow rate of granule: 4.4 kg/hr Flow rate of N_2: 12 kg/hr	A continuous process for production of aluminium nitride by the carbonitriding process of alumina.
1996	Ravenel et al. [134 p] (ELF Atochem SA)	$Al_2O_3 + 3C + N_2 = 2AlN + CO$ Exchange surface area/volume, 5-50 m⁻¹. C/ Al_2O_3 = 3 Granules Feed Rate: 5 kg/h. N_2 Feed Rate: 20 kg/h Yield: 100% Time: 12 hrs Temperature: 1350-2000°C.	Continuous production of aluminium nitride by carbonitriding of alumina in a moving bed reactor reaction zone comprising at least one conduit.
1993	Dorn et al. [133 p] (Hoechst)	Calcination of mixture at 400-1000°C Nitridation at 1400-1700°C (1-100 hrs)	Production of fine aluminium nitride by reaction between aluminium hydroxide with carbon in the presence of flowing nitrogen.
1992	Dunn et al. [132 p] (Dow Chemical Co)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ Temperature: 1650-1750°C. Time: 90 min Frequency: 1100 vibration/min. Yield: 97%wt.	Purification of aluminium nitride produced by carbothermal reaction of aluminium oxide, carbon and nitrogen. Significant amount of the surface portions are removed by mechanical agitation or mechanical abrasion to leave behind aluminium nitride pellets having significantly increased purity.
1991	Nakano et al. [131 p] (Sumitomo Chemical Co Ltd)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ Temperature: 1500-1700°C. Time: 2-10 hrs, starting materials < 5μm O, <2 wt.% Fe, <20 ppm	Production of aluminium nitride by firing and reacting alumina and carbon mixture in a nitrogen containing atmosphere.

1989	Bolt [130 p] (Du Pont)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ T nitridation = 1550-1800°C	Production of aluminium nitride fibers/films through carbontiridation of precursor fibers/films containing source of alumina and carbon.
1986	Kuramoto *et al.* [129 p] (Tokuyama)	$Al_2O_3 + 3C + N_2 (NH_3) = 2AlN + 3CO$ Temperature: 1400-1700°C Yield: 94 wt%.	Production of aluminium nitride fine powder (not more than 2 microns) by firing alumina carbon mixture after optionally drying it.
1963	Paris and Perieres [128 p] (Pechiney)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ $nAl_2O_3 + 3C_nH_{2n+2} + nN_2 = 2nAlN + 3nCO + 3(n+1) H_2$ $CH_4 + \frac{1}{2} O_2 + 2N_2 = CO + 2N_2 + 2H_2$ $Al_2O_3 + 3CH_4 + N_2 = 2AlN + 3CO + 6H_2$ Temperature: 1200-1750°C.	Manufacturing of aluminium nitride from the aluminium ores reacting with nitrogen and a reducing agent (hydrocarbon), which is relatively free of impurities and unreacted components.
1962	Clair [127 p] (Pechiney)	T = 1750°C	Development of reactors for continuous production of aluminium nitride. Counter current reactor, vertical shaft. A mixture of alumina, carbon and calcium aluminate binder.
1961	Perieres and Bollack [113 p] (Pechiney)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ $AlN + C = AlCN$ Yield: 99% Temperature: 1700°C (nitridation) 700-800°C (roasting) Time: 2 hrs Nitrogen Flow: 100 L/min.	A process for making aluminium nitride having a degree of purity above 97%, particularly free from any substantially amounts of alumina or carbon.
1918	Shoeld [126 p] (Armour Fert. Works)	$Al_2O_3 + 3C + N_2 = 2AlN + 3CO$ Temperature of 1800-2000°C Time: 3-4 hrs.	Production of aluminium nitride from comminuted carbon, alumina, and a binder mixture, and a nitrogen-containing gas travelling in opposite directions by passing a heating current of electricity.

4. Concluding Remarks

Many researchers have pursued an alternative commercial method for aluminium production. Although carbothermal reduction of alumina or aluminous ores (direct or indirect) offers the potential for lower energy consumption and improved productivity, compared to existing process, none of these proposed processes have been successfully commercialized. In the case of direct carbothermal reduction of alumina/aluminous ores, a mixture of aluminium carbide and metallic aluminium is formed. Equilibrium studies show that the driving forces for both aluminium carbide and aluminium metal formation by carbothermic reduction of alumina are similar, therefore it is difficult to obtain high yield of pure aluminium. This route has other difficulties, including a high operating temperature and yield problems associated with aluminium vapour back reactions with carbon monoxide forming aluminium oxides and carbides. The recent technology in this area has shifted to a multi stage process, the Alcoa-Elkem process, where a slag of Al_2O_3 -Al_4C_3 is first produced followed by extraction of aluminium.

In the case of multistage production of aluminum through the formation of intermediate compounds; there had been intense developments of the chloride route in the 60's and throughout the 70's with major players including Alcoa and Toth Al Corporation. At one stage, the Alcoa chloride process (carbohclorination followed by electrolysis) was used to produce Al commercially. This however was halted in the mid 80's due to problems associated with production and handling of pure aluminium chloride and chlorine at high temperatures.

In the sulphide route, $Al_2S_{3(l)}$ can be produced by carbosulphidation of alumina or aluminous ores. Aluminium metal can be extracted from $Al_2S_{3(l)}$ by disproportionation and electrolysis processes. In the 2000's, Corus developed a process for making aluminium through carbosulphidation followed by electrolysis. This, however, is not yet commercialised.

There is also the nitride route where $AlN_{(s)}$ is produced from alumina-graphite mixture reacted at 1700°C in nitrogen containing gas. One of the major challenges is to find the economical route to extract Al from $AlN_{(s)}$. The nitride is a very stable phase but can be dissociated to aluminium metal at above 2400°C at 0.1 MPa pressure. The theoretical decomposition voltage of aluminium nitride to aluminium and nitrogen is 0.75V at 700°C. It is the lowest compared to the decomposition voltage of $AlCl_{3(l)}$, $Al_2S_{3(s)}$ and $Al_2O_{3(s)}$ at the same temperature. Therefore, electrolysis has potential to be used for extracting aluminum from aluminium nitride. However, to date no appropriate electrolytes are available to dissolve the very stable AlN.

In summary, direct carbothermic reduction has yet to be commercialized because of problems with extreme operating conditions and yield, whilst, two stage indirect carbothermic reduction using Cl, S, and N sources to form intermediates have been investigated but still require significant development. No systematic thermodynamic examination of all the options has been published in the literature.

5. Acknowledgement

6. References

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