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**A PRELIMINARY STUDY OF THE ELECTROLYSIS  
OF ALUMINUM SULFIDE IN MOLTEN SALTS**

by

**Nguyen Quang Minh, Raouf O. Loutfy,  
and Neng-Ping Yao**

**MASTER**



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**ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS**

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Chemical Technology Division

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ABSTRACT

A preliminary laboratory-scale study of the electrolysis of aluminum sulfide in molten salts (a low-energy alternative for aluminum production) investigated the (1) solubility of  $\text{Al}_2\text{S}_3$  in molten salts, (2) electrochemical behavior of  $\text{Al}_2\text{S}_3$ , and (3) electrolysis of  $\text{Al}_2\text{S}_3$  with the determination of current efficiency as a function of current density. The solubility measurements show that  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic electrolyte at 1023 K can dissolve up to 3.3 mol % sulfide. The molar ratio of sulfur to aluminum in the eutectic is about one, which suggests that some sulfur remains undissolved, probably in the form of  $\text{MgS}$ . The experimental data and thermodynamic calculations suggest that  $\text{Al}_2\text{S}_3$  dissolves in the eutectic to form  $\text{AlS}^+$  species in solution. Addition of  $\text{AlCl}_3$  to the eutectic enhances the solubility of  $\text{Al}_2\text{S}_3$ ; the solubility increases with increasing  $\text{AlCl}_3$  concentration. The electrode reaction mechanism for the electrolysis of  $\text{Al}_2\text{S}_3$  was elucidated by using linear sweep voltammetry. The cathodic reduction of aluminum-ion-containing species to aluminum proceeds by a reversible, diffusion-controlled, three-electron reaction. The anodic reaction involves the two-electron discharge of sulfide-ion-containing species, followed by the fast dimerization of sulfur atoms to  $\text{S}_2$ . Electrolysis experiments show that  $\text{Al}_2\text{S}_3$  dissolved in molten  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic or in eutectic containing  $\text{AlCl}_3$  can be electrolyzed to produce aluminum and sulfur. In the eutectic at 1023 K, the electrolysis can be conducted up to about 300  $\text{mA}/\text{cm}^2$  for the saturation solubility of  $\text{Al}_2\text{S}_3$ . The current efficiency of aluminum deposition from 2 wt %  $\text{Al}_2\text{S}_3$  in the eutectic increases with increasing current density up to a maximum current efficiency of about 80%. In molten eutectic that contains  $\text{AlCl}_3$ , much higher current densities (0.2-1.2  $\text{A}/\text{cm}^2$ ) can be used to obtain the same current efficiency (80%) for the electrolysis of 5 wt %  $\text{Al}_2\text{S}_3$ . Although these preliminary results are promising, additional studies are needed to elucidate many critical operating parameters before the technical potential of the electrolysis can be accurately assessed.

## I. INTRODUCTION

Aluminum is the second most widely used metal in the world. The extensive use of aluminum is the result of both relatively low prices and certain physical characteristics such as corrosion resistance, conductivity, and high strength-to-weight ratio. The aluminum industry has undergone rapid growth since the end of World War II. Table I-1 highlights the performance of aluminum during this time. This table shows that both world and U.S. consumption of aluminum increased considerably more than the consumption of other major metals such as copper, zinc, nickel, and lead. In 1977, the U.S. industrial consumption represented 33% of total world primary aluminum production.<sup>2</sup>

Table I-1. Percentage Growth Rate for Selected Metals during Post-World War II Era<sup>1</sup>

	Aluminum	Copper	Zinc	Nickel	Tin
United States	6.7	2.3	0.3	2.2	-1.6
World	8.2	4.4	3.1	4.9	0.6

The overall outlook for aluminum markets during the 1980's is encouraging; the aluminum industry is still expected to grow (Table I-2), although at a smaller rate than that recorded during the past three decades.

Table I-2. Estimated Aluminum Consumption, 1980-1990<sup>1</sup> (10<sup>6</sup> Mg)<sup>a</sup>

	1980	1985	1990	Predicted % Growth 1980-1990
World	12.15	15.41	19.59	4.9
United States	4.72	5.75	6.92	3.9

<sup>a</sup>One megagram (Mg) equals one metric ton (tonne).

The aluminum industry is the largest electrolytic industry and consumes about 5% of the electrical energy generated in the United States. Aluminum-reduction plants use a large amount of electrical power (about 14,000-17,500 kWh ac per Mg aluminum in modern plants), and capital costs are high.

Table I-3<sup>3</sup> lists energy costs as percentages of metal prices for the production of aluminum and other metals. It can be seen that, relative to other metals, the price of aluminum is more vulnerable to energy costs, so that high energy costs have adverse effects on the aluminum industry. With the continuing shortage of energy, both currently as well as in future

Table I-3. Energy Cost as Percentage of Metal Price  
for Production of Selected Metals<sup>3</sup>

Metal	Energy Cost as % of Metal Price
Copper	5.3
Nickel (sulfide ore)	5.4
Zinc	7.5
Lead	8.0
Steel	16.0
Nickel (laterite ore)	16.0
Aluminum	36.0

projections, the aluminum industry is clearly headed for a considerable period of limited energy availability and high energy cost. Also, the U.S. aluminum industry depends on imports of raw material for over 90% of its production. As a result, production of aluminum ingots in less industrialized nations with abundant quantities of the raw materials (bauxite and energy) has increased. Therefore, in order to remain competitive with foreign producers, the U.S. aluminum industry must become more efficient in its use of energy.

Primary aluminum is currently produced exclusively by the Hall-Héroult process. Since about 60% of the total energy used in this process is consumed in the form of electrical power, electrical-power usage is a good target for energy reduction. In the past 40 years, the aluminum industry has cut its electrical power requirements for smelting nearly in half. Prior to World War II, about 26 kWh were needed to produce one kilogram of aluminum. Today the average smelters use 17-18 kWh and the most efficient about 13-14 kWh. These improvements may be attributed almost entirely to a continuing increase in the size of the electrolytic cell, accompanied by increased mechanization and better process control. The aluminum industry is continuing to cut its energy use. The Aluminum Association reported a 10.33% reduction in the amount of energy needed to make one kilogram of aluminum during 1979, as compared to the base year of 1972.<sup>4</sup> The industry also made a voluntary commitment to cut its unit energy consumption by a total of 20% by the end of 1985, as compared with the base year. In addition to efforts to improve the Hall-Héroult cell, many projects have been undertaken by aluminum companies and other organizations to develop alternative technologies for higher energy efficiencies. Some methods which have been studied include carbothermic reduction, subhalide disproportionation, and aluminum chloride electrolysis. Many processes, however, offer no economic advantage over the Hall-Héroult process. At present, the Alcoa Smelting Process (ASP) in which aluminum is produced by the electrolysis of aluminum chloride is probably the only alternative route under active research and development by the industry. A 14,000-Mg pilot plant has been in operation in Texas since 1976.

In the past few years, Argonne National Laboratory (ANL), under the auspices of the U.S. Department of Energy (USDOE), has been actively engaged in a program to identify and assess methods for improving energy efficiencies of industrial electrochemical processes. Arthur D. Little, Inc., under a contract with ANL, has critically evaluated potential processes for the production of aluminum.<sup>5</sup> The purpose of the survey was to identify (1) practical opportunities that exist for reducing electrical energy consumption in the aluminum industry, (2) areas where research and development are necessary to implement these opportunities, and (3) the capital investment involved. One of the major conclusions of the survey is that the ASP is the only alternative technology at present which can compete with respect to electrical energy consumption with the Hall-Héroult. However, for long-term research and development, aluminum sulfide, and probably aluminum nitride, electrolysis may also offer potential advantages. The Office for Electrochemical Project Management (OEPM) at ANL is presently evaluating the feasibility of the aluminum sulfide process.

The electrolysis of aluminum sulfide, like the ASP, possesses many advantages over the conventional Hall-Héroult process: lower operating temperature, lower decomposition voltage, and elimination of the consumable carbon anode (thus permitting a more efficient bipolar cell design). Another advantage of the sulfide process (like the ASP) is that low-cost nonbauxite domestic sources such as clay, kaolin, and flyash may be suitable for feed material. Moreover, the theoretical decomposition voltage of  $\text{Al}_2\text{S}_3$  is well below that of  $\text{AlCl}_3$  used in the ASP. The sulfide process may also tolerate a higher oxide impurity concentration than the ASP.

A preliminary thermodynamic assessment of processes to produce aluminum *via* the electrolysis of  $\text{Al}_2\text{S}_3$  and the disproportionation of aluminum subsulfide ALS has been carried out.<sup>6</sup> The aluminum sulfides  $\text{Al}_2\text{S}_3$  and ALS can be produced by direct sulfurization of aluminous ores such as bauxite or by sulfurization of pure alumina. Figure I-1 shows an overview of the process steps used to produce aluminum with aluminum sulfide as an intermediate product.

Thermodynamic calculations suggest that these processes could be low-energy alternatives for the production of aluminum. The projected energy requirements compare favorably with that for the conventional Hall-Héroult process and even with the figures indicated for the ASP. The ALS disproportionation processes consume less energy than the  $\text{Al}_2\text{S}_3$  electrolysis processes; however, very little is known about the chemistry of the ALS disproportionation. Although the electrolysis of  $\text{Al}_2\text{S}_3$  in molten salts has not been studied extensively, previous studies on the electrolysis of  $\text{Al}_2\text{S}_3$  and other metal sulfides seem to suggest that  $\text{Al}_2\text{S}_3$  electrolysis could be technically feasible if conducted under the proper conditions. Also, the electrolysis of  $\text{Al}_2\text{S}_3$  has fewer unknown or critical steps than the disproportionation process. Therefore, it has been decided to undertake experimental studies on the electrolytic production of aluminum from  $\text{Al}_2\text{S}_3$ .

In general, the  $\text{Al}_2\text{S}_3$  electrolysis process involves the sulfurization of aluminous ores or alumina (for example, with carbon and sulfur at high temperatures) followed by the electrolysis of  $\text{Al}_2\text{S}_3$  in a molten salt. A simplified flow sheet of the proposed process is presented in Fig. I-2. The two critical operations in the proposed process are the sulfurization of

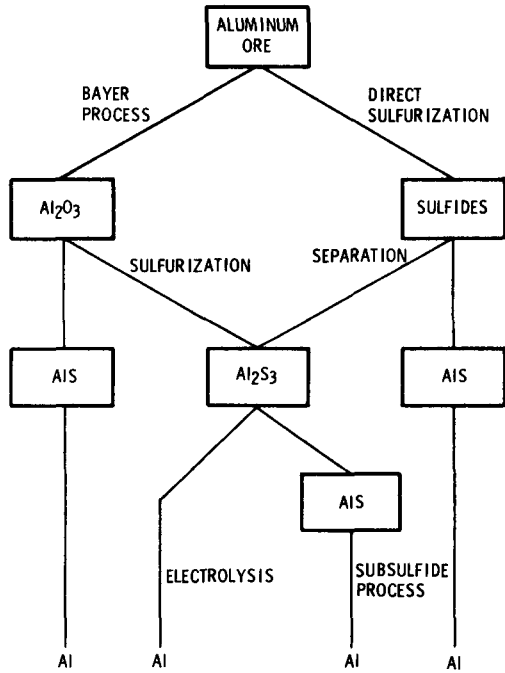


Fig. I-1.

Process Steps Needed to Produce Aluminum with Aluminum Sulfide as an Intermediate Product

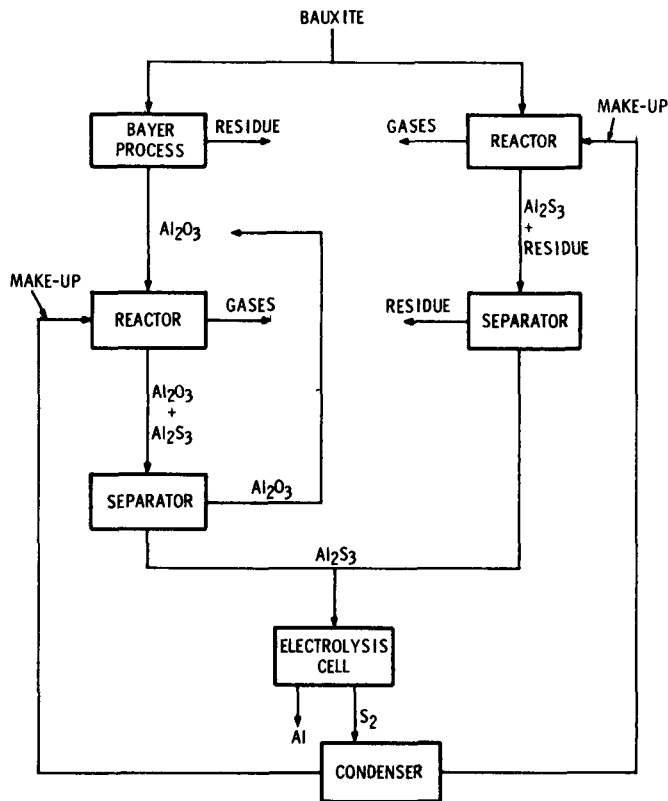


Fig. I-2. A Simplified Flow Sheet of the Proposed  $Al_2S_3$  Electrolysis Process



alumina or aluminous ores and the electrolysis of  $\text{Al}_2\text{S}_3$ . Experimental studies at ANL were concentrated in these two areas. This report deals with the electrolysis of  $\text{Al}_2\text{S}_3$  in molten-salt media; the results of the investigation on sulfurization of alumina will be presented elsewhere.<sup>7</sup> In this preliminary study, only three areas were investigated: (1) the solubility of  $\text{Al}_2\text{S}_3$  in molten salts, (2) the electrochemical behavior of  $\text{Al}_2\text{S}_3$ , and (3) the electrolysis of  $\text{Al}_2\text{S}_3$  with the determination of current efficiency as a function of current density. No attempt was made to optimize electrolysis through the use of different electrolytes, and the variation of some operating parameters that affect the electrolysis were not investigated.

As background for the present study, Section II gives a brief description of the Hall-Héroult and other electrolytic processes, together with their projected energy consumption. Section III is devoted to a literature survey on the electrolysis of metal sulfides, the electrochemical behavior of aluminum and sulfide ions, and the solubility of metal sulfides in molten salts. In Section IV, the results of the study on the electrolysis of  $\text{Al}_2\text{S}_3$  in chloride melts are given. Conclusions and recommendations are detailed in Section V.

## II. ELECTROLYTIC PROCESSES FOR ALUMINUM PRODUCTION

### A. The Hall-Héroult Process

Essentially all the primary metallic aluminum in the world is produced by the Hall-Héroult process. The principle of this process is the electrolytic dissociation of alumina ( $\text{Al}_2\text{O}_3$ ) dissolved in a molten bath of cryolite ( $3\text{NaF}\cdot\text{AlF}_3$ ). The fundamental process has been in use for more than 90 years; the only modifications to occur during this period have been technological.

The cross section of a typical Hall-Héroult cell is shown in Fig. II-1. The cell consists of a consumable carbon anode, a molten alumina-cryolite electrolyte, a pool of liquid aluminum, and a carbon-lined steel vessel to hold the metal and electrolyte. The anode is suspended from a superstructure extending over the cell and is connected to a movable anode bus so that its vertical position may be adjusted. Normally the anode-cathode distance is about 5 cm. The molten electrolyte consists principally of cryolite plus some excess  $\text{AlF}_3$ , 2 to 8 wt % of fluorspar ( $\text{CaF}_2$ ) and 2 to 8 wt %  $\text{Al}_2\text{O}_3$ . Commonly, lithium carbonate is added to the cell to improve the conductivity. A typical modern cell takes 150 kA or more at an anode current density of approximately  $0.7 \text{ A/cm}^2$  and operates at 1213-1253 K. There are two types of anodes, the prebaked and the Söderberg. Prebaked anode blocks are manufactured from a mixture of low-ash calcined petroleum coke and pitch or tar, formed in hydraulic presses, and baked at 1373 K. Söderberg anodes consist of a single large anode housed in an open steel casing through which it is fed down into the electrolyte. The anode is formed continuously by baking the coke-pitch mixture until it is fully carbonized at the working surface of the bath.

During operation of the cell, a frozen crust forms over the surface of the molten bath. Alumina is added on top of this crust, where it is preheated to drive off absorbed moisture. Alumina is then added to the bath by periodic breaking of the crust. When the alumina in the bath is

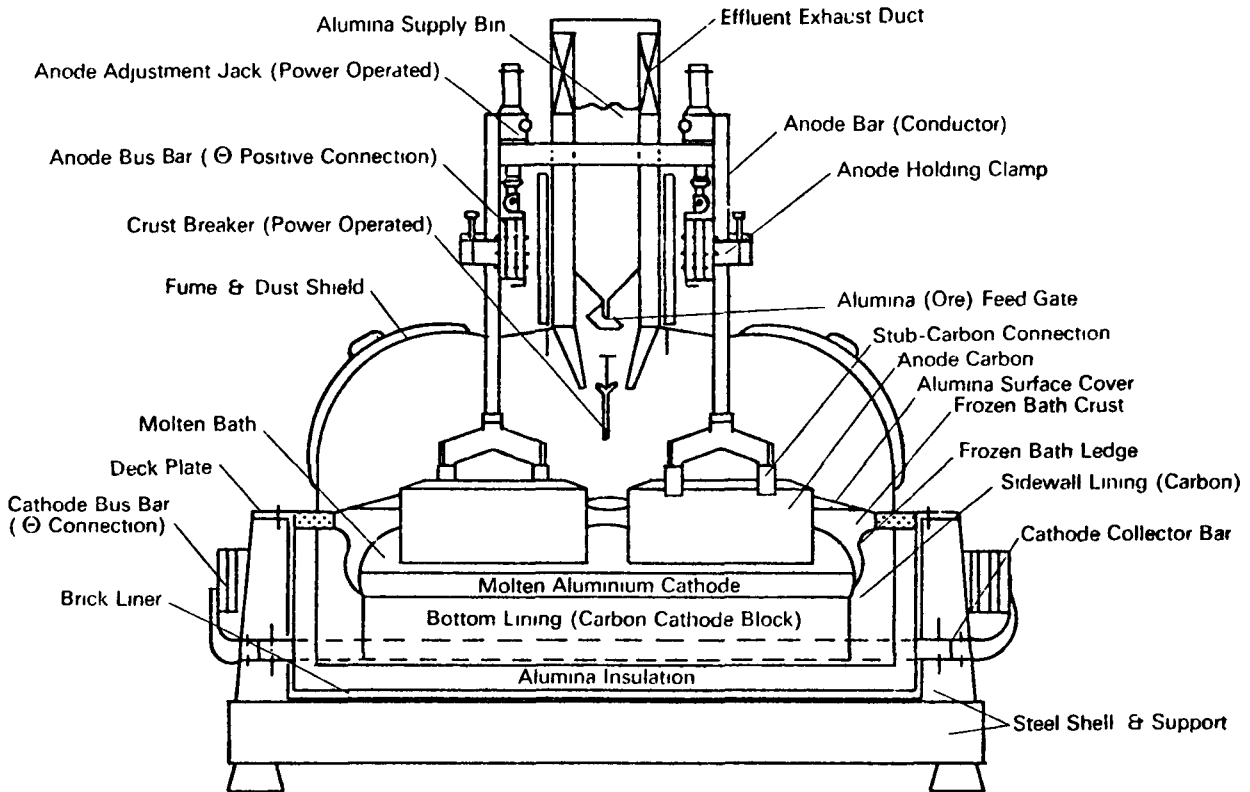
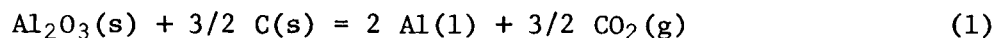


Fig. II-1. A Cross Section of a Typical Hall-Héroult Cell (Reproduced from Minerals Science and Engineering, Vol. II, p. 84, by permission of the publisher, the National Institute for Metallurgy)

depleted, the so-called anode effect occurs, which causes an abrupt rise in cell voltage. When this happens, alumina is stirred into the cell, the electrolysis process resumes, and cell voltage returns to normal.

The production of aluminum in the cell occurs according to the following simplified reaction:

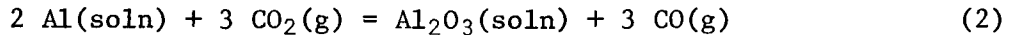


The theoretical energy requirement is 5.64 kWh/kg aluminum produced, compared with a requirement of 8.69 kWh/kg for the decomposition of oxide without the use of carbon as a reducing agent. In actual practice, some energy is used to bring reactants up to temperature and some energy is lost through ohmic resistance, overvoltage, and side reactions. Thus, the actual energy usage amounts to from 12 to 17 kWh for the production of one kilogram of aluminum.

At 100% current efficiency in an aluminum-reduction cell,  $\text{CO}_2$  should be the only anode product. However, the composition of the anode gas normally varies between 60 and 90%  $\text{CO}_2$  with the remainder being mainly  $\text{CO}$ . The rate of consumption of the carbon anodes is usually in the range of 0.44 to 0.50 kg carbon consumed/kg aluminum, which lies between the theoretical

values of 0.33 kg carbon consumed/kg aluminum if both Al and CO<sub>2</sub> were produced with 100% efficiency and 0.67 kg carbon consumed/kg aluminum if CO were the primary anode product.

The extent to which the current efficiency is lower than the theoretical value is determined principally by temperature, current density, interpolar distance, composition of the electrolyte, and cell design. The lowering of the current efficiency is caused primarily by back reaction between aluminum dissolved in some form in the electrolyte and carbon dioxide formed at the anode:



This reaction accounts for most of the carbon monoxide in the anode gases and for about a 4.5% loss in current efficiency. Other minor reactions are aluminum carbide formation (1%) and sodium uptake (1%).

The energy efficiency, EE, of the Hall-Héroult process as a function of the current efficiency, x, and the cell voltage, V<sub>cell</sub>, is given by<sup>8</sup>

$$\text{EE} = \frac{0.481 + 1.65x}{V_{\text{cell}}} \quad (3)$$

From Eq. 3, it can be seen that most of the decreases in energy efficiency can be attributed to an increase in cell voltage, and a smaller amount to a decrease in current efficiency. It seems that 95% current efficiency is probably the upper limit imposed by the losses inherent in the process, and this can be achieved by very careful operational control. On the other hand, much improvement in the energy efficiency of the aluminum cell can be achieved by reducing the cell voltage.

Contributions to the voltage drops in typical 72-kA and 150-kA reduction cells<sup>9</sup> are shown in Table II-1.

The cathodic overpotential is very small; therefore, the overpotential in an aluminum cell is primarily anodic. It can be seen clearly from Table II-1 that most of the energy inefficiency is attributable to the resistance loss, especially the resistance of the electrolyte between anode and cathode. Considerable research and development have been carried out to reduce voltage losses. The following paragraphs describe the principal ways of reducing these voltage losses.

The voltage associated with the ohmic drop in the electrolyte depends on the conductivity of the molten bath and the distance between the anode and cathode. The electrical conductivity can be improved by the use of salt additives. Addition of LiF, Li<sub>2</sub>CO<sub>3</sub>, or NaCl has a positive influence on conductivity,<sup>10</sup> and these additives are being used in several aluminum plants. A minimum separation between anode and cathode should be maintained to prevent a short-circuit caused by bath movements. Two principal factors responsible for movements in the bath are evolution at the anode of bubbles of gas and surges in the aluminum pad that result from the magnetic field in and around the cell. Techniques are available for calculating improvements in the magnetic field aimed at stabilizing the metal pad. Such improvements may permit some reduction in cathode-anode distance. A potential significant improvement can be realized by using titanium diboride (TiB<sub>2</sub>) cathodes in the

Table II-1. Voltage Drops in 72-kA and 150-kA Hall-Héroult Reduction Cells

Parameters	Voltage Drop, V	
	72 kA	150 kA
Ohmic Voltage Drop		
Anode Bus to Electrolyte (Metal and carbon conductors and contact resistance)	0.98	0.70
Electrolyte	1.70	1.27
Molten Aluminum Cathode to Cathode Bus (Metal and carbon conductors and contact resistance)	0.54	0.45
	3.22	2.42
Electrolysis Polarization		
Reversible Decomposition Potential	1.16	1.16
Cathode and Anode Overpotentials	0.64	0.64
	1.80	1.80
	5.02	4.22

Hall-Héroult cell.<sup>11,12</sup> Titanium diboride can be wet by aluminum, and with a  $TiB_2$  cathode, the metal pad can be reduced to a thin continuous film on the cell bottom. Because this thin film does not surge, the anode-cathode spacing can be narrowed to less than 2.5 cm. Titanium diboride still suffers cracking problems in a cell environment, however.

Steel is being used for conductors in reduction cells. Although many other metals have lower resistivities than steel, their price and their tendency to melt, alloy, or react with carbon make them less attractive for use as conductors. The most common technique used to minimize contact resistance is cleaning metal oxide and carbide film from the steel rod by sand blasting.<sup>13</sup> The resistance of carbon electrodes can be reduced by improving the quality of carbon (thermal treatment or graphitization).

There is a fairly large overpotential at the anode. It is theoretically possible to lower the overpotential by altering the structure of the anode or by treatment of the anode material with catalysts.<sup>10</sup> Gas depolarization has also been attempted to reduce the anodic overpotential. The latter approach is attractive but difficult to realize in practice.

The potential for reducing the energy usage for aluminum production using Hall-Héroult cells is summarized in Table II-2.<sup>14</sup>

Table II-2. Potential for Reduction of Energy Usage in Hall-Héroult Cells (Base = 13.2 kWh/kg Al)<sup>14</sup>

Parameters	Existing	Potential	Potential Savings, kWh/kg Al
Faraday Efficiency	90%	95%	0.66
Reaction Voltage	2.65 V	2.65 V	0
Overvoltage	1.43 V	1.21 V	0.22
Voltage Loss in Conductor	0.44 V	0.33 V	0.11
Voltage Loss in Anode	0.44 V	0.33 V	0.11
Voltage Loss across Electrolyte (current density effect)	3.09 V	2.75 V	0.34
Voltage Loss across Electrolyte (TiB <sub>2</sub> )	3.09 V	1.54-2.20 V	0.89-1.55
Voltage Loss across Lining	0.77 V	0.66 V	0.11

Another possible improvement in the process is associated with the use of permanent anodes. In theory, the use of a chemically inert and nonconsumable anode (for example, ceramic oxides) would save the cost of anode carbon and offer certain possibilities for more compact cell designs, for example, bipolar cells. On the other hand, the depolarizing effect of carbon would no longer be present. However, this could be offset by reduced ohmic resistance and other advantages. Many patents on the use of inert anodes are available.<sup>15</sup> The major problem in the development of an inert anode is the stability of the material and the life of the anode in alumina-cryolite melts.

Generally, about 50% of the energy added to the cell must be removed as heat. Some heat is removed by tapping the liquid aluminum, but more heat is transported away with the anode gases. Most of the heat is lost from the cell by radiation. A correct heat balance ensures good operation and longer life of the cell.

#### B. Other Electrolytic Processes

It is anticipated that the Hall-Héroult process will remain the main process for the industrial production of aluminum for many years. Improvements in the energy efficiency of the Hall-Héroult cell have been made in the past and continue to be developed in the present. On the other hand, numerous research programs have been undertaken by aluminum producers and others over the years to develop alternative technologies which could replace the energy-intensive and capital-demanding Hall-Héroult process. To date, none has been as successful as the Hall-Héroult or has reached commercial production. The discussion in this section will be limited to some alternative molten-salt electrolytic processes for the production of aluminum. Information relating to other processes can be found in the open literature.<sup>5,16-19</sup>

The theoretical decomposition voltages for compounds practical for use in aluminum production are shown in Table II-3.

Table II-3. Theoretical Decomposition Voltages for Aluminum Compounds

Compounds	Temperature, K	Decomposition Voltage, V
$\text{Al}_2\text{O}_3 = 2 \text{ Al} + 3/2 \text{ O}_2$	1273	2.19 <sup>a</sup>
$\text{Al}_2\text{O}_3 + 3/2 \text{ C} = 2 \text{ Al} + 3/2 \text{ CO}_2$	1243	1.17 <sup>a</sup>
$\text{AlCl}_3 = \text{Al} + 3/2 \text{ Cl}_2$	1000	1.84 <sup>a</sup>
$\text{Al}_2\text{S}_3 = 2 \text{ Al} + 3/2 \text{ S}_2$	1023	0.98 <sup>b</sup>
$\text{AlN} = \text{Al} + 1/2 \text{ N}_2$	1000	0.79 <sup>a</sup>

<sup>a</sup>Reference 20.

<sup>b</sup>Reference 21.

From the viewpoint of energy utilization, the electrolysis of  $\text{Al}_2\text{S}_3$  and  $\text{AlN}$  would be very attractive because of their low theoretical decomposition voltages as compared with that of  $\text{Al}_2\text{O}_3$ . The electrolysis of these compounds could be carried out at lower temperatures using bipolar electrodes. The high reversible voltage for  $\text{AlCl}_3$  represents a disadvantage with respect to energy usage; however, the overall energy of the  $\text{AlCl}_3$  electrolysis can still be low due to the low operating temperature and the use of bipolar cells.

### 1. $\text{AlCl}_3$ Electrolysis

Aluminum may be obtained *via* the electrolytic decomposition of  $\text{AlCl}_3$  in a fused salt. The possibility of producing aluminum by the electrolysis of  $\text{AlCl}_3$  has been under investigation since 1854. Failure in the past to develop commercial processes can be attributed to unfavorable economics and problems with construction materials associated with the hygroscopicity of aluminum chloride. In 1973 The Aluminum Company of America (Alcoa) reported that it had developed an electrolytic process based on the electrolysis of  $\text{AlCl}_3$  in melts of alkali and alkaline-earth chlorides. Alcoa has spent \$25 million over 15 years of research and is currently operating a 14,000-Mg/y pilot plant in Texas. According to Alcoa, an approximately 30% reduction in electrical energy requirements *vs.* the conventional Hall-Héroult process is obtained. However, an additional step, the formation of aluminum chloride from alumina, requires more energy than the formation of prebaked anodes for the Hall-Héroult cell. The net effect is that the total energy consumption of the Alcoa Smelting Process (ASP) may be only marginally better than that of Hall-Héroult.

Alcoa has described two different cell designs: a monopolar cell, similar to the conventional Hall-Héroult cell, and a novel bipolar cell. The monopolar cell is operated at 3.3 V and 13,000 A/m<sup>2</sup> to give an electrical energy consumption of 11.5 kWh/kg Al.

A bipolar cell is shown in Fig. II-2. The cell contains bipolar carbon electrodes stacked horizontally with small electrode spacing (about 1.3 cm compared with 5 cm in a Hall-Héroult cell). Each bipolar electrode behaves as a cathode on its top surface and an anode on its bottom surface. The chlorine formed on the anode (the lower surface) moves in channels towards a central space where it causes circulation of the electrolyte by a gas-lift action. The aluminum flows downwards counter-current to the chlorine gas but the back reaction is reported to be negligible. The electrolyte is composed of 51% NaCl, 40% LiCl, 2.5% MgCl<sub>2</sub>, and 6.5% AlCl<sub>3</sub> by weight, maintained at about 988 K.<sup>22,23</sup> Current densities of 0.8 to 2.3 A/cm<sup>2</sup> can be used, and Alcoa reported a voltage of 31 V for a cell of 12 bipolar electrodes, *i.e.*, 2.6 V per unit (compared with about 4 V for Hall-Héroult cell). The energy consumption of the ASP is about 10 kWh/kg Al. Aluminum chloride for the electrolysis should be very pure and water-free to prevent sludge formation and consumption of the anode face of the bipolar electrode. Other difficulties may involve the relatively high vapor pressures of several compounds in the electrolyte and intercalation of the carbon electrodes by chlorine or alkali metals. Nippon Light Metal Company Ltd. has patented a process similar to the ASP.<sup>23</sup> The Japanese proposed to use an electrolyte composed of NaCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>. The concentration of (CaCl<sub>2</sub> + MgCl<sub>2</sub>) is from 15 to 70 wt % and the MgCl<sub>2</sub>/NaCl ratio is greater than unity. Rectangular or cylindrical bipolar cells are recommended, with electrodes inclining at an angle of 15 to 45° from the vertical.

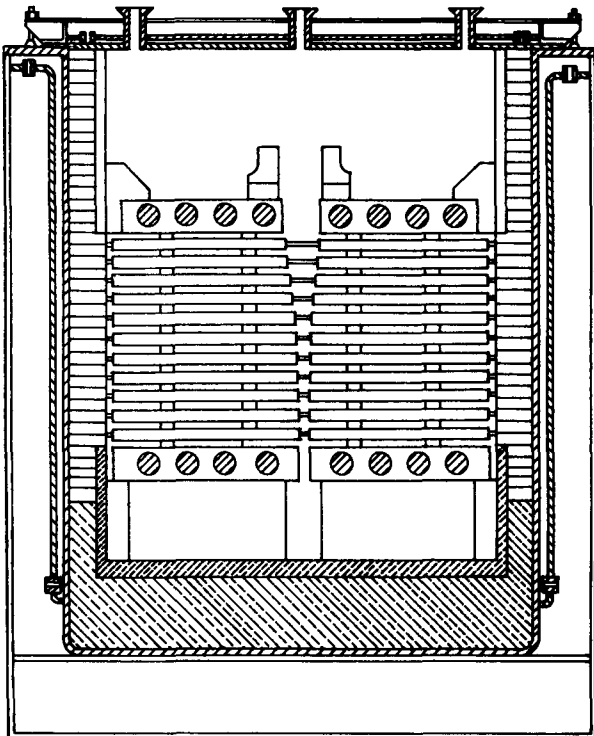


Fig. II-2.

Bipolar Cell for Alcoa  
Smelting Process

Note: Detailed description in U.S. Patent 4133727.

## 2. Al<sub>2</sub>S<sub>3</sub> Electrolysis

Aluminum can also be produced by the electrolysis of Al<sub>2</sub>S<sub>3</sub> dissolved in a molten electrolyte. As mentioned earlier (Table II-3), the main attractive feature of this process is the low theoretical decomposition voltage of Al<sub>2</sub>S<sub>3</sub>. At temperatures of 773-1073 K, the electrolysis would produce molten aluminum and elemental sulfur according to the overall reaction



and carbon electrodes would remain dimensionally stable.

The electrolysis of Al<sub>2</sub>S<sub>3</sub> is not a new idea. It can be traced back to 1892 when Bucherer<sup>24</sup> proposed to electrolyze sodium aluminum sulfide (Na<sub>6</sub>Al<sub>2</sub>S<sub>6</sub>) in an electrolyte of alkali or alkaline-earth fluorides or chlorides. More detailed work on Al<sub>2</sub>S<sub>3</sub> was done in the 1930's. A complete survey of the subject will be given in Section III.

## 3. AlN Electrolysis

Another route to aluminum from compounds other than Al<sub>2</sub>O<sub>3</sub> is *via* the electrolysis of aluminum nitride. Again, the electrolysis process possesses the advantages of low decomposition voltage and low operating temperature. The evolution of N<sub>2</sub> would eliminate consumption of the carbon anode. The AlN electrolysis has not been studied extensively. The only work reported in this area is that of the Battelle Geneva Research Center.<sup>25</sup> Aluminum nitride was electrolyzed in a molten mixture of Li<sub>3</sub>N and LiCl. No metallic aluminum was actually collected in the electrolysis. The faradaic efficiency determined by an indirect method increased with increasing current density and reached a value of about 83% at a cathodic current density of 1.55 A/cm<sup>2</sup> and temperature of 1023 K. The cell voltages recorded during the electrolysis were reported to be in reasonable agreement with the theoretical values. It seems that the electrolysis is not simple, and finding a suitable solvent for AlN would present a major problem.

## C. Energetics of Aluminum Production Processes

The total cell voltage,  $V_{\text{cell}}$ , of an aluminum cell is given by the following relationship:

$$V_{\text{cell}} = V_{\text{rev}} + \Sigma\eta + \Sigma IR \quad (5)$$

where  $V_{\text{rev}}$  is the reversible decomposition voltage,  $\Sigma\eta$  is the sum of cell operating overpotentials, and  $\Sigma IR$  is the sum of ohmic voltages through the various cell components.

At a current efficiency of  $x\%$ , the electrical-energy requirement, EER, in kWh/kg Al may be represented by the following equation:

$$\text{EER} = 3.086 \frac{F V_{\text{cell}}}{x} \quad (6)$$

where  $F$  is the faraday.



Table II-4 compares the voltage drops in the ASP cell,  $\text{Al}_2\text{S}_3$  electrolysis cell, and  $\text{AlN}$  electrolysis cell with that for the Hall-Héroult cell. For the  $\text{Al}_2\text{S}_3$  and  $\text{AlN}$  electrolysis cells, it is assumed that: (1) sulfur ( $\text{Al}_2\text{S}_3$ ) or nitrogen ( $\text{AlN}$ ) is formed at the anode, and (2) ohmic losses and overpotential drops are the same as those of the ASP.

Table II-4. Voltage and Energy Comparison for Various Aluminum Cells

Parameter	Hall-Héroult (1223 K)	ASP (1000 K)	$\text{Al}_2\text{S}_3$ (1000 K)	$\text{AlN}$ (1000 K)
Decomposition Voltage, V	1.20	1.84	0.98	0.73
Anode and Cathode Overpotentials, V	0.64	0.40	0.40	0.40
Ionic (Electrolyte) Resistance Drop, V	1.27	0.55	0.55	0.55
Electronic (Electrode) Resistance Drop, V	<u>1.15</u>	<u>0.20</u>	<u>0.20</u>	<u>0.20</u>
Total Cell Voltage, V	4.26	2.99	2.13	1.88
Assumed Current Efficiency	90%	90%	90%	90%
dc kWh/kg Al (GJ/Mg)	14.1 (50.8)	9.9 (35.6)	7.0 (25.2)	6.2 (22.3)
Fossil-Fuel Energy Equivalent, GJ/Mg <sup>a</sup>	154	108	76	68

<sup>a</sup>The efficiency of combustion of a fuel to generate electrical energy is taken to be about 33%.

As can be seen from Table II-4, the amount of electrical energy required per kilogram of aluminum is substantially lower for the electrolysis of  $\text{Al}_2\text{S}_3$  and  $\text{AlN}$  than for the ASP or the Hall-Héroult process. However, the total energy required for each process must include the thermal-energy requirement. For the Hall-Héroult, the thermal energies are the energies of the Bayer process, the mining and ore beneficiation, the carbon anodes and their preparation. This is about 80 GJ/Mg. The thermal energy for the ASP (the energies of the Bayer process and the chlorination of alumina) is at least 80 GJ/Mg. The thermal energy demand for the  $\text{Al}_2\text{S}_3$  and  $\text{AlN}$  electrolysis processes can be estimated thermodynamically. The compounds  $\text{Al}_2\text{S}_3$  or  $\text{AlN}$  could be formed by the reaction between  $\text{Al}_2\text{O}_3$ , C, and  $\text{S}_2$  or  $\text{Al}_2\text{O}_3$ , C, or  $\text{N}_2$ , respectively. The computer program developed by NASA-Lewis Research Center was used to calculate the equilibrium composition of these reactions,<sup>6</sup> and the thermal-energy requirements were estimated at the necessary temperature and pressure for 90% conversion of  $\text{Al}_2\text{O}_3$  to the intermediate salt. The estimates for the  $\text{Al}_2\text{S}_3$  and  $\text{AlN}$  processes are 120 and 140 GJ/Mg, respectively. If a less energy-consuming route can be devised, the thermal energy for these processes would be reduced. For example,  $\text{Al}_2\text{S}_3$  could be formed from  $\text{Al}_2\text{O}_3$  and  $\text{CS}_2$  in a molten salt<sup>7</sup> at a lower temperature;  $\text{AlN}$  could be produced by the reaction between  $\text{AlCl}_3$  and ammonia.<sup>25</sup> Table II-5 shows the estimates of energy requirements for various aluminum processes.

It must be emphasized here that the reliability of these estimates is very limited. The comparison, however, is useful in demonstrating that there is a possibility of energy savings in the alternative technologies (ASP,  $\text{Al}_2\text{S}_3$ , and  $\text{AlN}$ ) as compared to the Hall-Héroult process. The  $\text{AlN}$  process represents

Table II-5. Estimates of Energy Requirements for Various Processes for the Production of Aluminum

	Hall-Hérout	ASP	Al <sub>2</sub> S <sub>3</sub>	AlN
Equivalent Electrical Energy, GJ/Mg	154	108	76	68
Thermal Energy, GJ/Mg	<u>80</u>	<u>80</u>	<u>80-120</u>	<u>80-140</u>
Total, GJ/Mg	234	188	156-196	148-208

a long shot for low energy in the future, but many uncertainties exist in both the production and the electrolysis of AlN. For example, finding a suitable solvent for AlN poses a formidable problem. On the other hand, the Al<sub>2</sub>S<sub>3</sub> electrolysis process has less uncertainty since more knowledge is presently available regarding the electrolysis of metal sulfides in molten salts. Synthesizing the Al<sub>2</sub>S<sub>3</sub> from alumina or aluminous ores would still require considerable developmental work; however, the energy-consumption estimate for the Al<sub>2</sub>S<sub>3</sub> electrolysis process is sufficiently attractive to warrant experimental studies to better understand the complete electrolytic process and to determine its technical feasibility.

### III. LITERATURE SURVEY

As mentioned in Section I, the experimental effort of the present study on the electrolysis of Al<sub>2</sub>S<sub>3</sub> was directed at three areas: (1) the solubility of Al<sub>2</sub>S<sub>3</sub> in molten salts, (2) the electrochemical behavior of Al<sub>2</sub>S<sub>3</sub>, and (3) the electrolysis of Al<sub>2</sub>S<sub>3</sub> with the determination of current efficiency as a function of current density. These experiments were preceded by a literature survey. The survey begins with a description of previous work on sulfide electrolysis with emphasis on practical aspects such as operating conditions and current efficiencies. The survey then summarizes the published information on the anodic oxidation of sulfide ions and the solubility of metal sulfides in molten salts.

#### A. Metal Production by the Electrolysis of Metal Sulfides

A thorough literature search on the electrolysis of metal sulfides in molten salts was carried out to provide a background to the present study. The electrolysis of molten metal sulfides to give the metal and sulfur has been known since 1833, when Michael Faraday<sup>26</sup> electrolyzed fused "Sulphuret of Antimony" in an attempt to determine the electrochemical equivalent of sulfur and antimony. Electrolysis of many pure molten sulfides was later found to be impractical due to their high melting points and appreciable electronic conductivity in their molten state. The proposed use of a solution of metal sulfides in a fused-salt electrolyte for the extraction of metals goes back to the late 19th century. In the year 1892, Bucherer<sup>24</sup> was issued a patent on the electrolysis of sodium aluminum sulfide (Na<sub>6</sub>Al<sub>2</sub>S<sub>6</sub>) in an electrolyte of alkali or alkaline-earth fluorides or chlorides. Since that time, research on sulfide electrolysis has been conducted by many investigators. To date, there has been no commercial production of metals

based on this principle; and except for pilot-scale studies on the electrolysis of galena (PbS) in fused chlorides, the work has been limited to laboratory-scale studies.

Because of its comparatively low theoretical energy requirement, the extraction of metals by the electrolysis of their sulfides in molten salts has long been commercially attractive. Many metal sulfides of practical interest have theoretical decomposition voltages well below the decomposition voltages of most chlorides and oxides. For metals which do not occur as natural sulfides, the use of this extraction would also require an economical way of converting the corresponding ore to sulfide. Fortunately, however, raw materials for many nonferrous metals are sulfide minerals. Thus, the simplest scheme is to dissolve the sulfide mineral directly in a suitable melt; electrolysis then yields metal at the cathode and sulfur at the anode. In addition to having low energy requirements, this process is attractive from the pollution-control standpoint since it directly converts sulfide ores to elemental sulfur without undesirable SO<sub>2</sub> emissions. The process is also useful for low-grade ores that cannot be processed by conventional metallurgical methods.

### 1. Aluminum Sulfide

The electrolysis of aluminum sulfide in molten salts was first proposed by Bucherer<sup>24</sup> in 1892. He suggested dissolving sodium aluminum sulfide (Na<sub>6</sub>Al<sub>2</sub>S<sub>6</sub>) in an electrolyte of alkali or alkaline-earth fluorides or chlorides and electrolyzing the molten bath. Aluminium Industrie, A.-G.<sup>27</sup> recommended using aluminum sulfide instead of sodium aluminum sulfide. In 1894 Jaenniger<sup>28</sup> prepared aluminum sulfide by fusing a mixture of alumina and sodium carbonate in carbon disulfide and then electrolyzing the fused bath in an atmosphere of carbon disulfide. Peniakoff<sup>29</sup> stated that aluminum sulfide was formed by the double decomposition taking place between anhydrous aluminum salts and the sulfides of alkalies or alkaline-earths in a suitable flux. The aluminum sulfide could then be electrolyzed directly in the molten bath.

According to Blackmore,<sup>30</sup> the electrolysis of aluminum sulfide could be carried out in a molten electrolyte of sodium and potassium sulfide containing alkali thiocarbonates. Gin<sup>31</sup> proposed an electrolyte composed of aluminum fluoride and sodium sulfide. Keogh<sup>32</sup> added anhydrous aluminum sulfate and carbon to fused sodium chloride. The sulfate was thought to be reduced by the carbon to aluminum sulfide which could then be reduced to aluminum by electrolysis of the mixture. Kissock<sup>33</sup> suggested converting alumina to aluminum carbide and followed by heating with sulfur or a sulfide to form aluminum sulfide. The compound was dissolved and electrolyzed in a molten bath of alkaline earth chlorides or fluorides.

In the 1930's, German and Russian scientists initiated a revival of research into aluminum sulfide electrolysis. Röntgen and Borchers<sup>34</sup> prepared aluminum sulfide by melting Al with FeS (or ZnS, PbS, CuS) without the use of flux and found that the recovery of aluminum sulfide was very high. Aluminum sulfide was then electrolyzed in NaCl (60% Al<sub>2</sub>S<sub>3</sub>, 40% NaCl)\* at 973 K.

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\* All concentrations are given in mole percent unless stated otherwise.

Their preliminary experiments indicated that the decomposition voltage of  $\text{Al}_2\text{S}_3$  is 1 V lower than that of  $\text{Al}_2\text{O}_3$  in cryolite with little attack on C anodes. In 1937, the authors took out a patent<sup>35</sup> on a process in which an  $\text{Al}_2\text{S}_3$ -containing melt was prepared from aluminous material such as clay or bauxite by heating with sulfur or a metal sulfide. Metallic aluminum was recovered by electrolysis. Khazanov and Belyaev<sup>36</sup> carried out a more detailed study of the electrolysis of  $\text{Al}_2\text{S}_3$  in various melts such as  $\text{Al}_2\text{S}_3$  in NaCl, and  $\text{Al}_2\text{S}_3$  in a mixture of cryolite with either NaCl or KCl. They reported the current efficiency of the electrolysis in 30% cryolite-70% NaCl as a function of  $\text{Al}_2\text{S}_3$  concentration, anode and cathode current densities, and electrolyte temperature. Optimum electrolysis conditions were found to be: sulfide concentration, 7%  $\text{Al}_2\text{S}_3$ ; anode current density, 1 A/cm<sup>2</sup>; cathode current density, 0.7 A/cm<sup>2</sup>; electrolyte temperature, 1073 K. The maximum current efficiency obtained for these optimum conditions was reported to be 55%. Addition of  $\text{Al}_2\text{O}_3$  to the molten salt did not affect the current efficiency whereas the addition of FeS reduced the efficiency sharply.

Gardner<sup>37</sup> patented a process in which aluminum is produced by electrolyzing  $\text{Al}_2\text{S}_3$  in a fused alkali fluoride or mixture of fluorides in a closed cell. Khazanov and Komarov<sup>38</sup> investigated the electrolytic refining of aluminum in 56% cryolite-37% NaCl-7%  $\text{Al}_2\text{S}_3$ . Their best results were obtained using an anodic current density of 1 A/cm<sup>2</sup> and a cathodic current density of 1.5 A/cm<sup>2</sup>.

Röntgen and Giesen<sup>39</sup> attempted to repeat Khazanov and Belyaev's experiments; however, they reported experimental difficulties and carried out further work with 83% cryolite-2% NaCl-15%  $\text{Al}_2\text{S}_3$ . These experiments were carried out at high cathodic current densities (1.3-2.6 A/cm<sup>2</sup>). The current efficiencies achieved were 46-54%, very close to values obtained by these authors for  $\text{Al}_2\text{O}_3$  electrolysis in 88% cryolite-2% NaCl-10%  $\text{Al}_2\text{O}_3$  under similar conditions (48-54%).

In 1976, the Light Metal Smelters Association of Japan undertook basic studies on the production of aluminum electrolytically from aluminum sulfide,<sup>40</sup> but the effort was later discontinued because of some problems encountered during their electrolysis work.

## 2. Other Metal Sulfides

### a. Antimony

The principal antimony mineral is the sulfide. Therefore, many attempts have been made to extract antimony metal from its sulfide *via* electrolysis. Problems with the electrolysis of molten antimony sulfide arise from (1) the mutual solubility of the liquid metal and sulfide phases which results in very low current efficiency and (2) the high electronic conductivity of the melt. Vivian<sup>41</sup> improved the ionic conductivity of the molten sulfide by adding  $\text{Na}_2\text{S}$  to the melt; however, the current efficiency of his electrolysis barely exceeded 10%. Better yields were obtained by Yanagase and Derge<sup>42</sup> who performed the electrolysis of a metal-saturated solution of the sulfide.

A new attempt at antimony deposition from a solution of the sulfide in chloride mixtures has yielded improved current efficiency.<sup>43</sup> Also, Weiss<sup>44</sup> studied the electrolysis of  $\text{Sb}_2\text{S}_3$  in oxysalts ( $\text{NaPO}_3\text{-NaCl}$  and  $2\text{B}_2\text{O}_3, \text{Na}_2\text{O-NaF}$ ) and reported the current efficiency to be about 45%. The Russian school<sup>45-51</sup> concentrated their efforts on studies of the electrical conductivity and current efficiency during electrolysis of binary melts of  $\text{Sb}_2\text{S}_3\text{-Na}_2\text{S}$ . They found that a critical concentration of  $\text{Na}_2\text{S}$  in the melt mixture was required for successful electrolysis of  $\text{Sb}_2\text{S}_3$ . The maximum current efficiency of the electrolysis of 15%  $\text{Na}_2\text{S}$ -85%  $\text{Sb}_2\text{S}_3$  was reported to be about 64% at 0.5  $\text{A/cm}^2$  and 993 K. Colom and de la Cruz<sup>52</sup> achieved a current efficiency of up to 100% for antimony deposition from molten 33 mol %  $\text{Na}_2\text{S}$ -67 mol %  $\text{Sb}_2\text{S}_3$  at 1173 K with a cathodic current density of 1  $\text{A/cm}^2$ .

#### b. Copper

As in the cases of many other metal sulfides, the electrical conductivity of cuprous sulfide is predominantly electronic, rather than ionic, in nature, so that electrodeposition from the pure molten sulfide is not feasible. The results obtained by Yang *et al.*,<sup>53</sup> indicate that  $\text{Cu}_2\text{S-CuCl}$  solutions, of concentrations up to about 30 mol %  $\text{Cu}_2\text{S}$  and temperatures below 1273 K, are essentially ionic conductors. The electrolysis of  $\text{Cu}_2\text{S}$  in  $\text{CuCl}$  by Garbee and Flengas<sup>54</sup> yielded copper metal at the cathode with high current efficiencies. Current efficiencies of about 80% were obtained in the low-temperature range 723-773 K with low apparent current densities ( $\leq 15 \text{ mA/cm}^2$ ) and with  $\text{Cu}_2\text{S}$  concentration  $\leq 30$  mol %. Velikanov *et al.*<sup>55,56</sup> electrolyzed a molten mixture of  $\text{Na}_2\text{S-Cu}_2\text{S}$  with cathodic current densities of 5-7  $\text{A/cm}^2$  at 923 K and 1023 K.

#### c. Indium

Velikanov and coworkers<sup>57</sup> measured the electrical conductivity of the  $\text{In}_2\text{S}_3\text{-Na}_2\text{S}$  system over a wide range of temperatures and concentrations. The electrolysis of melts containing 50-90%  $\text{Na}_2\text{S}$  was carried out at different voltages and cathodic current densities. Indium metal was deposited and detected at the cathode.

#### d. Iron

The only reported work on iron sulfide is that of Velikanov and coworkers.<sup>58</sup> Iron was recovered from 35%  $\text{FeS}$ -65%  $\text{Na}_2\text{S}$  melts at 1243 K by electrolysis in Alundum cells using graphite anodes, at a current density of 1.5  $\text{A/cm}^2$ . The current efficiency was 29%.

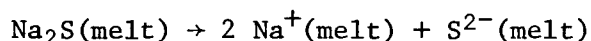
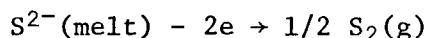
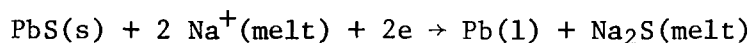
#### e. Lead

The electrolysis of galena ( $\text{PbS}$ ) has been extensively studied. In 1906 Townsend<sup>59</sup> was issued a patent for the reduction of sulfidic ores, especially of galena, by electrolysis using a molten mixture of lead and sodium halide salts as solvent.

The electrolysis has been developed to pilot-plant scale at three separate locations. The first of these plants was at Halkyn in Wales, U.K. and operated for some years up to the outbreak of World War II in 1939. Subsequently, plants were built in Canada and Port Pirie, Australia.

The process was based on a patent granted to Gibson and Robson<sup>60</sup> and Richardson,<sup>61</sup> and Newall<sup>62</sup> gave a limited amount of additional information. Bipolar electrodes were used at a voltage of 1.2-1.4 V per stage and an energy consumption of 740-790 Wh/kg, which implies an efficiency of the order of 50%. The concentration of dissolved PbS in PbCl<sub>2</sub> was 3-5%, the temperature 823 K, and the current density 0.6-0.75 A/cm<sup>2</sup>. The bath was agitated, and the addition of feed and removal of gangue took place in a special compartment.

Laboratory studies of the electrolysis have been reported by a number of investigators. Izgaryshev and Grigor'ev<sup>63</sup> recommended the electrolysis of galena suspension in a melt of mixed sodium and potassium chlorides, and Gul'din and coworkers<sup>64-67</sup> suggested a similar electrolyte containing a small quantity of dissolved sodium sulfide. They described a pilot cell working 1500 A at 903-1003 K with a liquid lead cathode. The current efficiency was reported to be 96-97%. The mechanism of the process is represented by the following equations:



The formation of Na<sub>2</sub>S was shown not to affect the kinetics of discharge of the metal.<sup>68</sup>

Vlasenko *et al.*<sup>69</sup> discussed the feasibility of a method for the treatment of PbS raw material by electrolysis in NaCl-KCl melts. Based on their conductivity data, Velikanov and coworkers<sup>70</sup> suggested that lead could be recovered electrolytically from PbS-Na<sub>2</sub>S. Winterhager and Kammel<sup>43,71,72</sup> demonstrated the feasibility of the PbS electrolysis in molten alkali chlorides on a small scale. They gave yield data and details of cell construction, current, voltage, temperature, and energy consumption.

Japanese investigators<sup>73-75</sup> favored the addition of alkali chloride to molten PbCl<sub>2</sub> to improve the conductivity and lower the temperature at which electrolysis can be conducted. Alkali chlorides also reduce metal loss due to fogging. The current efficiency of their electrolysis approached 95%. Furukawa<sup>76</sup> has patented the use of a pressed anode of fused or partly fused galena suspended in a fused lead chloride bath. The PbS is then electrolyzed at about 773 K to deposit lead at the cathode.

Detailed studies of Welch and coworkers<sup>77-81</sup> on the electrolysis of PbS in PbCl<sub>2</sub>-NaCl show the effects of temperature, sulfide concentration, and current density on current efficiencies. It has been shown that high current efficiency is favored by a low concentration of lead sulfide, high current density, and a low temperature. These authors pointed out that the primary cause for the loss in current efficiency is lead reoxidation, either from sulfur dissolving in the melt or from the formation of subsulfide or polysulfide ions at the anode. The polysulfide or subsulfide products have a limited solubility in the melt and can give rise to a buildup of solid material. Further studies show that other sulfides contaminating the galena

will not dissolve in  $\text{PbCl}_2$  or  $\text{PbCl}_2\text{-NaCl}$  but will form an insoluble gangue; thus, low-grade ores might be amenable to treatment if the problem of the separation of gangue could be solved.

f. Magnesium

A completely new process was proposed by Winterhager, Krajewski, and Nawab-Teherani<sup>82</sup> who produced magnesium of 99.9% purity, by electrolysis of  $\text{MgS}$  dissolved in an  $\text{MgCl}_2\text{-3% NaF}$  electrolyte. At 1023 K, the solubility of  $\text{MgS}$  in the electrolyte is about 4-5%. At an anodic current density of  $0.5 \text{ A/cm}^2$  and 15%  $\text{MgS}$ , the current efficiency was about 42%. The authors claimed that better current efficiency could be achieved for larger-scale electrolysis. They detected  $\text{S}_2\text{Cl}_2$  during the electrolysis at high potentials, but only  $\text{S}_2$  at low potentials.

g. Molybdenum

An attractive technique for molybdenum production by electro-extraction directly from technical-grade molybdenum disulfide ( $\text{MoS}_2$ ) was proposed by Mukherjee and Gupta.<sup>83</sup> The process involved molybdenum disulfide-carbon soluble-anode electrolysis in a  $\text{KCl-K}_3\text{MoCl}_6$  electrolyte. Metal recovery of 82% at an average current efficiency of 50% was achievable at 1173 K with a cathode current density of about  $1.5 \text{ A/cm}^2$  and an operating voltage of 0.7 to 0.8 V. The process yielded molybdenum of >99% purity. Electrolysis with a molybdenum sesquisulfide ( $\text{Mo}_2\text{S}_3$ ) or  $\text{Mo}_2\text{S}_3$ -graphite anode<sup>84</sup> gave higher current efficiencies (up to 87%).

h. Nickel

Nickel was reported to be recovered from a 3.5%  $\text{Ni}_3\text{S}_2\text{-96.5% Na}_2\text{S}$  melt at 1173 K by electrolysis at  $0.5 \text{ A/cm}^2$ .<sup>58,85</sup> The current efficiency was 14% and decreased with increasing current density and increasing temperature.

i. Silver

Electrolysis of a  $\text{Ag}_2\text{S-Na}_2\text{S}$  melt was investigated by Velikanov *et al.*<sup>86-89</sup> as part of their studies on metal sulfide-alkali sulfide systems. Experiments were conducted for two compositions at various temperatures and current densities. Silver was isolated in all cases.

j. Thallium

The electrolysis of molten  $\text{Tl}_2\text{S}$ ,  $\text{Tl}_2\text{S}_3$ , and  $\text{Tl}_2\text{S-K}_2\text{S}$  has been studied by the Russians.<sup>90,93</sup> The addition of alkali sulfide to molten  $\text{Tl}_2\text{S}$  greatly improved the electrolysis due to the reduction of nonionic conductivity. The best current efficiency of 70% was obtained at 723-773 K in 55%  $\text{Tl}_2\text{S-45% K}_2\text{S}$  with a current density of  $1.5\text{-}2.0 \text{ A/cm}^2$ .

k. Tin

Velikanov and coworkers demonstrated that tin could be extracted from  $\text{SnS-Na}_2\text{S}$  or  $\text{SnS-KCl}$  melts.<sup>70,94-96</sup> The efficiency, however, was low ( $\sim 33\%$ ), and cell voltage was high ( $\sim 9 \text{ V}$ ) in the  $\text{Na}_2\text{S}$ -containing melt.

A better yield (70%) with a tin cathode and a carbon anode was reported for the SnS-KCl system at 1073 K and 1-A/cm<sup>2</sup> current density.

### 1. Zinc

The principal source material for zinc is the naturally occurring sulfide, sphalerite (ZnS). The direct electrolysis of sphalerite dissolved in a molten salt has been studied only on a laboratory scale. A survey by Kammel<sup>97</sup> on molten-salt electrolysis methods for zinc recovery indicated that ZnS electrolysis was possible with good current efficiency and high metal yield. In 1978, Fullam and Hartley<sup>98</sup> carried out an experimental program to evaluate the production of zinc *via* molten-salt electrolysis of ZnS. They found that electrolysis with chloride or fluoride melts had to be conducted at low current densities because the zinc sulfide content of the melts was too low. In a mixed chloride-fluoride system, KF-LiF-NaF-NaCl-ZnF<sub>2</sub>, anode current densities of up to 0.3 A/cm<sup>2</sup> could be employed. Current efficiency in the melt at an anodic current density of 0.2 A/cm<sup>2</sup> and 923 K was 95% and cell voltage was 2.9-3.3 V. One process modification investigated was the electrolysis of a thick slurry of ZnS in a chloride melt. In this case the electrolytic cell could be operated at higher anodic current density without the evolution of S<sub>2</sub>Cl<sub>2</sub> or Cl<sub>2</sub>.

### B. Electrochemical Behavior of Aluminum and Sulfide Ions in Molten Salts

The electrolytic decomposition of Al<sub>2</sub>S<sub>3</sub> is believed to involve the reduction of aluminum ions (or aluminum-ion-containing species) at the cathode and the oxidation of sulfide ions (or sulfide-ion-containing species) at the anode. Therefore, a literature search on the electrochemical behavior of these two ions was carried out and is summarized below.

#### 1. Cathodic Reduction of Aluminum Ions in Molten Salts

Aluminum chloride-alkali chloride and cryolite melts have been the most commonly used electrolytes for studies of the electroreduction of aluminum ions.<sup>99</sup> Studies in chlorides are often in connection with aluminum plating and aluminum refining and production (Alcoa Smelting Process), while aluminum deposition from cryolite-based melts is the basis of the present commercial aluminum electrowinning.

Data are available on electrode potential for aluminum in a number of fused-salt systems.<sup>100</sup> In such fused-salt electrolytes, oxide films are considered to be of little importance, and the aluminum electrode reactions are quite reversible. Kinetic studies of the aluminum electrode in molten-salt systems have also been carried out by many investigators.<sup>99</sup> The solvent equilibria have been described in a manner similar to that used for aqueous electrolytes. Boxall *et al.*,<sup>101</sup> Fannin *et al.*,<sup>102</sup> and others<sup>103-105</sup> have examined solvent equilibria in AlCl<sub>3</sub>-alkali metal chloride melts, while Rey<sup>106</sup> has considered equilibria in cryolite-Al<sub>2</sub>O<sub>3</sub> melts.

The reduction of aluminum ions appears to be quite straightforward in AlCl<sub>3</sub>-containing melts.<sup>99</sup> Senderoff<sup>107</sup> claimed deposition of Li-Al from AlCl<sub>3</sub>-LiCl, and attributed the formation of Li-Al alloy to the existence of a



stable intermetallic phase and the mutual solubility of Li and Al. In contrast, the Na-Al and K-Al phase diagrams show no mutual solubility or intermetallic phases. At lower temperatures (that is, below the melting point of aluminum) deposition of aluminum from aluminum chloride-alkali chloride melts is often accompanied by dendrite formation. Aluminum deposition has also been postulated to occur from  $\text{Al}_2\text{Cl}_7^{2-}$  rather than  $\text{AlCl}_4^-$ .<sup>108</sup> The ions  $\text{Al}^+$  and  $\text{Al}^{2+}$  have been postulated in kinetic studies of aluminum electrode; however, their existence has not been positively established and is open to further experimentation. At higher temperatures (that is, above the melting point of aluminum) the electrolysis of  $\text{AlCl}_3$  in  $\text{AlCl}_3$ -alkali chlorides produces liquid aluminum metal which has very low solubility in the solvents. The back reaction between Al and  $\text{Cl}_2$  is small since chlorine is hardly soluble in molten chlorides.

The cathodic reaction of aluminum in cryolite melts has been the subject of rather few experimental studies, probably because the reaction occurring at the cathode has been considered to be simple. Early studies of the cathodic reaction were centered on the question of whether sodium or aluminum is the primary cathodic product. The magnitude as well as the nature of the overvoltage is a matter of controversy. While  $\text{Na}^+$  has been shown to be the main current-carrying species in the electrolysis of  $\text{Al}_2\text{O}_3$  in cryolite, the nature of the anionic species is still the subject of some controversy.<sup>10</sup> In cryolite, the existence of  $\text{Al}^+$  appears to be well established.

A complete review of the cathodic reaction in  $\text{AlCl}_3$ -containing chloride and in  $\text{Al}_2\text{O}_3$ -cryolite can be found in monographs by Plambeck<sup>100</sup> and by Grjotheim and coworkers,<sup>10</sup> respectively.

## 2. Anodic Oxidation of Sulfide Ions in Molten Salts

The oxidation of sulfide ions in molten salts is rather complex. The mechanism of the reaction is still controversial and cannot be interpreted in an unambiguous manner. Attention has been focused mainly on the oxidation of sulfide in molten chlorides. The identity of the sulfur species involved has also been investigated. Other sulfide-related studies include electrode processes in sulfide and polysulfide melts,<sup>109,110</sup> the mechanism of  $\text{FeS}_2$  electrodes in molten chlorides,<sup>111</sup> and the electrochemical behavior of sulfide and polysulfide ions in molten alkali thiocyanates.<sup>112,113</sup> The literature survey in this section centers on the electrochemical reaction of sulfide in molten chlorides.<sup>114-129</sup>

Delarue<sup>114,115</sup> was one of the first workers to investigate redox reactions involving sulfur and sulfide in LiCl-KCl eutectic. According to Delarue, sulfide ion is oxidized electrochemically to sulfur *via* a simple reaction,  $\text{S}^{2-} - 2e \rightarrow \text{S}$ . The half-wave potential was located at -0.45 V *vs.* a Pt/Pt<sup>2+</sup> reference electrode.

Bodewig and Plambeck<sup>116</sup> studied the sulfur-sulfide reaction in LiCl-KCl eutectic at 693 K using coulometry, potentiometry, and chronopotentiometry. The sulfur-sulfide couple showed Nernstian behavior, with 1.86 for the number of electrons involved in the reaction. Weaver and Inman<sup>117</sup> found that the oxidation of sulfide ions in LiCl-KCl up to 723 K was complex; their chronopotentiometric results indicated an overall diffusion-controlled

and reversible reaction. The oxidation appeared to be controlled by the extensive formation of a polymeric sulfur film, and a mixture of various soluble polysulfides was ultimately formed. Calcium sulfide was reported to dissolve in LiCl-KCl eutectic and oxidize in three steps<sup>118</sup> yielding a final oxidation product of  $S^+$ .

Other workers<sup>120-122</sup> have investigated the behavior of sulfides in  $AlCl_3$ -NaCl. According to Marassi *et al.*,<sup>121</sup> the oxidation of sulfide ions in NaCl-saturated  $AlCl_3$ -NaCl melt at 448-530 K occurred in two steps. The oxidation product was either  $S_2^{2+}$  or  $S^{2+}$ , depending on the temperature, the higher oxidation state being formed at higher temperatures. Paulsen and Osteryoung<sup>120</sup> found that the solubility of metal sulfides increased markedly as the melt was made more acid, *i.e.*, as  $AlCl_3$  was added. They deduced the acid-base equilibrium involving the sulfide and the solvent to be  $AlCl_4^- + S^{2-} = AlSCl + 3Cl^-$ . Raman spectroscopic measurements by Berg *et al.*<sup>123</sup> have shown that in LiCl-CsCl and CsCl- $AlCl_3$  melts, dissolved tetrachloroaluminate and sulfide ions at  $\sim 673$  K react in a ratio close to 1:1.

The electrochemical oxidation of sulfide in  $PbS$ - $PbCl_2$ -NaCl and  $PbS$ - $PbCl_2$ -KCl melts has been studied by several investigators<sup>79,81,124-129</sup> to obtain a better understanding of the anode reaction in the electrowinning of lead. Detailed studies by Welch and coworkers<sup>79,81,124,125</sup> showed that the oxidation of  $PbS$  occurred *via* an irreversible two-electron process in  $PbCl_2$ -NaCl at 713 K. The product formed on glassy carbon was of limited solubility but reacted with the melt to form a new product that was not electrochemically reduced. The follow-up reaction was first-order with a rate constant of  $8\text{ s}^{-1}$ . It was reported by deGuibert *et al.*<sup>126-129</sup> that in  $PbCl_2$ -KCl,  $PbS$  was oxidized in two steps. The first step was a two-electron transfer controlled by the diffusion of sulfide ion; the final product in the second, complex step was reported to be sulfur formed without intermediate formation of polysulfide.

Greenberg, Sundheim, and Gruen<sup>130</sup> interpreted the blue solution formed by the dissolution of sulfur in LiCl-KCl as being caused by diatomic sulfur molecules in the triplet state. This explanation was supported by Delarue<sup>115</sup> who observed an intense blue color when sulfides were oxidized in LiCl-KCl. Bodewig and Plambeck,<sup>131</sup> however, found that in highly purified LiCl-KCl melt at 673 K, the solution of sulfur was colorless and that the blue color appeared only when either sulfur was reduced or sulfide ions were added, suggesting that coloration arises from a polysulfide ion formed by the reaction,  $S^{2-} + S_{2x-1} = 2S_x^-$ . On the other hand, Gruen *et al.*<sup>132</sup> carried out spectrophotometric measurements on the sulfur-sulfide system in LiCl-KCl at 873 K. The blue color was attributed to the  $S_3^-$  ion and the green color to  $S_2^-$ . Giggenbach<sup>133,134</sup> concluded from his spectrophotometric studies in LiCl-KCl that  $S_2^-$  is responsible for the blue color.

### C. Solubility of Metal Sulfides in Molten Salts

One of the principal requirements for a viable  $Al_2S_3$  process for aluminum is a suitable molten-salt electrolyte having a high enough solubility of  $Al_2S_3$  to allow acceptable cell operation. The only data relating to the amount of  $Al_2S_3$  dissolved in molten salts are those reported in work on the molten-salt electrolysis of  $Al_2S_3$ <sup>36,39</sup> and on the solubilization of  $Al_2S_3$  by  $AlCl_3$ .<sup>135</sup> Khazanov and Belyaev<sup>36</sup> carried out the electrolysis of  $Al_2S_3$  in

cryolite-sodium chloride at 1013-1123 K with concentrations of  $\text{Al}_2\text{S}_3$  up to 15 mol %. Röntgen and Giesen<sup>39</sup> used cryolite containing 25 mol %  $\text{Al}_2\text{S}_3$  in their electrolysis investigation at 1123 K; however, it is not clear whether all the  $\text{Al}_2\text{S}_3$  used was soluble. Recently, Nagy *et al.*<sup>135</sup> titrated  $\text{AlCl}_3$  with  $\text{Li}_2\text{S}$  in  $\text{LiCl-KCl}$  eutectic at 723 K and indicated that  $\text{Al}_2\text{S}_3$  was soluble in the molten salt as long as there was a significant excess of  $\text{AlCl}_3$ . In  $\text{AlCl}_3\text{-NaCl}$  (54.5-45.5 mol %) at 513 K, the solubility of  $\text{Al}_2\text{S}_3$  was reported to be 0.26 mol %.<sup>136</sup>

There is not a great deal of systematic information available on melt systems containing sulfides. Phase diagrams are available for a few systems, for example,  $\text{AgCl-Ag}_2\text{S}$ ,<sup>137,138</sup>  $\text{PbCl}_2\text{-PbS}$ ,<sup>139,140</sup>  $\text{CuCl-Cu}_2\text{S}$ ,<sup>54</sup>  $\text{FeCl}_2\text{-FeS}$ ,<sup>54</sup>  $\text{ZnF}_2\text{-ZnS}$ ,<sup>141</sup>  $\text{SnS-SnCl}_2$ ,<sup>142</sup>  $\text{Tl}_2\text{S-TlCl}$ ,<sup>143</sup> and  $\text{NaCl-PbCl}_2\text{-PbS}$ .<sup>72-75</sup> Also, not much data have been reported on solubilities of other metal sulfides in molten salts. Mohapatra, Alcock, and Jacob<sup>144</sup> determined the solubilities of  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ , and  $\text{Cu}_2\text{S}$  in the  $\text{NaCl-KCl}$  eutectic melt. The solubilities of these sulfides were found to be small; for example, at 1123 K the solubilities were less than 1 mol %. Sodium sulfide addition was observed to enhance these solubilities, the effect being largest for  $\text{Cu}_2\text{S}$  followed by  $\text{Sb}_2\text{S}_3$ ,  $\text{Bi}_2\text{S}_3$ , and  $\text{PbS}$ . Using the method of decantation and analysis, Pelton and Flengas<sup>145</sup> measured the solubility of  $\text{PbS}$  in  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ , and  $\text{CsCl}$ . The solubility of  $\text{PbS}$  was found to increase as the solvent was changed in the series from  $\text{NaCl}$  to  $\text{CsCl}$ .

Gashurov and Levine<sup>146</sup> investigated the solubility of  $\text{ZnS}$  in  $\text{ZnCl}_2$  at various temperatures and in certain other halides at specific temperatures. The solubility of  $\text{ZnS}$  in  $\text{ZnCl}_2$  in molality,  $m$ , at temperature  $T$ , is given as  $\log m = -2520/T + 2.06$ . Fullam and Hartley<sup>98</sup> reported the maximum solubility of  $\text{ZnS}$  in a large number of chlorides containing  $\text{ZnCl}_2$  to be about 3 wt % at temperatures up to 973 K. They found appreciable  $\text{ZnS}$  solubility in certain fluoride and mixed fluoride-chloride systems, up to 20 wt %  $\text{ZnS}$  in  $\text{ZnF}_2\text{-NaCl-KF-LiF-NaF}$  (30-28-25-12-5 wt %) at 1073 K.

An electrode composed of the eutectic mixture of  $\text{NiS}$  and  $\text{Ni}$  (1:1 mole ratio) was employed by Liu and coworkers<sup>147</sup> to study the solubility behavior of  $\text{NiS}$  and  $\text{Li}_2\text{S}$  in  $\text{LiCl-KCl}$  eutectic. Saboungi *et al.*<sup>148,149</sup> measured the solubilities of  $\text{Li}_2\text{S}$  and the solubility product of  $\text{FeS}$  and  $\text{PbS}$  in  $\text{LiCl-KCl}$  eutectic and  $\text{LiCl-LiF}$  eutectic using an electrochemical titration technique. At 823 K, the solubility of  $\text{Li}_2\text{S}$  in  $\text{LiCl-LiF}$  is much larger than in  $\text{LiCl-KCl}$  ( $1.95 \times 10^{-2}$  compared with  $3.50 \times 10^{-3}$  mole fraction). These authors reported a value of  $1.0 \times 10^{-10}$  for the  $K_{\text{sp}}$  of  $\text{PbS}$  at 823 K and  $1.3 \times 10^{-11}$  for the  $K_{\text{sp}}$  of  $\text{FeS}$  at 773 K. In References 148 and 149, an exact thermodynamic cycle was used to calculate *a priori* the solubility products of several transition- and heavy-metal sulfides.

#### D. Summary of Literature Survey

The background information provided by the literature survey is summarized below.

It can be seen that the principle of metal and sulfur production via the electrolysis of metal sulfides in molten salts has been experimentally demonstrated by many studies. However, many practical problems have not been resolved. All electrolyses of metal sulfides reported in the literature have

been carried out in either molten halides or alkali sulfides. For aluminum sulfide, molten halides are probably the most suitable electrolytes. The contribution of electronic conductivity to the total conductivity is insignificant in halide melts containing low concentration of metal sulfide. Operating variables such as temperature, current density, metal sulfide concentration, and electrolyte composition play a major part either directly or indirectly in determining the current efficiency of the sulfide electrolysis.

The electrolytic decomposition of a metal sulfide in halide melts involves the reduction of metal ions at the cathode and the oxidation of sulfide ions at the anode. For the case of aluminum ions at the cathode, the reduction appears to be quite straightforward. Although information reported in the literature on fused-salt electrolysis of metal sulfides indicates that sulfur is the principal product at the anode, little is known regarding the mechanism of the anode reaction. Most of the investigations on the mechanism of the sulfide oxidation have been carried out in connection with work on high-temperature batteries. These investigations show that the oxidation of sulfide ions at temperatures up to 823 K is rather complex. The mechanism of the reaction is still controversial and cannot be interpreted in an unambiguous manner. From the survey, it appears that the lowering of the current efficiency and the difficulties in cell operation in the electrolysis of metal sulfides in halides are caused primarily by the sulfur-producing anode reactions. Sulfur generated at the anode can dissolve chemically in the electrolyte to polysulfides, which have a deleterious effect on the electrolysis. Work on PbS electrolysis shows that polysulfide formation is favored by a high concentration of sulfide in the melt. Two other conditions that are important to the stability of polysulfides in molten chlorides are the pH and temperature of the melt. The solubility of metal sulfides in molten salts has not been well studied. Generally, metal sulfides have low solubilities in halide melts. At present, little is known of the factors that contribute to the dissolution of metal sulfides in molten salts. It is apparent, however, that the common ion effect has a strong influence on metal sulfide solubility. Complex formation and melt composition are other factors affecting the solubility.

#### IV. THE ELECTROLYSIS OF $Al_2S_3$ IN MOLTEN CHLORIDES

In general, any molten salt to be used in an electrolytic operation should have the following properties: (1) a low vapor pressure, (2) a low viscosity, (3) a high ionic conductivity, and (4) a large decomposition voltage. The composition should have as low a melting point as possible. Corrosion, ease of handling and purification, and cost should also be considered. For electrolytic extraction of metals, liquid metal deposits are ideal (as for aluminum electrowinning). Thus, the difference in density between the electrolyte and the electrowon liquid metal must be sufficient to cause rapid gravity separation.

From an examination of the literature and from experience with the electrolysis of aluminum and other metal compounds in molten salts, it seemed that the choice of an electrolyte for  $\text{Al}_2\text{S}_3$  electrolysis would be limited to mixtures of alkali and alkaline-earth chlorides or fluorides. Data on phase diagrams and physical and electrochemical properties<sup>150-153</sup> indicate that these melts possess most of the properties listed above. Mixtures of two or more alkali and alkaline-earth chlorides or fluorides are probably most suitable for the electrolysis of  $\text{Al}_2\text{S}_3$ . The most commonly used chlorides are  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ , and  $\text{CaCl}_2$ .

There is a very wide range of mixture compositions of the above chlorides which can be used for  $\text{Al}_2\text{S}_3$  electrolysis. Since aluminum would be recovered in liquid form, the operating temperature of the electrolysis should be above the melting point of aluminum (933 K) and preferably not over 100 degrees above the melting point of aluminum. This would exclude a number of very low- and very high-temperature melts. The electrolysis of  $\text{Al}_2\text{S}_3$  in many aspects resembles the electrolysis of  $\text{AlCl}_3$  in the Alcoa Smelting Process. The electrolyte in the ASP is composed mainly of  $\text{NaCl}$  and  $\text{LiCl}$ , with a few percent  $\text{MgCl}_2$ . Recently, Japanese investigators found that the addition of  $\text{MgCl}_2$  increased aluminum deposition efficiency.<sup>154</sup> Thermodynamic considerations, which will be described later in this report, also indicated that  $\text{MgCl}_2$  might help solubilize  $\text{Al}_2\text{S}_3$ . Therefore, it was decided to use an electrolyte composed of alkali chlorides and  $\text{MgCl}_2$  for the electrolysis of  $\text{Al}_2\text{S}_3$ . In the present investigation,  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic (50 mol %  $\text{MgCl}_2$ -30 mol %  $\text{NaCl}$ -20 mol %  $\text{KCl}$ ) was chosen. The melting point of the eutectic is 669 K. Although  $\text{LiCl}$  is known to improve the electrical conductivity of the electrolyte,  $\text{KCl}$  was used instead because some electrochemical data for  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic are available in the literature.<sup>100</sup>

Three types of studies were carried out: (1) solubility studies to determine the solubility of  $\text{Al}_2\text{S}_3$  in the eutectic and to develop a molten salt having sufficient  $\text{Al}_2\text{S}_3$  solubility to allow acceptable cell operation; (2) electrochemical studies to investigate the mechanism of the electrolysis of  $\text{Al}_2\text{S}_3$  in the molten salt; and (3) electrolysis studies to demonstrate the production of aluminum and sulfur and to determine the current efficiency of the cell. These experiments were conducted at a temperature of 1023 K.

## A. Solubility Studies

### 1. Experimental

The solubility of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  at 1023 K was determined by the two-phase liquid equilibration method. The method was based on saturation of the melt with  $\text{Al}_2\text{S}_3$ . The melt was rapidly quenched and the  $\text{Al}_2\text{S}_3$  content of the melt was then analyzed.

The following experimental procedure was used. A closed-end fused silica tube (10-mm-dia) was cleaned, degassed, and dried under vacuum. The evacuated tube was transferred into a glove box (Vacuum Atmospheres Corporation). The glove box, together with the purification system (VAC MO-40),

maintained a high-purity helium atmosphere, *i.e.*, less than 5 ppm contaminants. The fused silica tube was filled with about 3 g purified MgCl<sub>2</sub>-NaCl-KCl eutectic powder (supplied by Anderson Physics Laboratories, Champaign, Illinois). Approximately 10 wt % Al<sub>2</sub>S<sub>3</sub> (Cerac Pure) was added to the tube and the solids were mixed thoroughly. A preliminary run showed that the solubility of Al<sub>2</sub>S<sub>3</sub> was less than 10 wt %; in each run, 10 wt % Al<sub>2</sub>S<sub>3</sub> was used to ensure the presence of excess Al<sub>2</sub>S<sub>3</sub> in the melt.

The tube was brought out of the glove box under helium atmosphere, evacuated, and then sealed. It was then heated and kept at the desired temperature inside a cylindrical furnace (Mellen Model C2-311). Its temperature was controlled by a controller (Mellen Model 919), using a chromel-alumel thermocouple. Temperatures were measured with a chromel-alumel thermocouple in an alumina sheath held close to the tube.

Undissolved Al<sub>2</sub>S<sub>3</sub>, which was heavier than the molten salt, settled to the bottom of the tube. At the conclusion of a run, the tube was quickly removed from the furnace and quenched in water to solidify the salt. The tube was opened inside the glovebox and the solidified clear salt was removed for analysis of the aluminum and sulfur contents. The sulfur content of the samples from the experiments was oxidized to sulfate and determined as BaSO<sub>4</sub>. The aluminum content was analyzed by atomic absorption.

The time to attain equilibrium was established in a set of preliminary experiments in which the samples were equilibrated for different lengths of time, quenched, and analyzed. It was found that equilibrium could be attained in eight hours. However, the tube was generally held at the specified temperature for 48 h to ensure equilibrium.

The solubility of Al<sub>2</sub>S<sub>3</sub> in the eutectic was also determined by using a rocking furnace. The tube was prepared as described earlier. It was placed in a rocking furnace and agitated for at least 5 h. Agitation was then stopped and the contents of the tube were allowed to settle before removal from the furnace and quenching.

The solubility of Al<sub>2</sub>S<sub>3</sub> in MgCl<sub>2</sub>-NaCl-KCl eutectic containing varying amounts of AlCl<sub>3</sub> was also measured. Aluminum chloride was supplied by Anderson Physics Laboratories. In each run of this series, 20 wt % Al<sub>2</sub>S<sub>3</sub> was used.

## 2. Results and Discussion

Table IV-1 shows the results of the Al<sub>2</sub>S<sub>3</sub> solubility determinations in MgCl<sub>2</sub>-NaCl-KCl eutectic at 1023 K. Except for samples 3 and 13 where the results are uncertain (trapping of some Al<sub>2</sub>S<sub>3</sub> in the solidified salt was observed), the average solubility of Al and S from these determinations is about 3.3 mol %. The molar ratios of S/Al are shown by chemical analysis to be about 1 (average value: 1.04), which is lower than the value of 1.5 expected for a true dissolution of Al<sub>2</sub>S<sub>3</sub>. One possible mode for the dissolution of Al<sub>2</sub>S<sub>3</sub> in the MgCl<sub>2</sub>-NaCl-KCl eutectic can be written as

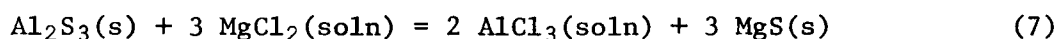


Table IV-1. The Solubility of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic Melt at 1023 K

Sample	Mol % S	Mol % Al	Molar Ratio S/Al
1	2.8	3.0	0.93
2	3.5	3.3	1.08
3	4.8	3.3	1.45
4 <sup>a</sup>	3.8	3.4	1.12
5	3.0	3.1	0.97
6 <sup>a</sup>	2.9	3.2	0.92
7	3.3	3.4	0.96
8 <sup>b</sup>	---	---	---
9	3.9	3.5	1.12
10	3.7	3.2	1.16
11	3.1	3.0	1.05
12	3.4	3.1	1.12
13	5.1	4.9	1.05

<sup>a</sup>Rocking furnace

<sup>b</sup>Failed

Since there is a large excess of  $\text{MgCl}_2$  in the solvent, the chemical potential of  $\text{MgCl}_2$  is fixed. Thus, in the presence of the solid  $\text{Al}_2\text{S}_3$  and  $\text{MgS}$ , the chemical potential of  $\text{AlCl}_3$  is also fixed. If one chooses as standard states, solid for  $\text{Al}_2\text{S}_3$  and  $\text{MgS}$ , and liquid for  $\text{MgCl}_2$ , and a reference state so that the activity coefficient of  $\text{AlCl}_3$  is unity at infinite dilution in the melt, the standard free-energy change for Reaction 7,  $\Delta G_7^\circ$ , is expressed as follows:

$$\Delta G_7^\circ = -RT \ln \frac{a_{\text{MgS}}^3 a_{\text{AlCl}_3}^2}{a_{\text{Al}_2\text{S}_3} a_{\text{MgCl}_2}^3} \quad (8)$$

The compounds  $\text{Al}_2\text{S}_3$  and  $\text{MgS}$  are present as solids, so that  $a_{\text{Al}_2\text{S}_3} = 1$  and  $a_{\text{MgS}} = 1$ . At 50 mol %  $\text{MgCl}_2$  in the eutectic,  $a_{\text{MgCl}_2} = 0.15$ .<sup>155</sup> Thus,

$$\Delta G_7^\circ = -2RT \ln 17.2 a_{\text{AlCl}_3} \quad (9)$$

On the other hand,  $\Delta G_7^\circ$  is also given by

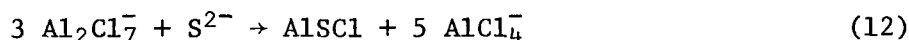
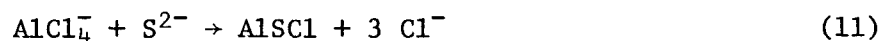
$$\Delta G_7^\circ = 3 \Delta G_{\text{MgS}(s)}^\circ + 2 \Delta G_{\text{AlCl}_3(\text{soln})}^\circ - 3 \Delta G_{\text{MgCl}_2(\text{soln})}^\circ - \Delta G_{\text{Al}_2\text{S}_3(s)}^\circ \quad (10)$$

At 1023 K,  $\Delta G_{\text{MgS}(s)}^\circ = -3.07 \times 10^5$  J/mol from the JANAF Tables.<sup>20</sup> The quantities  $\Delta G_{\text{AlCl}_3(\text{soln})}^\circ$  and  $\Delta G_{\text{MgCl}_2(\text{soln})}^\circ$  can be derived from the standard formation potentials of  $\text{AlCl}_3$  and  $\text{MgCl}_2$  in the  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic.

From the emf data at 748 K compiled by Plambeck,<sup>100</sup> the difference  $(2 \Delta G^\circ_{\text{AlCl}_3} - 3 \Delta G^\circ_{\text{MgCl}_2})$  equals  $4.24 \times 10^5$  J/mol. If it is assumed that the temperature effect on this difference is small, then the same value can be used at 1023 K. A value of  $-5.60 \times 10^5$  J/mol for  $\Delta G^\circ_{\text{Al}_2\text{S}_3(\text{s})}$  at 1023 K was deduced from the thermodynamic data of Ferrante and coworkers.<sup>21</sup> With the above information and Eqs. 9 and 10, the activity of  $\text{AlCl}_3$  was calculated to be 0.00143. This gives a solubility of about 0.07 mol %  $\text{Al}_2\text{S}_3$  in the eutectic.

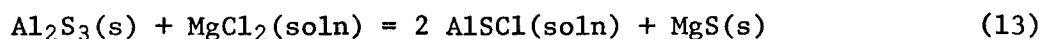
The above thermodynamic calculations show that the solubility of  $\text{Al}_2\text{S}_3$  in the eutectic would be low, accompanied by the formation of  $\text{MgS}$  as a precipitate if there were no complex formation between  $\text{Al}^{3+}$  and  $\text{S}^{2-}$ . The uncertainties in the thermodynamic data preclude a definitive statement about complex formation; however, the experimental molar ratio of unity for  $\text{S}/\text{Al}$  strongly suggests that the dissolution of  $\text{Al}_2\text{S}_3$  leads to the formation of the  $\text{AlS}^+$  species.

The  $\text{AlS}^+$  species has been proposed by Paulsen and Osteryoung<sup>120</sup> and Robinson *et al.*<sup>156</sup> to exist in sodium tetrachloroaluminate melts at 448 K. They deduced from their electrochemical studies that sulfide is involved in an acid-base equilibrium, with the solvent acting as a tribasic species in acidic melts and as a dibasic species in basic melts, according to the equations



The formation of solid  $\text{AlSCl}$  from  $\text{AlCl}_3$  and metal sulfides under anhydrous conditions at about 573 K is well established.<sup>157,158</sup> Recently, Raman spectroscopic measurements by Berg *et al.*<sup>123</sup> on  $\text{LiCl}-\text{CsCl}$  and  $\text{CsCl}-\text{AlCl}_3$  melts have shown that dissolved tetrachloroaluminate and sulfide ions at temperatures around 673 K react in a ratio close to 1:1. Chain species  $[\text{AlSCl}_2]_m^{m-}$  seem to be formed in basic systems. A similar type of complex,  $\text{AlO}^+$ , has also been reported to be involved in the dissolution of  $\text{Al}_2\text{O}_3$  in chloride melts.<sup>159-161</sup>

If the  $\text{AlS}^+$  complex is formed, the reaction could then be written as



and one can derive the following equation

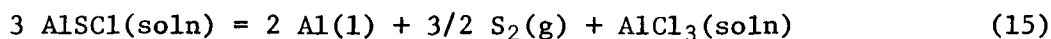
$$-RT \ln \frac{a_{\text{AlSCl}}^2}{a_{\text{MgCl}_2}} = \Delta G^\circ_{\text{MgS}(\text{s})} + 2 \Delta G^\circ_{\text{AlSCl}(\text{soln})} - \Delta G^\circ_{\text{MgCl}_2(\text{soln})} - \Delta G^\circ_{\text{Al}_2\text{S}_3(\text{s})} \quad (14)$$

where  $\Delta G^\circ_{\text{AlSCl}}$  is the free energy of formation of a standard state, defined so that the activity coefficient is unity at infinite dilution. The value of  $\Delta G^\circ$  for  $\text{AlSCl}$  in  $\text{MgCl}_2-\text{NaCl}-\text{KCl}$  eutectic is not known. Nagy and coworkers<sup>135</sup> have shown that in the  $\text{LiCl}-\text{KCl}$  eutectic,  $\Delta G^\circ_{\text{AlSCl}}$  is less than  $-3.89 \times 10^5$  J/mol.



In the Henry's law region,  $a_{\text{AlSCl}}$  is equal to the mole fraction of AlSCl obtained from the solubility measurements, so that one can deduce the standard free energy of formation of AlSCl in solution. The value of  $\Delta G_{\text{AlSCl}}^{\circ}$  was calculated to be  $-3.75 \times 10^5$  J/mol. However, because of the difficulty of sampling and detecting MgS in the melt, we have not experimentally confirmed our assumption that MgS is the product and not some other sulfide such as a double salt of MgS and  $\text{Al}_2\text{S}_3$ . Consequently, our value of  $\Delta G_{\text{AlSCl}}^{\circ}$  must be considered a lower limit and could be less negative.

The voltage of the following reaction can also be used to calculate  $\Delta G_{\text{AlSCl}}^{\circ}$ .



A decomposition voltage of about 0.95 V was obtained from voltage-current density curves for the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic at 1023 K. The value of  $\Delta G_{\text{AlSCl}}^{\circ}$  is then deduced to be  $-3.75 \times 10^5$  J/mol, in agreement with the value calculated from the solubility measurements, considering the uncertainties in the decomposition voltage and  $\Delta G^{\circ}$  of  $\text{AlCl}_3$  in solution.

As shown in Table IV-1, the solubility of  $\text{Al}_2\text{S}_3$  based on the Al content is about 3 wt %. Based on the results of the electrolysis experiments, which are discussed in a subsequent section, it appeared that this solubility would be too low to allow a current density high enough for practical application. Thus, it is necessary to develop a molten salt having sufficient  $\text{Al}_2\text{S}_3$  solubility to permit acceptable cell operation.

From the above data and the literature survey in Section III, it appears that  $\text{Al}_2\text{S}_3$ , and metal sulfides in general, are not highly soluble in molten chlorides. It is evident from the literature that the solubility of metal sulfides is generally greatest in the fused halide of the same metal or in mixtures of the halide of the same metal and other metal halides. Therefore, the addition of  $\text{AlCl}_3$  to the  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic could enhance the  $\text{Al}_2\text{S}_3$  solubility. Also, the results of solubility measurements in the eutectic suggest that the dissolution of  $\text{Al}_2\text{S}_3$  leads to the formation of  $\text{AlS}^+$  species. If that is the case,  $\text{AlCl}_3$ -containing melts should solubilize enough  $\text{Al}_2\text{S}_3$  to result in a S/Al molar ratio of about unity. Thus, besides the common ion effect,  $\text{AlCl}_3$  increases the solubility of  $\text{Al}_2\text{S}_3$  *via*  $\text{AlS}^+$  complex formation.

In fact, this enhancement was observed by Nagy *et al.*<sup>135</sup> in the  $\text{LiCl}$ - $\text{KCl}$  eutectic melt. Also, Paulsen and Osteryoung<sup>120</sup> found that the solubility of metal sulfides in  $\text{NaCl}$ - $\text{AlCl}_3$  melts increased markedly as the melt was made more acid, *i.e.*, as  $\text{AlCl}_3$  was added. They deduced the acid-base equilibrium involving  $\text{S}^{2-}$  and the solvent to be  $\text{AlCl}_4^- + \text{S}^{2-} = \text{AlSCl} + 3 \text{ Cl}^-$ .

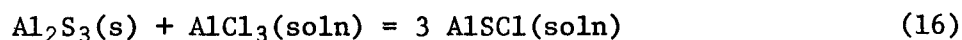
The solubility of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic containing  $\text{AlCl}_3$  was determined at four different concentrations of  $\text{AlCl}_3$ : 2, 5, 10, and 15 wt %  $\text{AlCl}_3$ . For each  $\text{AlCl}_3$  wt %, three or more determinations of the solubility were carried out. These determinations are listed in Table IV-2.

Table IV-2. Solubility of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic Containing  $\text{AlCl}_3$  at 1023 K

Wt % $\text{AlCl}_3$ in Eutectic	Mole Fraction $\text{AlCl}_3$ in the Eutectic	Mole Fraction S in Salt	Mole Fraction Al in Salt	Molar Ratio S/Al
2	0.0108	0.113	0.100	1.13
2	0.0110	0.123	0.107	1.15
2	0.0111	0.126	0.102	1.24
5	0.0275	0.133	0.111	1.20
5	0.0279	0.138	0.111	1.24
5	0.0281	0.135	0.102	1.32
5	0.0279	0.141	0.117	1.20
5	0.0272	0.130	0.117	1.11
5	0.0272	0.136	0.116	1.17
10	0.057	0.175	0.168	1.04
10	0.057	0.173	0.166	1.04
10	0.057	0.179	0.186	0.96
15	0.087	0.184	0.200	0.92
15	0.084	0.184	0.199	0.93
15	0.086	0.193	0.197	0.98

It is clearly seen from Tables IV-1 and IV-2 that the addition of  $\text{AlCl}_3$  increases the solubility of  $\text{Al}_2\text{S}_3$  in the eutectic at 1023 K and that the solubility increases with increasing  $\text{AlCl}_3$  additions. The molar ratio S/Al is also about unity in the presence of added  $\text{AlCl}_3$ . This suggests the formation of an  $\text{AlS}^+$  complex.

However, the ratios appear to be somewhat greater than unity in the measurements made with 2% and 5%  $\text{AlCl}_3$  additions. This deviation could be related to experimental uncertainties, but one cannot exclude the possibility of the formation of  $\text{AlS}_2$  species or the mechanical entrainment of a small amount of undissolved  $\text{Al}_2\text{S}_3$ . In view of the molar ratio of S/Al in the measurements made with no  $\text{AlCl}_3$  added, the second possibility appears to be the more probable. This is supported by the fact that the apparent enhancement of the solubility of  $\text{Al}_2\text{S}_3$  is greater than one would expect even if all the  $\text{AlCl}_3$  added reacted to form the  $\text{AlS}^+$  species. In the measurements at 10 wt % added  $\text{AlCl}_3$ , it is probable that a significant fraction of free  $\text{AlCl}_3$  is present in solution. Thus, it is hypothesized that  $\text{AlCl}_3$  in the melt dissolves  $\text{Al}_2\text{S}_3$  according to the reaction



The equilibrium constant  $K_e$  for Reaction 16 is given as

$$K_e = \frac{a_{\text{AlS}}^3}{a_{\text{Al}_2\text{S}_3} a_{\text{AlCl}_3}} \quad (17)$$

where, in the Henry's law region,  $K_e$  is given by the expression

$$\Delta G_{16}^{\circ} = \left( 3 \Delta G_{\text{AlSCl}}^{\circ} - \Delta G_{\text{AlCl}_3}^{\circ} - \Delta G_{\text{Al}_2\text{S}_3}^{\circ} \right) = -RT \ln K_e = -RT \ln \left( \frac{X_{\text{AlSCl}}^3}{X_{\text{AlCl}_3}} \right) \quad (18)$$

where the  $X$ 's are the mole fractions of the indicated components. Since values of  $X_{\text{AlSCl}}^3$  are larger with added  $\text{AlCl}_3$ , values of  $X_{\text{AlCl}_3}$  are then larger than is fixed by Eq. 7 and no solid  $\text{MgS}$  (or double sulfide) will be present. The value of  $K_e$  is calculated to be 0.025 using the activity of  $\text{AlCl}_3$  at saturation with  $\text{Al}_2\text{S}_3$  and  $\text{MgS}$  in the eutectic and the solubility of  $\text{Al}_2\text{S}_3$ . In principle,  $K_e$  can also be calculated from the data in Table IV-2 and Eq. 18. However, the mole fraction of free  $\text{AlCl}_3$  in solution is very small and very much dependent on the accuracy of the chemical analysis of aluminum and sulfur contents of the samples and also on the contamination of the melt with fine particles of undissolved  $\text{Al}_2\text{S}_3$ . In the present work, the chemical analysis is not accurate enough to allow the determination of free  $\text{AlCl}_3$  by the difference between mole fractions of Al and S in the melt. Thus,  $K_e$  cannot be deduced from data in Table IV-2. It seems that the best way to determine  $K_e$  with confidence would be to devise a method which directly measures the mole fraction of free  $\text{AlCl}_3$  in the  $\text{AlCl}_3$ -containing eutectic (for example, an emf method).

## B. Electrochemical Studies

### 1. Experimental

The voltammetric study of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic was carried out inside the VAC glove box under helium atmosphere. The cell consisted of an alumina crucible (Coors Porcelain, approximately 35-mm-dia, 64-mm high) containing  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic melt. The alumina crucible was placed inside a secondary alumina container which, in turn, was placed inside a protective nickel liner. The liner was slipped into a furnace tube (made of RA 303 nickel alloy) attached by a flange to the bottom of the glove box.

A three-electrode system was used for all measurements. The working electrode was a 6.3-mm-dia graphite rod (Ultra Carbon Corporation, Ultra "F" Purity), insulated with boron nitride (The Carborundum Company) so that only a defined surface area was exposed to the molten salt. Another graphite rod immersed in the melt was employed as the counter electrode. The reference electrode was a  $\text{Ni}/\text{Ni}_3\text{S}_2$  electrode, fabricated according to the design developed by Redey.<sup>162</sup> The electrode consisted of high-purity nickel wire in contact with a saturated heterogeneous mixture of  $\text{Al}_2\text{S}_3$  and the melt. This was contained in a 1.6-mm alumina tube closed at one end by yttria felt pressed in place. Nickel ions were generated by the anodic dissolution of nickel at about 20  $\mu\text{A}$  for about two hours. Thus, the concentration of nickel ions was fixed by the  $\text{S}^{2-}$  ions present in the melt.

The cell assembly was heated by a single-zone Lindberg furnace (5600 Series) equipped with a Platinel II thermocouple. The thermocouple, in conjunction with a Lindberg control console (Model 59344), maintained the furnace temperature at the desired value, within  $\pm 1$  K, after reaching steady

state. The actual temperature of the melt was monitored by a chromel-alumel thermocouple inside an alumina sheath.

The voltammetric circuit was conventional. A universal programmer (PAR Model 175) was used to provide an external control voltage for a potentiostat (PAR Model 173) which was connected directly to the cell. The current-voltage curves were recorded with an X-Y recorder (Hewlett-Packard Model 7044 A). The initial and upper- and lower-limit potentials were varied by manipulating the dials on the universal programmer. The initial or starting potential was chosen to be the point when no current passed through the cell.

The molten electrolyte was purified  $\text{MgCl}_2\text{-NaCl-KCl}$  eutectic obtained from Anderson Physics Laboratories. Pure  $\text{Al}_2\text{S}_3$  (Cerac) was added as required.

## 2. Results and Discussion

A blank experiment with no  $\text{Al}_2\text{S}_3$  in the melt was carried out to test the experimental procedure and the purity of the melt. A linear-sweep voltammogram illustrating the background current of the melt at 1023 K is shown in Fig. IV-1. The voltammogram showed no significant current within the potential range +1.0 V to -0.9 V *vs.* the  $\text{Ni/Ni}_3\text{S}_2$  reference electrode;

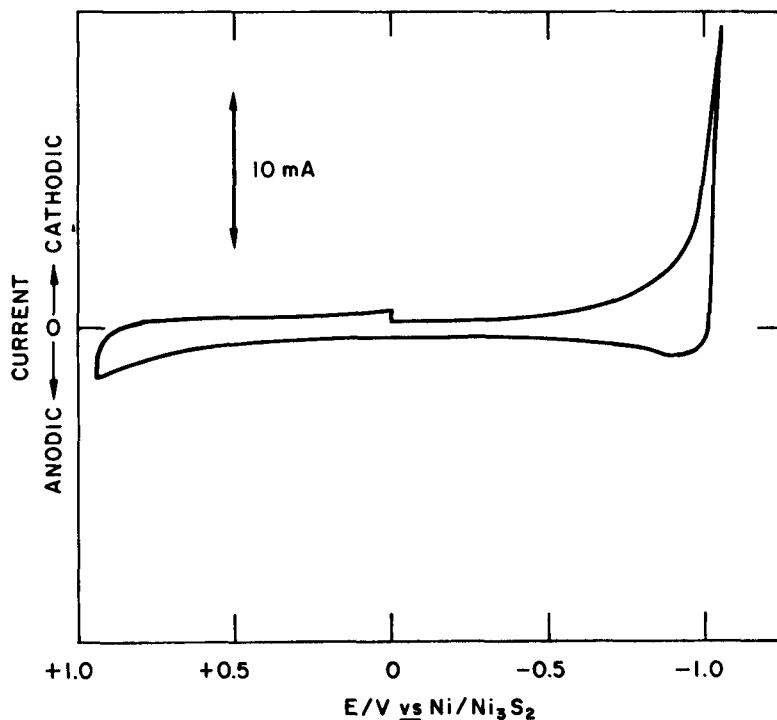


Fig. IV-1. Voltammogram of the  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic Melt Background at 1023 K. Electrode area  $2.10\text{ cm}^2$ ; sweep rate  $50\text{ mV/s}$ .

the eutectic was apparently pure and the level of electroactive impurities, if any, could be considered negligible. The current rising at about  $-1.1$  V was attributable to the deposition of Mg from  $\text{MgCl}_2$ . On the addition of  $\text{Al}_2\text{S}_3$ , four additional peaks were observed on the voltammogram. A typical voltammogram is shown in Fig. IV-2. The first couple, which occurred at a potential of about  $-0.70$  V *vs.* the Ni/Ni<sub>3</sub>S<sub>2</sub> reference electrode, was due to the reactions of aluminum. The identification of aluminum peaks was confirmed by the addition of  $\text{AlCl}_3$  to the  $\text{MgCl}_2$ -NaCl-KCl melt containing  $\text{Al}_2\text{S}_3$ , thus increasing the concentration of aluminum ions (or aluminum-ion-containing species).

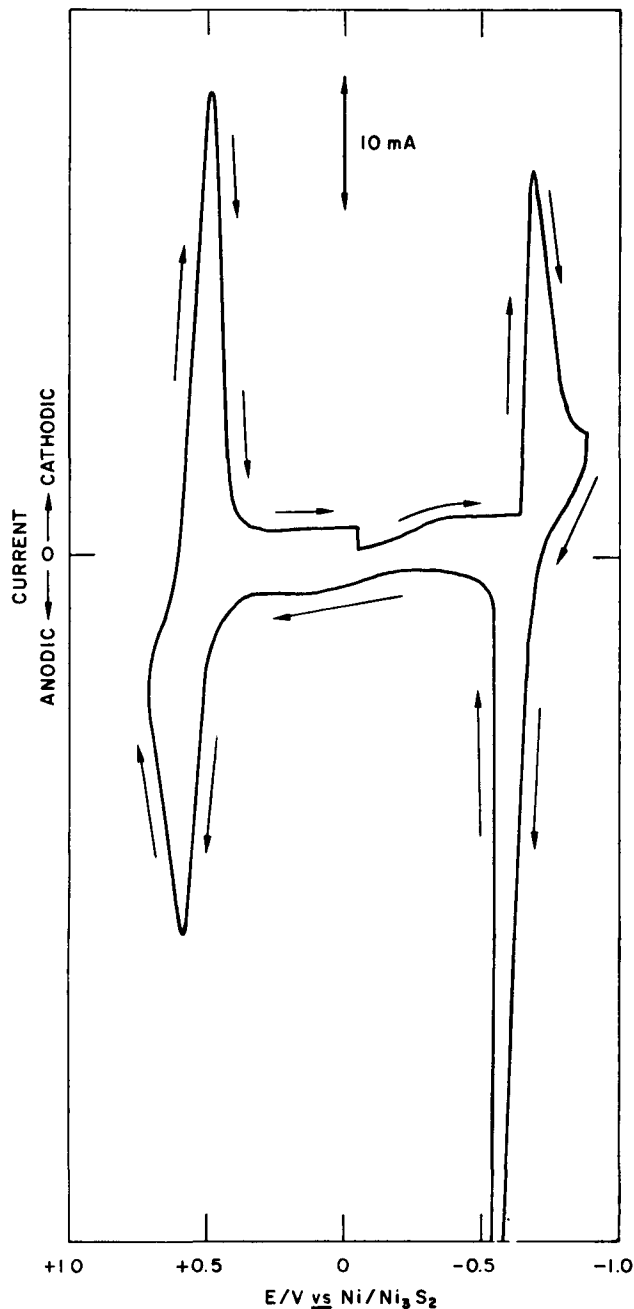


Fig. IV-2.

Typical Voltammogram of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ -NaCl-KCl Eutectic at 1023 K. Electrode area  $2.10 \text{ cm}^2$ ; sweep rate  $100 \text{ mV/s}$ ;  $\text{Al}_2\text{S}_3$  concentration  $5.40 \times 10^{-6} \text{ mol/cm}^3$ .

The addition of  $\text{AlCl}_3$  enhanced the aluminum peaks but had no effect on the other two peaks. The other two peaks located at about +0.55 V were attributed to the oxidation of sulfide and the reduction of its product.

The deposition of magnesium from  $\text{MgCl}_2$  occurs at about -1.1 to -1.2 V, which provides an adequate separation between the reduction of aluminum ions and the deposition of magnesium. Polcyn and Shain<sup>163</sup> have considered the theory of linear-sweep voltammetry for uncomplicated multistep reversible and irreversible electrochemical reactions. As discussed by these authors, for the voltammograms to behave as independent waves, a certain minimum potential separation is required between the formal reduction (or oxidation) potentials. The minimum separation is  $4.595 RT/nF$  or  $405/n$  millivolts at 1023 K where  $R$  is the universal gas constant ( $\text{J/mol}\cdot\text{K}$ ),  $T$  is the temperature (K),  $n$  is the number of electrons involved in the process, and  $F$  is the faraday ( $\text{C/mol}$ ). In the present study, the approximate potential separation between the reduction of aluminum ions and the magnesium deposition was much greater than 135 mV at the experimental temperature used. Consequently, the deposition of magnesium had no effect on the reduction wave for aluminum ions. In voltammetric experiments, the cathodic and anodic potentials were limited to -0.9 V and +0.7 V, respectively. It should be noted that the use of the terms "aluminum ion" or "sulfide ion" is a simplification since, in the melt, complex forms of aluminum ion or sulfide ion may exist.

#### a. The Reduction of Aluminum Ions

The reduction of aluminum ions was studied at two different  $\text{Al}_2\text{S}_3$  concentrations: 5.40 and  $8.47 \times 10^{-6}$  mol/cm<sup>3</sup>. The appropriate concentration of the electroactive species in the molten salt was obtained by adding a weighed amount of  $\text{Al}_2\text{S}_3$  to the melt. Figure IV-3 shows typical voltammograms of the reduction of aluminum ions in the eutectic at different sweep rates. The shape of the curve for the reduction suggests a reversible electrochemical reaction involving an insoluble product. The anodic peak is very sharp, and its height is much greater than the height of the cathodic peak. This indicates the formation of an insoluble product: the anodic dissolution of the product is unlikely to be diffusion-controlled, and thus the anodic current increases until all the deposit is stripped.

For a reversible deposition of an insoluble product under diffusion-controlled mass-transport conditions, the equation for the peak current is<sup>164</sup>

$$i_p = 0.541 \frac{2}{\pi^{1/2}} \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A_s D^{1/2} C^\circ v^{1/2} \quad (19)$$

where  $i_p$  is the peak current (A),  $n$  is the number of electrons involved in the process,  $C^\circ$  is the initial concentration of the electroactive species ( $\text{mol/cm}^3$ ),  $A_s$  is the electrode area ( $\text{cm}^2$ ),  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $F$  is the faraday ( $\text{C/mol}$ ),  $T$  is the temperature (K),  $R$  is the universal gas constant ( $\text{J/mol}\cdot\text{K}$ ), and  $v$  is the potential sweep rate ( $\text{V/s}$ ).

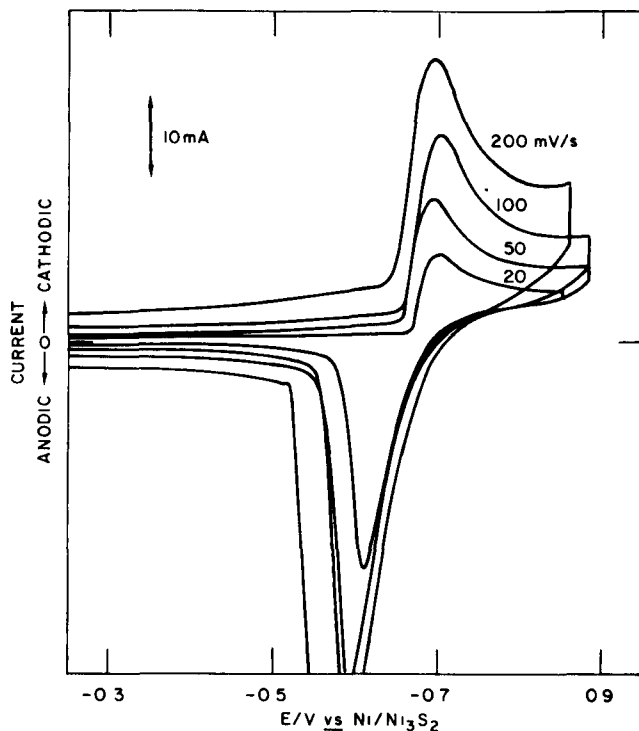


Fig. IV-3.

Voltammograms of the Reduction of Aluminum Ions in Molten  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic at Different Sweep Rates. Temperature 1023 K; electrode area  $2.10 \text{ cm}^2$ ;  $\text{Al}_2\text{S}_3$  concentration  $5.40 \times 10^{-6} \text{ mol/cm}^3$ .

Equation 19 shows that, at constant temperature, the peak current or peak current density should be proportional to the square root of the potential sweep rate. This was the case in the reduction of aluminum ions, as shown in Fig. IV-4 by the plots of  $i_p/A_s$  vs.  $v^{1/2}$  at two different  $\text{Al}_2\text{S}_3$  concentrations. The slope of the lines is proportional to the  $\text{Al}_2\text{S}_3$  concentration. In addition, the peak potential,  $E_p$ , was independent of the sweep rate, indicating the reversibility of the charge-transfer reaction.

Theoretical consideration of the shape of the voltammogram shows that, for a reversible electrochemical reaction involving an insoluble product, the difference between the peak potential  $E_p$  and half-peak potential  $E_{p/2}$  is related to the number of electrons by the following equation:<sup>164</sup>

$$\Delta E_p = E_p - E_{p/2} = \frac{-0.7725 RT}{nF} \quad (20)$$

The peak-to-half-peak potential separations of the recorded voltammograms were measured and are summarized in Table IV-3. The values are in agreement with the theoretical value of 22.7 mV calculated from Eq. 20 for a three-electron reversible process at 1023 K.

Mamantov and coworkers<sup>165</sup> have shown that an  $n$ -value for a reversible deposition of an insoluble product may be obtained from  $\log(i_p - i)$  vs.  $E$  plots where  $i$  represents the current at potential  $E$ . The relationship should be linear in the approximate range 0.5-0.9  $i_p$ . The slope of this line corresponds to a value of  $2.2 nF/RT$ . Plots of  $\log(i_p - i)$  vs.  $E$  ( $E$  at 0.5  $i_p$  was taken as zero) are shown in Fig. IV-5. The slopes of these plots were of the order of 14-15 mV, compared to the theoretical value of 13.3 mV for  $n = 3$ .

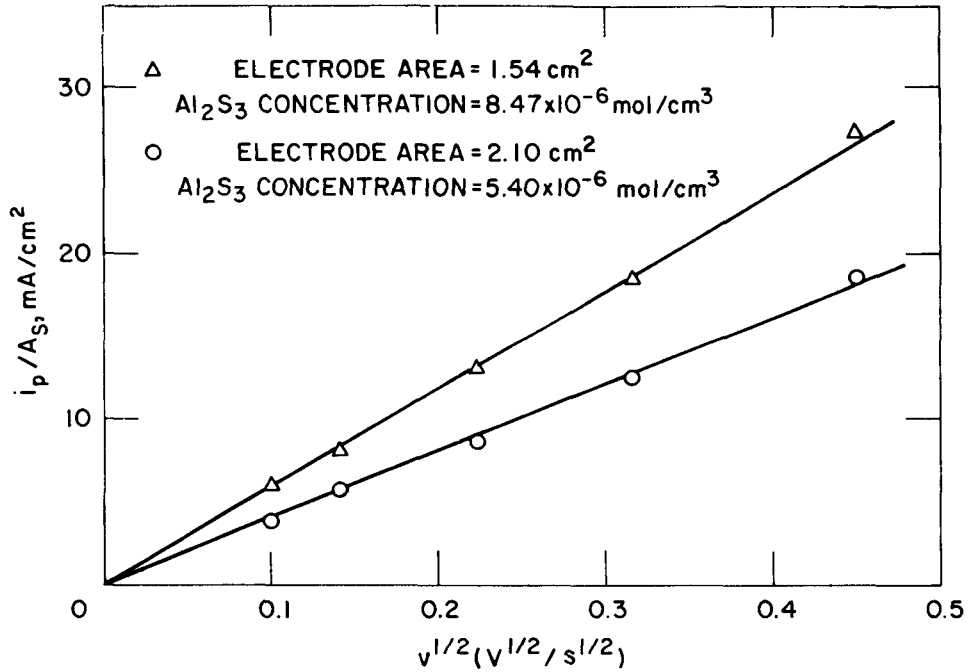


Fig. IV-4. Voltammetric Peak Current Densities vs. Square Root of Sweep Rate for the Reduction of Aluminum Ions at 1023 K

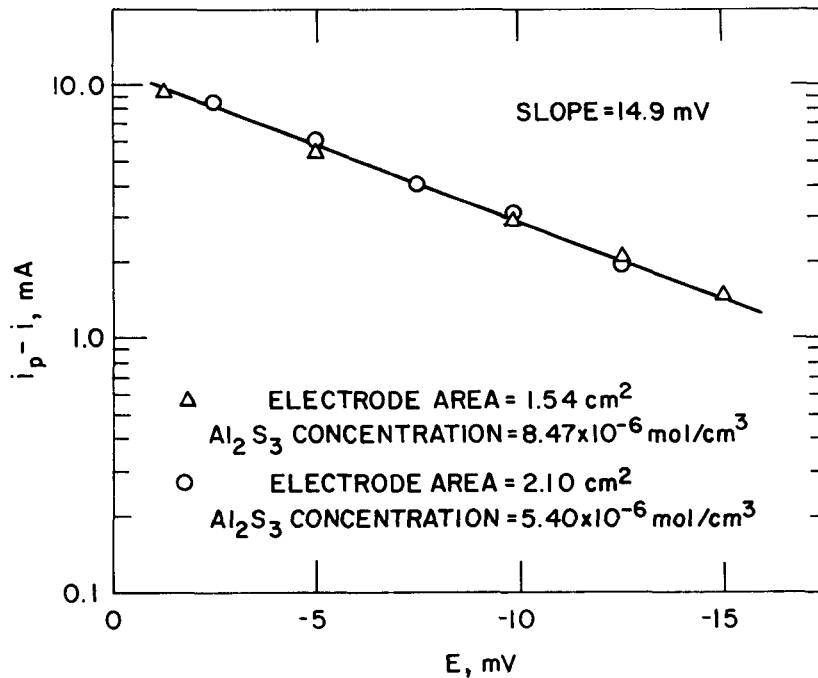


Fig. IV-5. Plot of  $\log(i_p - i)$  vs.  $E$  for the Reduction of Aluminum Ions at 1023 K. Sweep rate 50 mV/s.



Table IV-3. Voltammetric Peak-to-Half-Peak Potential Separation for the Reduction of Aluminum Ions in MgCl<sub>2</sub>-NaCl-KCl Eutectic at 1023 K

v, mV/s	$\Delta E_p$ ( $\pm 5$ mV), mV	
	[Al <sub>2</sub> S <sub>3</sub> ] = $5.40 \times 10^{-6}$ mol/cm <sup>3</sup>	[Al <sub>2</sub> S <sub>3</sub> ] = $8.47 \times 10^{-6}$ mol/cm <sup>3</sup>
10	-20	-20
20	-25	-20
50	-25	-25
100	-25	-25
200	-30	-25

Thus, the results obtained show that the reduction of aluminum ions at a graphite electrode is diffusion-controlled and proceeds *via* a reversible, three-electron charge transfer forming an insoluble product. Aluminum metal as the cathode product was confirmed in laboratory-scale electrolysis of Al<sub>2</sub>S<sub>3</sub> which will be discussed later in Section IV-C.

Once the reaction has been established as a reversible, diffusion-controlled process involving three-electrons, the value of the diffusion coefficient can be calculated using Eq. 19. The diffusion coefficients for aluminum deposition from aluminum sulfide were calculated to be  $1.12 \times 10^{-5}$  cm<sup>2</sup>/s at  $5.40 \times 10^{-6}$  mol/cm<sup>3</sup> and  $0.93 \times 10^{-5}$  cm<sup>2</sup>/s at  $8.47 \times 10^{-6}$  mol/cm<sup>3</sup>, with an estimated experimental error of  $\pm 0.1 \times 10^{-5}$  cm<sup>2</sup>/s. Within this uncertainty, the concentration dependence of the diffusion coefficient cannot be defined.

#### b. The Oxidation of Sulfide Ions

A series of voltammograms at different sweep rates were recorded for the oxidation of sulfide ions at a graphite electrode. Figure IV-6 shows typical voltammograms. The peak current for the sulfide oxidation is linearly proportional to the square root of the sweep rate (Fig. IV-7). Also, the slope of the plots is proportional to the concentration of Al<sub>2</sub>S<sub>3</sub>. The result indicates a diffusion-controlled process. The oxidation is also reversible, as indicated by the constancy of the peak potential as the potential sweep rate is varied.

It is possible that the anodic oxidation of sulfide proceeds *via* a mechanism based on the following two steps:



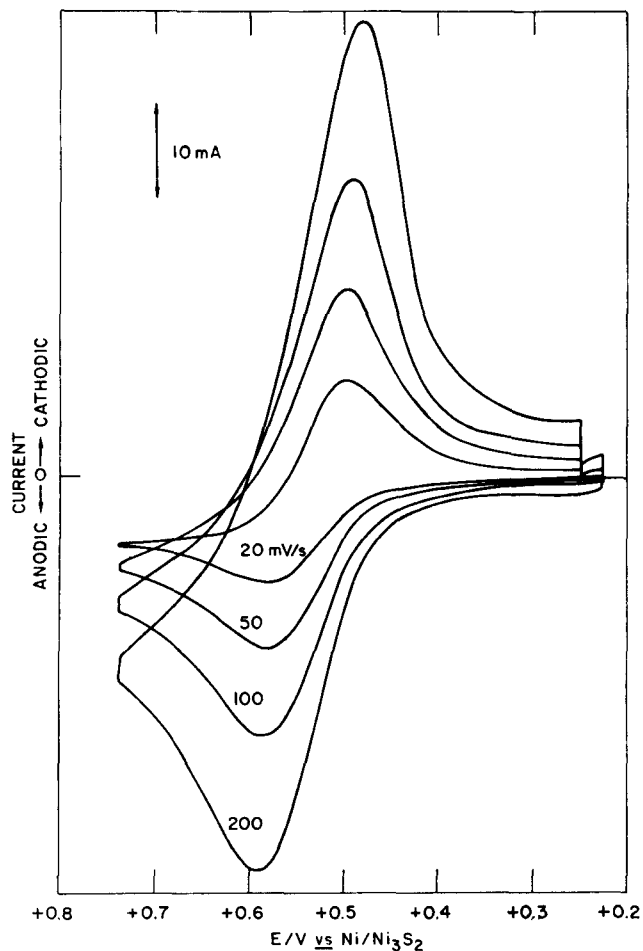


Fig. IV-6.

Voltammograms for the Oxidation of Sulfide Ions in  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic at 1023 K. Electrode area  $2.10 \text{ cm}^2$ ;  $\text{Al}_2\text{S}_3$  concentration  $5.40 \times 10^{-6} \text{ mol/cm}^3$ .

where  $k_f$  and  $k_b$  are the forward and backward rate constants of the dimerization of sulfur atoms. Sulfide is discharged to sulfur, followed by the dimerization of sulfur atoms to  $\text{S}_2$ . At the experimental temperature and at one atmosphere pressure, the most stable and predominant species of sulfur is  $\text{S}_2$ .<sup>166</sup> Sulfur was actually detected during laboratory-scale electrolyses of  $\text{Al}_2\text{S}_3$  dissolved in the molten salt (See Section IV-C).

In the mechanism represented by Eqs. 21 and 22, the effect of the subsequent chemical reaction (dimerization of sulfur atoms) depends on the potential sweep rate and the rates of the chemical reaction. The theory of electrode processes involving dimerization of a charge-transfer product has been reported for linear-sweep voltammetry.<sup>167-171</sup> There are three limiting cases in which the peak current is linearly proportional to the square root of the sweep rate:

(1) In the first case, the chemical reaction is rapid and reversible; that is, the rate of reaction is high in comparison with the sweep rate. Equilibrium is very much displaced toward  $\text{S}_2$  with  $K_e \varepsilon^{1/2} = \infty$  where

$$K_e = \frac{k_b}{k_f} \quad \text{and} \quad \varepsilon = \frac{RT k_f C^0}{nFv}$$

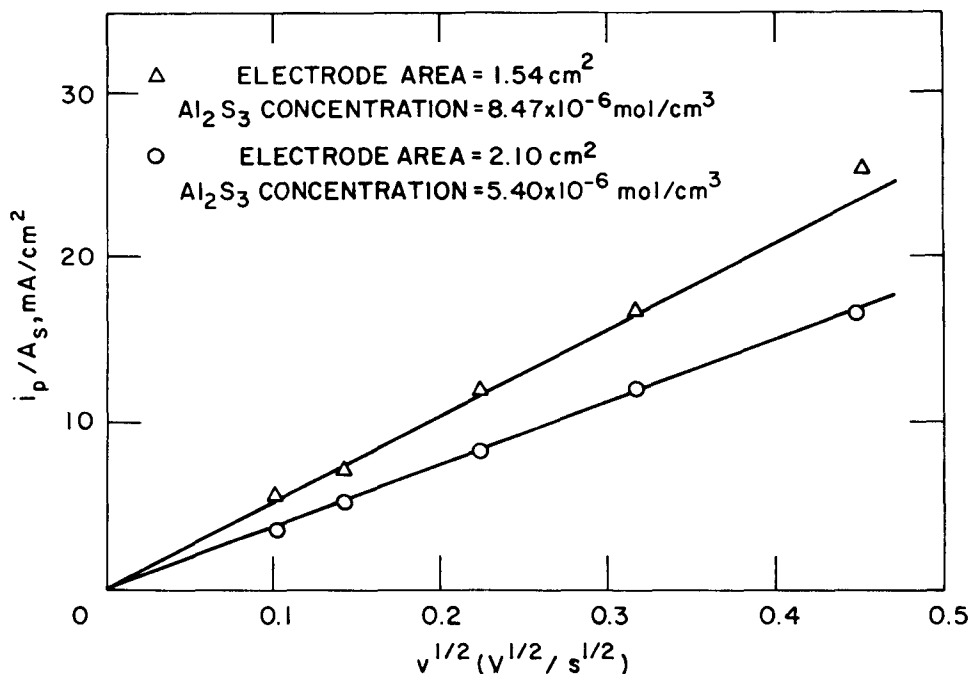


Fig. IV-7. Plots of  $i_p/A_s$  vs.  $v^{1/2}$  for the Oxidation of Sulfide Ions at 1023 K

(2) In the second case, the chemical reaction is fast and reversible. Equilibrium is very much displaced towards S with  $K_e^{1/2} = 0$ .

(3) In the third case, the chemical reaction is very slow in comparison with the sweep rate. The chemical reaction has no effect on the overall oxidation process. The simple model for diffusion-controlled reversible processes applies in this case.

Table IV-4 summarizes the peak current  $i_p$ , the peak potential  $E_p$ , the peak-to-half-peak potential  $\Delta E_p$ , and the peak-to-half-wave potential  $\Delta E$  (the half-wave potential  $E_{1/2}$  is measured at the potential corresponding to  $0.85 i_p$ ) for each of the above cases. The experimental voltammetric results at two  $\text{Al}_2\text{S}_3$  concentrations are shown in Table IV-5.

It is clear from Tables IV-4 and IV-5 that the experimental results are in good agreement with Case 1,  $n = 2$ . Therefore, it is concluded that the dimerization of sulfur atoms is fast and the equilibrium is very much displaced towards  $\text{S}_2$  during the potential sweep.

According to Shuman,<sup>170</sup> the ratio of reverse to forward peak current is 1.09 for the case of a reversible dimerization following a reversible electrochemical reaction. Voltammograms show that this ratio is greater than 1.09 for the anodic oxidation of sulfide ion. The ratio also increases with increasing sweep rate. The peak current ratio is very much dependent on switching potential. This behavior is indicative of weak product adsorption<sup>172</sup> or other nonfaradic processes.<sup>164</sup> Therefore, the ratio of reverse to forward peak current is greater than the theoretically predicted value.

Table IV-4. The Voltammetric Behavior of the Limiting Cases for a Dimerization Following an Electrochemical Reaction

	Kinetic Scheme: $S^{2-} \leftrightarrow S + 2e^-$ $S + S \leftrightarrow S_2$		
	Case (1)	Case (2)	Case (3)
Peak current $i_p$	$i_p \propto v^{1/2}$	$i_p \propto v^{1/2}$	$i_p \propto v^{1/2}$
Peak potential as function of sweep rate	$E_p$ is independent of $v$	$E_p$ is dependent on $v$	$E_p$ is independent of $v$
Peak-to-half-peak potential $\Delta E_p$	$1.57 \frac{RT}{nF}$ or $\frac{138}{n}$ mV at 1023 K	--	$2.20 \frac{RT}{nF}$ or $\frac{194}{n}$ mV at 1023 K
Peak-to-half-wave potential $\Delta E$	$0.70 \frac{RT}{nF}$ or $\frac{61.8}{n}$ mV at 1023 K	--	$1.11 \frac{RT}{nF}$ or $\frac{97.8}{n}$ mV at 1023 K

Table IV-5. Experimental Voltammetric Data on the Oxidation of Sulfide Ions in MgCl<sub>2</sub>-NaCl-KCl Eutectic at 1023 K

Al <sub>2</sub> S <sub>3</sub> added, mol/cm <sup>3</sup>	Peak Current $i_p$	Peak Potential $E_p$	Sweep Rate, mV/s	$\Delta E_p(\pm 5 \text{ mV})$ , mV	$\Delta E(\pm 5 \text{ mV})$ , mV
$5.40 \times 10^{-6}$	$i_p$ is linearly proportional to $v^{1/2}$	$E_p$ is independent of $v$	10	65	30
			20	65	30
			50	70	30
			100	70	35
			200	75	35
$8.47 \times 10^{-6}$	$i_p$ is linearly proportional to $v^{1/2}$	$E_p$ is independent of $v$	10	65	35
			20	70	30
			50	65	35
			100	70	35
			200	75	40

For Case 1, the equation for the peak current has been deduced and given as<sup>167-171</sup>

$$i_p = 0.500 \frac{n^{3/2} F^{3/2}}{R^{1/2} T^{1/2}} A_s D^{1/2} C^{\circ} v^{1/2} \quad (23)$$

The diffusion coefficient of sulfide ions can be calculated using the above equation. The concentration of the diffusing species is the apparent concentration of sulfide ions (*i.e.*, three times the  $\text{Al}_2\text{S}_3$  concentration). The apparent diffusion coefficients of sulfide ions in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic at 1023 K are calculated to be  $2.87 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $5.40 \times 10^{-6} \text{ mol/cm}^3$   $\text{Al}_2\text{S}_3$  and  $2.59 \times 10^{-5} \text{ cm}^2/\text{s}$  at  $8.47 \times 10^{-6} \text{ mol/cm}^3$   $\text{Al}_2\text{S}_3$ .

The mechanistic tests applied to the voltammograms for the sulfide oxidation also suggest that the reaction product is soluble. For the reaction product to be soluble, its solubility in the melt must be of at least a similar magnitude to the concentration of sulfide in the melt, that is, at least  $10^{-4}$ - $10^{-5} \text{ mol/cm}^3$ . Although no data have been reported on the solubility of sulfur in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic, this value is not unreasonable considering the data reported for the solubility of sulfur in molten salts.<sup>79,81,173-175</sup> For example, the solubility of sulfur in  $\text{PbCl}_2$ - $\text{NaCl}$  melt at 778 K is  $5 \times 10^{-4} \text{ mol/cm}^3$ .<sup>79</sup> Also, in gas-evolving reactions, supersaturation can occur and can reach several orders of magnitude of the solubility. Consequently, it is reasonable to assume that the sulfur product is soluble in the melt.

The diffusion coefficients reported in this report were calculated from the apparent concentrations of the electroactive species, assuming that  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic dissociates into aluminum and sulfide ions. However, aluminum and sulfide ions may exist as complexes in the molten salt. Chain species such as  $[\text{AlSCl}_2]_m^m$  have been shown to form in chloride melts.<sup>123</sup> The solubility data for  $\text{Al}_2\text{S}_3$  suggest that  $\text{Al}_2\text{S}_3$  is present in the eutectic as a complex of the form  $\text{AlS}^+$ , with the excess sulfide being precipitated as  $\text{MgS}$ . The formation of complexes would result in an increase in the calculated diffusion coefficient for sulfide ions, as reported earlier, because the concentration of the complex is less than that of the total sulfide.

In summary, the voltammetric study has elucidated the mechanisms of the cathodic reduction and the anodic oxidation of  $\text{Al}_2\text{S}_3$  dissolved in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic at 1023 K. The results have also demonstrated that for the time scale of the voltammetry experiments, the electrolytic decomposition of  $\text{Al}_2\text{S}_3$  produces aluminum at the cathode and diatomic elemental sulfur at the anode.

In the electrolysis experiments discussed in Section IV-C,  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic containing  $\text{AlCl}_3$  was also used as the electrolyte for the electrolysis of  $\text{Al}_2\text{S}_3$ . Therefore, linear-sweep voltammetry was used to study the effect, if any, of  $\text{AlCl}_3$  in the eutectic on the anodic oxidation of sulfide ions.

Figure IV-8 shows typical voltammograms of  $\text{Al}_2\text{S}_3$  in the eutectic containing  $\text{AlCl}_3$ . It can be seen from Figs. IV-2 and IV-8 that, with the addition of  $\text{AlCl}_3$ , the deposition of aluminum occurs at the cathodic limit on the voltammogram. This is expected since  $\text{AlCl}_3$  concentrations are high.

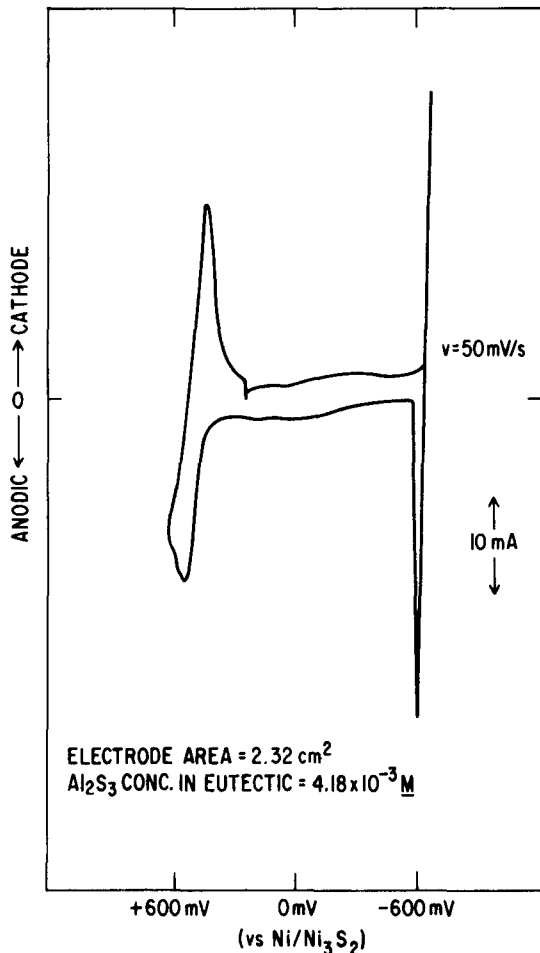


Fig. IV-8.

Typical Voltammogram of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic Containing 1 wt %  $\text{AlCl}_3$ .

Aluminum chloride in the eutectic has no effect on the mechanism of the oxidation of sulfide ions. All mechanistic tests applied to the voltammograms (Table IV-6) confirm that the oxidation occurs in a two-step mechanism, as in the case of  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic; *i.e.*, the oxidation involves the two-electron discharge of sulfide ions, followed by the dimerization of sulfur atoms to  $\text{S}_2$  which is very fast and very much displaced towards  $\text{S}_2$ .

Under the same conditions, the peak current of the sulfide oxidation increases with increasing  $\text{AlCl}_3$  content in the melt. Figure IV-9 shows plots of  $i_p$  vs.  $v^{1/2}$  at different  $\text{AlCl}_3$  concentrations. Since the peak current is given by Eq. 23, the increase in peak current is, then, due either to a change in concentration or diffusion coefficient, or both, because of the presence of  $\text{AlCl}_3$ .

Table IV-6. Voltammetric Data on the Oxidation of Sulfide Ions in  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic Containing  $\text{AlCl}_3$  at 1023 K

wt % $\text{AlCl}_3$	$i_p$	$E_p$	$\Delta E_p (\pm 5 \text{ mV}),$ mV	$\Delta E (\pm 5 \text{ mV}),$ mV
1	linearly proportional to $v^{1/2}$	independent of $v$	70	35
2			70	35
4			70	35
5			75	35

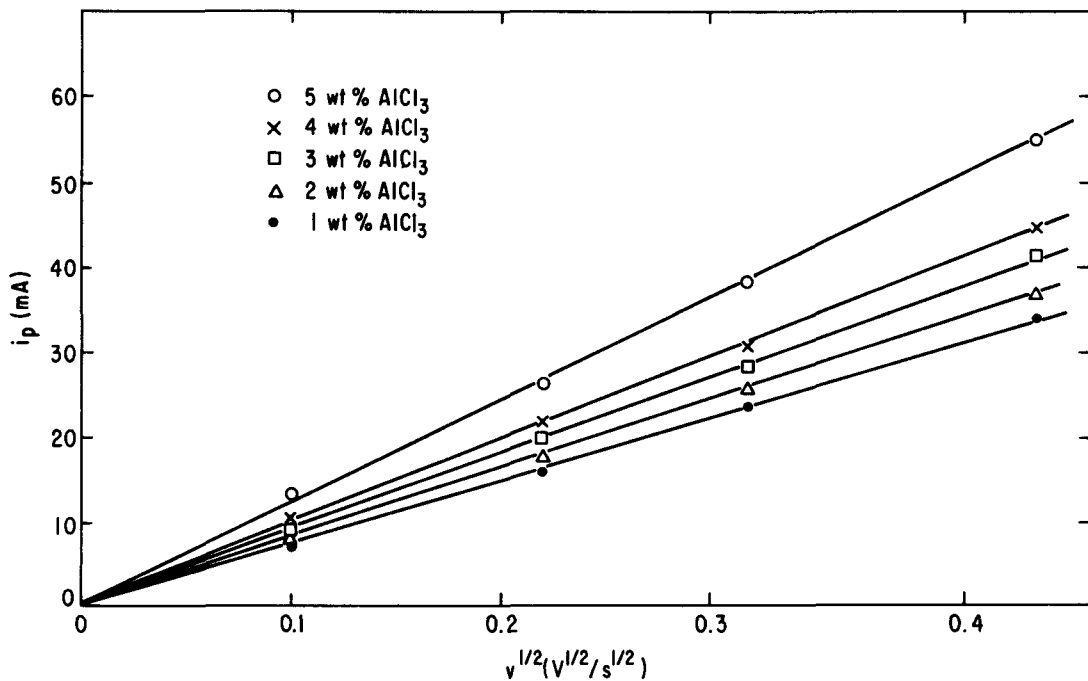


Fig. IV-9. Plots of  $i_p$  vs.  $v^{1/2}$  at Different  $\text{AlCl}_3$  Concentrations in  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic. Temperature 1023 K; electrode area  $2.32 \text{ cm}^2$ ;  $\text{Al}_2\text{S}_3$  concentration  $4.18 \times 10^{-6} \text{ mol/cm}^3$ .

In summary, the voltammetric results indicate that the same mechanism for the electrochemical reaction of  $\text{Al}_2\text{S}_3$  is operative in  $\text{MgCl}_2\text{-NaCl-KCl}$  eutectic with or without  $\text{AlCl}_3$ . One would, then, expect the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{AlCl}_3$ -containing melts to produce aluminum at the cathode and sulfur at the anode.

## C. Electrolysis Studies

### 1. Experimental

#### a. Basis for Cell Design

With  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic chosen as the principal solvent, it was then possible to proceed to the design of the cell. First, the construction materials were examined with regard to their suitability at the temperature used and their susceptibility to corrosion.

There are not many choices of electrode materials for the electrolysis of  $\text{Al}_2\text{S}_3$ . Graphite is probably the most suitable material for the cathode and the anode. There is a possibility of carbon disulfide ( $\text{CS}_2$ ) formation from a high-temperature reaction between the graphite anode and the sulfur. However, some results reported in the literature<sup>176,177</sup> indicate that the reaction between carbon and sulfur is so minor that graphite may be considered essentially inert towards sulfur at temperatures up to 1123 K.

Alumina is not attacked by the molten salt or by the electrolysis products. Thus, an alumina crucible is used to hold the electrolyte. Although no attempt will be made to collect all the sulfur produced, a means should be provided to condense the sulfur vapor. Molybdenum is considered to be the most suitable material for a sulfur collector, in view of the corrosive nature of sulfur gas.

Molten aluminum is collected in a boron nitride collector. Hot-pressed boron nitride is easily machinable, highly resistant to thermal shock, and does not react with halide salts or other reagents. It also exhibits little or no reaction with many molten metals, including aluminum. In later electrolysis runs, a graphite collector was also used because it was found that boron nitride, although stable in the molten salt and during electrolysis, was flaking during washing to collect aluminum metal. In these cases, care was taken to ensure there was no contact between the cathode and the collector.

The volume of electrolyte and the electrode area used in the electrolysis is estimated to ensure that enough aluminum is produced in a reasonable time for current efficiency determination.

#### b. Cell Description

The electrode assembly used in the electrolysis experiments is shown in Fig. IV-10. It consisted of two rectangular graphite-plate electrodes ( $5 \times 12.7$  cm, ATJ grade, Union Carbide Corporation). The parallel distance between the electrodes was held constant (3 cm) by a boron nitride spacer (HP grade, Carborundum Company). Electrical connection to the graphite plates was made using molybdenum rods (0.63-cm-dia). The electrodes were immersed from above in the molten electrolyte contained in an alumina crucible (9.3-cm-dia, 16.7-cm-high, Coors Porcelain).



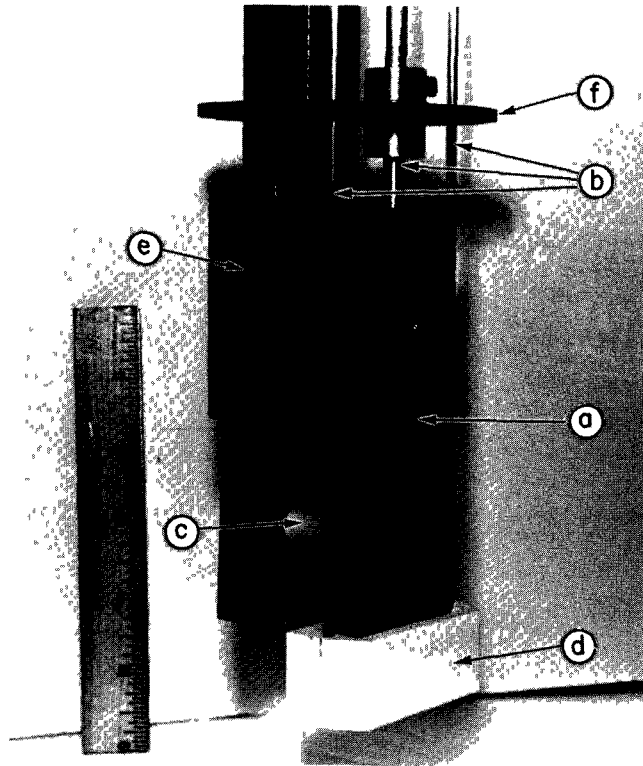


Fig. IV-10. Electrode Assembly for the Electrolysis of  $\text{Al}_2\text{S}_3$ .  
 (a) graphite electrode,  
 (b) molybdenum rods,  
 (c) boron nitride spacer,  
 (d) boron nitride collector,  
 (e) molybdenum hood,  
 (f) Lava radiation shield.

Molten aluminum produced at the cathode was collected in a boron nitride collector. The collector was placed directly under the cathode and could be raised or lowered by two molybdenum rods. A hood made of molybdenum was placed over the anode as shown in Fig. IV-10. Sulfur gas generated at the anode during the electrolysis passed into the hood and condensed on cool portions of the hood. A Lava radiation shield (American Lava Corporation) was used to reduce the amount of radiation heat loss. A chromel-alumel thermocouple inside an alumina sheath was inserted into the cell to monitor the actual temperature of the molten salt.

### c. Procedure

The electrolysis experiments were carried out in the helium-atmosphere glove box. The procedure was as follows: a feed mixture of the appropriate chloride salts and  $\text{Al}_2\text{S}_3$  was charged into the alumina crucible to be used in the experiment. The alumina crucible was placed inside a protective nickel liner. The liner was then slipped into the furnace tube. The heating was started, and, as soon as the salts melted, the thermocouple well

was inserted into the melt. The melt was held at the desired temperature (1023 K) for 8-20 h to ensure that the  $\text{Al}_2\text{S}_3$  was dissolved. The electrode assembly was then lowered into the melt, the electrical leads connected, and the electrolysis begun. Constant current was fed to the cell by means of a power supply (Sorensen SRL Model 20-25). The cell voltage was monitored during the run. At the end of the electrolysis, the electrode assembly and the thermocouple were withdrawn from the melt and allowed to cool in the inert atmosphere, while the electrolyte itself cooled and froze.

The electrode assembly was brought out of the glove box. The cathode deposit was separated by washing the assembly in water. The deposit was then dried and weighed for the current efficiency determination. The operating parameters for the electrolysis are: salt charge, 350-450 g; electrolysis time, 0.5-2 h; electrode area, 20-25  $\text{cm}^2$ , electrode spacing, 3 cm; and aluminum recovered, 0.5-2 g.

The cathodic and anodic components of the cell voltage were measured by inserting a  $\text{Ni}/\text{Ni}_3\text{S}_2$  reference electrode in the electrolyte and measuring the voltages at different current densities.

## 2. Results and Discussion

The cathodic and anodic components of the steady-state cell voltage of the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic were measured against a  $\text{Ni}/\text{Ni}_3\text{S}_2$  reference electrode at 1023 K and at three  $\text{Al}_2\text{S}_3$  concentrations (1, 2, and 3 wt %). As shown by the solubility measurements, the solubility limit of  $\text{Al}_2\text{S}_3$  in the eutectic at 1023 K is 3 wt %, based on Al content. The voltage components (uncorrected for ohmic drop) were plotted *vs.* the cathode/anode current density, as shown in Fig. IV-11, for each  $\text{Al}_2\text{S}_3$  concentration. The cathodic voltage increases with increasing current density until a limiting cathodic current density is reached, after which the voltage rises much more rapidly. The cathodic voltage varies rapidly toward more negative values at the limiting cathodic current density and no steady-state values can be measured. No such rapid rise is observed for the anodic voltage up to the limiting cathodic current density. This rapid rise of the cathodic voltage is caused by reaching the diffusion-limited rate of deposition of aluminum ions (or aluminum-ion-containing species) during the electrolysis and the start of magnesium deposition. Thus, the electrolytic cell should be operated below the limiting cathodic current density to prevent the codeposition of magnesium.

It should be noted that the cell voltage at a given current density is the sum of the anodic and cathodic components shown in Fig. IV-11. Extrapolations of cell voltage components to zero current density in Fig. IV-11 give the decomposition voltage of about 1 V for  $\text{Al}_2\text{S}_3$  at 1023 K, in good agreement with the value of 0.98 V estimated from Ferrante and coworkers' thermodynamic data.<sup>20</sup>

Electrolysis experiments to determine the current efficiency were carried out using the eutectic melt containing 2 wt %  $\text{Al}_2\text{S}_3$ . The cell was operated below the limiting cathodic current density for this concentration so that only aluminum was deposited at the cathode. Figure IV-12 shows the electrode assembly after the electrolysis. It can be seen that some of the metal deposits remained on the graphite. Aluminum metal was collected from

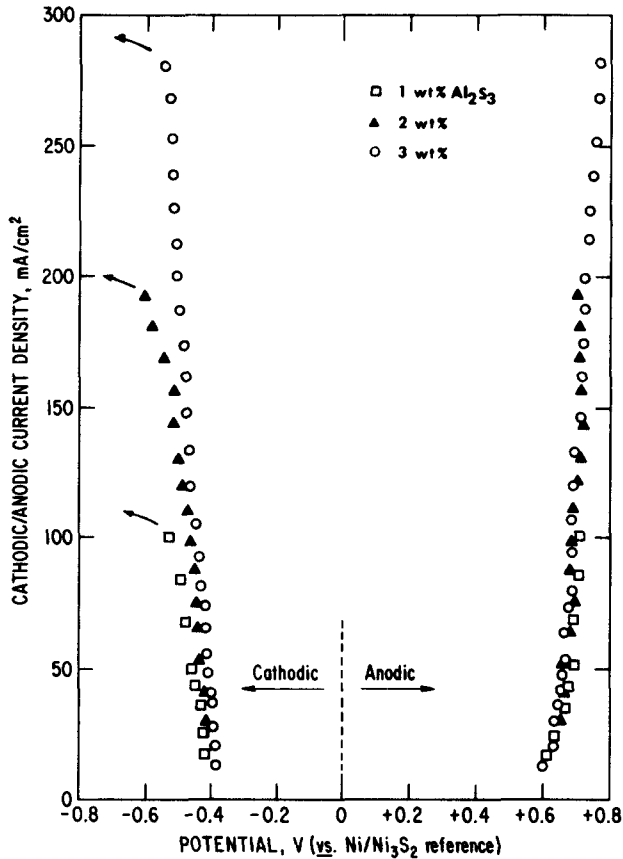


Fig. IV-11.

Plots of Current Density vs. Cathodic and Anodic Potentials (Uncorrected for Ohmic Drop) for the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2\text{-NaCl-KCl}$  Eutectic. Temperature 1023 K; electrode spacing 3 cm.

these runs as granules of varying size (Fig. IV-13). No attack on the graphite electrodes and no change in the color of the solidified salt were observed for the time scale of these experiments. Sulfur was detected as the anode product by X-ray analysis although no attempt was made to collect the sulfur to determine the anodic efficiency.

The operating conditions and results of two electrolysis experiments are presented in Table IV-7.

Figure IV-14 represents the cathodic current efficiencies as a function of anode/cathode current density for the electrolysis at 2 wt %  $\text{Al}_2\text{S}_3$ . Within the accuracy limits, it is clearly seen that there is a definite trend of increasing efficiency with increasing current density. A decrease in current efficiency at low current density is probably due to the recombination of the electrolysis products (reoxidation of metal or metal dissolved in the electrolyte by the anode gas or by the dissolved anode gas). An analogous situation exists in the Hall-Héroult cell where the recombination proceeds *via* dissolution of aluminum.<sup>13</sup> A similar trend was observed by Welch and coworkers<sup>78</sup> for the electrolysis of  $\text{PbS}$ . These investigators found that the dissolution reaction was most likely to involve the sulfur, and the recombination occurred at or near the cathode.

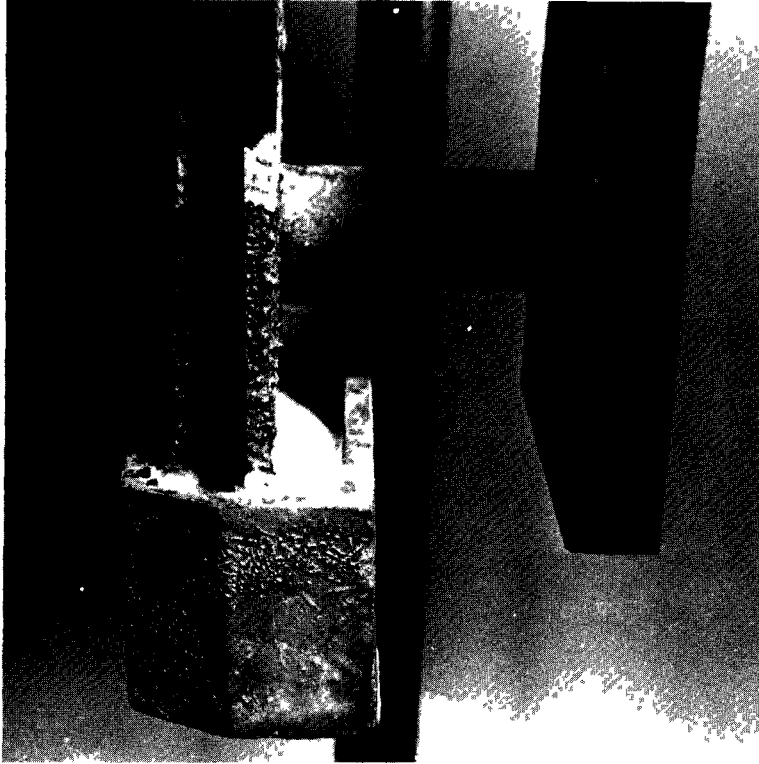


Fig. IV-12. The Electrolysis Assembly after a Constant-Current Electrolysis

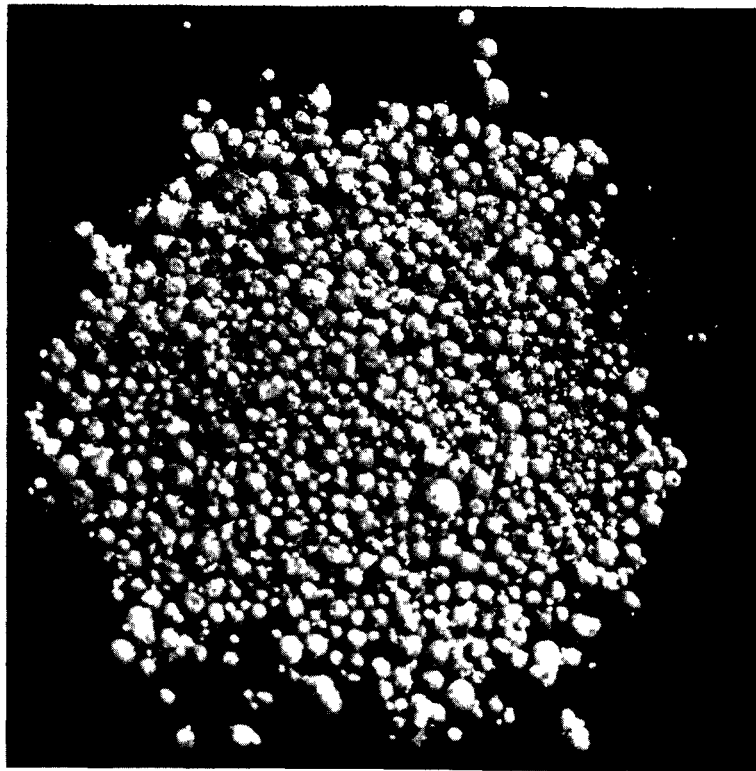


Fig. IV-13. Typical Examples of Granular Aluminum Products from the Electrolysis of  $\text{Al}_2\text{S}_3$

Table IV-7. Operating Parameters and Results Obtained for the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic

	Run E-1	Run E-2
Melt Composition	$\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$ Eutectic with 2 wt % $\text{Al}_2\text{S}_3$	$\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$ Eutectic with 2 wt % $\text{Al}_2\text{S}_3$
Temperature	1023 K	1023 K
Cathode	graphite, 21.1 $\text{cm}^2$	graphite, 20.9 $\text{cm}^2$
Anode	graphite, 21.1 $\text{cm}^2$	graphite, 20.9 $\text{cm}^2$
Electrode Spacing	3 cm	3 cm
Cell Current	4.10 A	3.10 A
Cathode Current Density	194 $\text{mA}/\text{cm}^2$	148 $\text{mA}/\text{cm}^2$
Faradays	20,910 C	10,044 C
Aluminum Recovered	1.60 g	0.59 g
Cathode Current Efficiency	82%	63%
Anode Current Efficiency	not determined	not determined

The analyses of the metal products from the two runs are shown in Table IV-8. The analyses show that the resultant metal has low levels of impurities.

The experimental results indicate that it is possible to produce aluminum and sulfur with good current efficiency *via* the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic melt. A current efficiency of over 80% was achieved at a current density of about 200  $\text{mA}/\text{cm}^2$ . The current efficiency obtained in the present study is much better than the efficiency of 55% for the electrolysis in cryolite-chloride melts reported by Russian and German investigators<sup>36,39</sup> in the 1930's. No reason for the difference can be given here except the fact that the previous studies were conducted using a different electrolyte, with different  $\text{Al}_2\text{S}_3$  concentration and current density. There is also a possibility of the presence of impurities in the Russian and German experiments.

As mentioned earlier, the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  has to be carried out below a limiting current density to prevent the codeposition of magnesium. At 3 wt %  $\text{Al}_2\text{S}_3$ , the saturation solubility in the melt, the limiting cathodic current density is about 300  $\text{mA}/\text{cm}^2$ . This cathodic current density limits the aluminum-production rate to a low level; this level may be too low to be of practical value. Present aluminum processes use much higher current densities. For example, the current density (anode) in the Hall-Héroult reduction cell is from 0.7 to 1.2  $\text{A}/\text{cm}^2$ . Also, for a

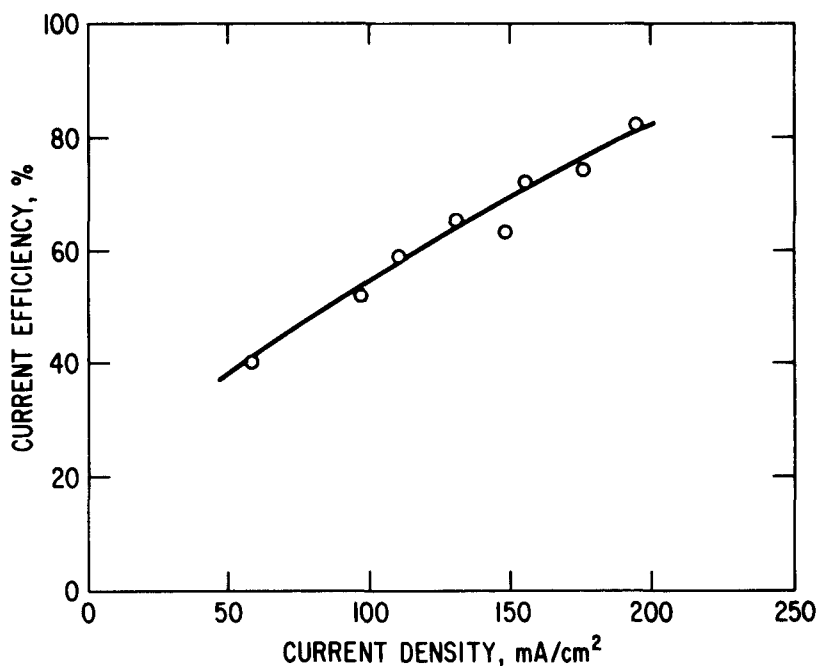


Fig. IV-14. Effect of Current Density on Cathodic Current Efficiency for the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic. Temperature 1023 K; electrode spacing 3 cm;  $\text{Al}_2\text{S}_3$  concentration 2 wt %.

Table IV-8. Spectrochemical Analysis of Aluminum Products Obtained from the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic. (Values in wt %)

Component	Run E-1	Run E-2
Al	VS <sup>a</sup>	VS
B	0.05	0.05
Ca	0.05	0.01
Cr	0.005	0.005
Cu	0.003	0.01
Fe	0.01	0.05
Mg	M <sup>b</sup>	M
Mn	0.01	0.01
Na	0.02	0.01
Pb	0.002	0.02
Si	M	M

<sup>a</sup>VS = very strong, approximate concentration 100 to 10 wt %.

<sup>b</sup>M = medium, approximate concentration 1 to 0.1 wt %.

batch operation, the limiting current density will decrease as the  $\text{Al}_2\text{S}_3$  content of the melt is depleted during electrolysis. In order to be able to operate the electrolytic cell at higher current densities, higher concentrations of aluminum ion (or aluminum-ion-containing species) in the molten salt are required. There are two possible ways to modify the process: (1) use of an electrolyte containing the common aluminum ion (*e.g.*, melts containing  $\text{AlCl}_3$  or  $\text{AlF}_3$ ); or (2) use of an electrolyte having higher  $\text{Al}_2\text{S}_3$  solubility.

The problem of a low concentration of aluminum ions (or aluminum-ion-containing species) has been eliminated by the addition of  $\text{AlCl}_3$  to the eutectic. The presence of  $\text{AlCl}_3$  in the melt provides common aluminum ions (or aluminum-ion-containing species) and increases the solubility of  $\text{Al}_2\text{S}_3$ , as shown by the solubility measurements. Thus, cells for the electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$ - $\text{AlCl}_3$  melts can be operated at higher current densities. It has also been shown in the electrochemical studies that the presence of  $\text{AlCl}_3$  in the eutectic has no effect on the anodic oxidation of sulfide ion (or sulfide-ion-containing species), *i.e.*, elemental sulfur ( $\text{S}_2$ ) is still the product at the anode.

A number of experiments were carried out with  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic/5 wt %  $\text{AlCl}_3$  to obtain cell voltages and cathodic and anodic potentials at different current densities. Difficulties were encountered in dissolving more than 3 wt %  $\text{Al}_2\text{S}_3$  in these melts, although the solubility of  $\text{Al}_2\text{S}_3$  in this mixture should be about 7.8 wt %. It appeared that volatilization of  $\text{AlCl}_3$  during heating was causing the loss of solubility. It was decided to carry out the electrolysis in melts containing 10 wt %  $\text{AlCl}_3$ . Those melts dissolved up to 5 wt %  $\text{Al}_2\text{S}_3$  without any problems. A significant amount of  $\text{AlCl}_3$  had been volatilized; however, enough  $\text{AlCl}_3$  remained in the melt to dissolve 5 wt %  $\text{Al}_2\text{S}_3$ .

Plots of anode and cathode components of the cell voltage (uncorrected for ohmic drop) *vs.* current density for three  $\text{Al}_2\text{S}_3$  concentrations (2, 3, and 5 wt %) are shown in Fig. IV-15. It is clear from these plots that higher current densities can be used for electrolytic cells with  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  + 10 wt %  $\text{AlCl}_3$ .<sup>\*</sup> This figure shows a steady but small rise in the cathodic potential, and a limiting anodic current density for each  $\text{Al}_2\text{S}_3$  concentration. The change in slope of the anode potential *vs.* current density curve indicates the approximate anode current density at which  $\text{S}_2\text{Cl}_2$  or  $\text{Cl}_2$  evolution begins. At 5 wt %  $\text{Al}_2\text{S}_3$ , the limiting anode current density is about 1.9 A/cm<sup>2</sup>. Extrapolations of these plots to zero current density also give about 1 V for the decomposition voltage of  $\text{Al}_2\text{S}_3$  at 1023 K.

The electrolysis of  $\text{Al}_2\text{S}_3$  to produce aluminum for efficiency determination was carried out in the eutectic/10 wt %  $\text{AlCl}_3$  containing 5 wt %  $\text{Al}_2\text{S}_3$ . Again, sulfur was detected as the anode product, condensed inside the molybdenum collection hood. The solidified electrolyte remained white after the electrolysis. Aluminum deposits were also collected as granules of varying sizes as in the case of the electrolysis of  $\text{Al}_2\text{S}_3$  in the pure eutectic. Because of the high current density used in these experiments, the electrolysis was started at a temperature about 5 to 10 degrees lower than the desired temperature (1023 K) to prevent overheating of the cell.

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\* Initial weight percent of  $\text{AlCl}_3$  added.

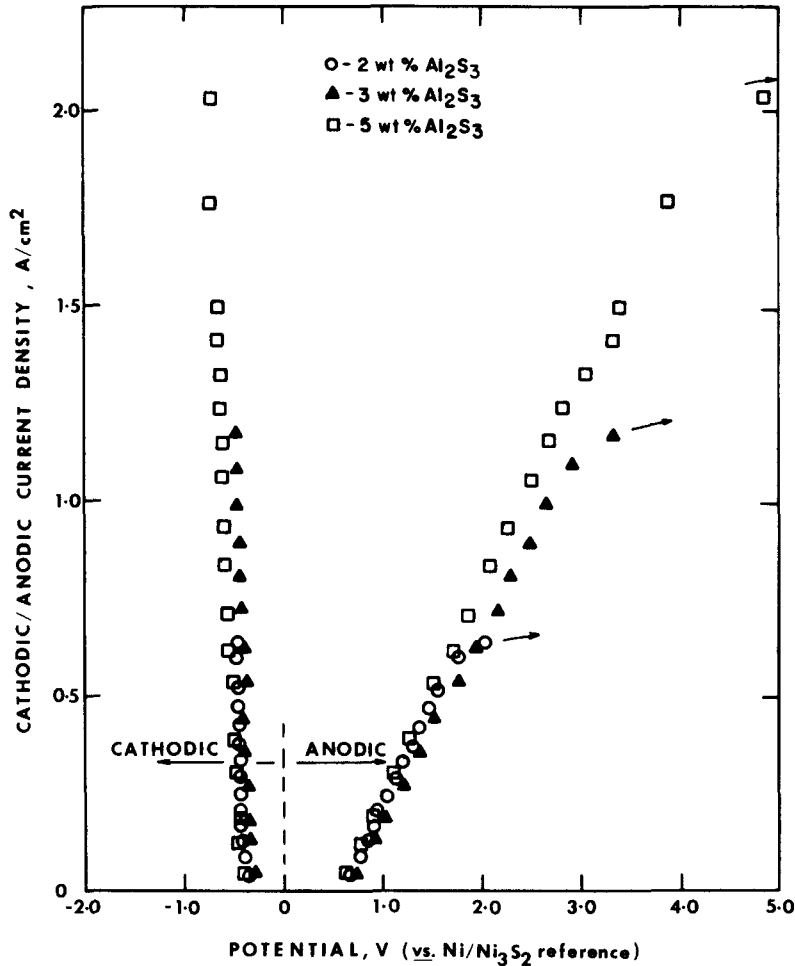


Fig. IV-15. Plots of Current Density *vs.* Cathodic and Anodic Potentials (Uncorrected for Ohmic Drop) for the Electrolysis of Al<sub>2</sub>S<sub>3</sub> in MgCl<sub>2</sub>-NaCl-KCl Eutectic/10 wt % AlCl<sub>3</sub>

Typical operating parameters and results obtained for the electrolysis of Al<sub>2</sub>S<sub>3</sub> in the MgCl<sub>2</sub>-NaCl-KCl-AlCl<sub>3</sub> melt are listed in Table IV-9.

The current efficiencies were determined at different current densities greater than 0.2 A/cm<sup>2</sup>. The results obtained are illustrated by the curve presented in Fig. IV-16. It appears that, within the current density range 0.2-1.2 A/cm<sup>2</sup>, the cathodic current efficiency for the electrolysis of Al<sub>2</sub>S<sub>3</sub> in MgCl<sub>2</sub>-NaCl-KCl eutectic containing AlCl<sub>3</sub> does not vary significantly with the current density; current efficiencies of about 75 to 85% were obtained. One possible explanation for this trend in current efficiency is that at those higher current densities (compared to those in MgCl<sub>2</sub>-NaCl-KCl eutectic), the limiting rate of the controlling step for the recombination of the electrode products has been reached. This explanation can only be verified by further experimentation.



Table IV-9. Operating Parameters for the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic/10 wt %  $\text{AlCl}_3$ 

Parameter	Run ALE-2	Run ALE-5
$\text{Al}_2\text{S}_3$ Concentration	5 wt %	5 wt %
Salt Charge (eutectic + $\text{AlCl}_3$ )	400 g	400 g
Temperature	1023 K ( $\pm 10$ K)	1023 K ( $\pm 10$ K)
Cathode	Graphite, 18.1 $\text{cm}^2$	Graphite, 16.7 $\text{cm}^2$
Anode	Graphite, 18.1 $\text{cm}^2$	Graphite, 16.7 $\text{cm}^2$
Electrode Spacing	3 cm	3 cm
Cell Current	10 A	20 A
Anode/Cathode Current Density	0.55 $\text{A}/\text{cm}^2$	1.20 $\text{A}/\text{cm}^2$
Cell Voltage	$\sim 2.2$ V	$\sim 3.4$ V
Faradays	48,060	36,000
Aluminum Recovered	3.81 g	2.72 g
Cathodic Current Efficiency	85%	81%
Anode Current Efficiency	not determined	not determined

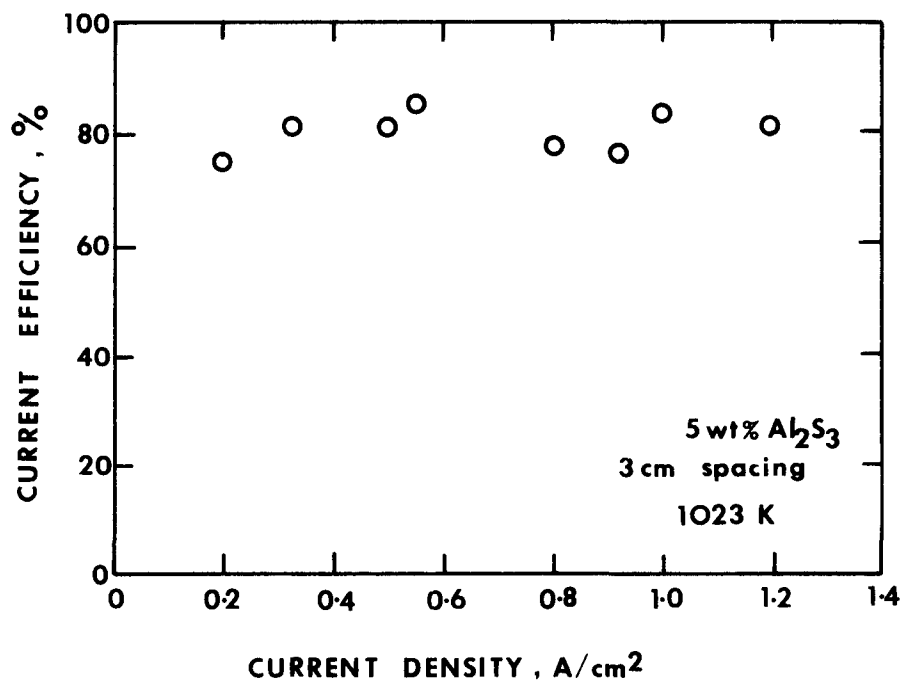


Fig. IV-16. Current Efficiency of the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic/10 wt %  $\text{AlCl}_3$  at Varying Current Density. Temperature 1023 K; electrode spacing 3 cm;  $\text{Al}_2\text{S}_3$  concentration 5 wt %.

The assay of the aluminum produced indicated that its purity was better than 99% and its magnesium content was low (less than 0.1%) (Table IV-10). However, the largest granule from one of the runs at higher current was analyzed separately; it showed an unusually high magnesium content (6%). Perhaps in some cases the diffusion-limited current for aluminum deposition was surpassed locally during electrolysis.

Table IV-10. Spectrochemical Analysis of Aluminum Products from the Electrolysis of  $\text{Al}_2\text{S}_3$  in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  Eutectic/10 wt %  $\text{AlCl}_3$ . (Values in wt %)

Component	Run ALE-4	Run ALE-6	Run ALE-7
Al	VS <sup>a</sup>	VS	VS
B	0.00	0.00	0.01
Ca	0.03	0.03	0.03
Cr	0.00	0.00	0.00
Cu	0.00	0.00	0.01
Fe	0.00	0.00	0.00
Mg	0.00	0.00	0.1
Mn	0.01	0.01	0.01
Na	0.1	0.1	0.1
Pb	0.01	0.00	0.03
Si	0.1	0.1	0.2

<sup>a</sup>VS = very strong, approximate concentration 100 to 10 wt %.

## V. CONCLUSIONS AND RECOMMENDATIONS

The results of the experiments on the electrolysis of aluminum sulfide are very encouraging and demonstrate that  $\text{Al}_2\text{S}_3$  dissolved in a molten chloride can be electrolyzed to produce aluminum and elemental sulfur. This indicates that the aluminum sulfide route may be a potential alternative process for the production of aluminum if a feasible method for synthesizing  $\text{Al}_2\text{S}_3$  from alumina or aluminous ores can be developed. (The synthesis of  $\text{Al}_2\text{S}_3$  should be carried out with good yield, should produce  $\text{Al}_2\text{S}_3$  with an acceptable quality for electrolysis, and above all should have low energy requirements.) Although the electrolysis of  $\text{Al}_2\text{S}_3$  has been shown to produce aluminum with reasonable current efficiency, these results are quite preliminary. Detailed studies of many operating parameters are lacking, and additional laboratory studies are needed before the technical potential of the electrolysis can be accurately assessed.

The solubility, linear-sweep voltammetry, and electrolysis studies carried out in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic and in the eutectic containing  $\text{AlCl}_3$  have shown many interesting and important results. The molar ratios of aluminum and sulfur in  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic are shown by the solubility measurements to be about unity, which is lower than the value of 1.5 expected for a true dissolution of  $\text{Al}_2\text{S}_3$ . This important finding suggests that the dissolution of  $\text{Al}_2\text{S}_3$  in the eutectic leads to the formation of  $\text{AlS}^+$  species

and that some sulfur remains undissolved, probably as MgS. The precipitation of MgS has not been confirmed experimentally because of the difficulty of sampling and detecting MgS in the melt. If the formation of MgS is significant for the dissolution of  $\text{Al}_2\text{S}_3$ , MgS will form sludge and its buildup may have a deleterious effect on the continuous operation of the electrolysis. The MgS problem, however, can be eliminated by the addition of  $\text{AlCl}_3$  to the eutectic, which dissolves MgS into the molten salt by the reaction  $\text{MgS(s)} + \text{AlCl}_3(\text{soln}) = \text{AlSCl(soln)} + \text{MgCl}_2(\text{soln})$ . The addition of  $\text{AlCl}_3$  to the eutectic has been found to enhance the solubility of  $\text{Al}_2\text{S}_3$  and the solubility increases with increasing  $\text{AlCl}_3$  concentration. The molar ratio S/Al is also about unity for the solubility of  $\text{Al}_2\text{S}_3$  in the presence of added  $\text{AlCl}_3$ . This result, at least, gives some support for the  $\text{AlS}^+$  hypothesis. Practically, the solubility data imply that sufficient  $\text{Al}_2\text{S}_3$  can be solubilized in a molten chloride for electrolysis. Thus, a viable electrolyte for  $\text{Al}_2\text{S}_3$  electrolysis would be composed of alkali and/or alkaline-earth chlorides and aluminum chloride. The concentration level of  $\text{AlCl}_3$ , of course, is dictated by many factors which can be determined only by experimentation and testing. The  $\text{AlCl}_3$  content, however, should not be too high because the volatilization of the  $\text{AlCl}_3$  then becomes a serious problem.

The linear-sweep voltammetric studies have elucidated the mechanism of the electrode reactions for the electrolysis of  $\text{Al}_2\text{S}_3$ . The electrode reactions in both  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic and in  $\text{AlCl}_3$ -containing eutectic are shown to be reversible and diffusion-controlled. The reduction of aluminum ions is a three-electron process to form aluminum metal. The sulfide oxidation is a two-electron electrochemical reaction followed by the fast dimerization of sulfur atoms to  $\text{S}_2$ . Thus, on the time and  $\text{Al}_2\text{S}_3$ -concentration scales of voltammetry, the electrolytic decomposition of  $\text{Al}_2\text{S}_3$  produces aluminum at the cathode and elemental sulfur at the anode. No evidence of polysulfide formation is observed for these scales. This may be one of the explanations for the good current efficiency obtained in this work. This is contrary to the general belief that the efficiency of the sulfide electrolysis in chlorides might be poor due to polysulfide species formed between sulfur at the anode and the sulfide in the melt. This belief is based mainly on the fact that a variety of polysulfides have been identified in chloride melts at temperatures of 473-823 K (Section III-B-2). It may be possible that, at the temperature of the present work (higher than those of previous works), the polysulfides are not stable. Also, the stability of polysulfides depends very much on the acidity of the melt. Also,  $\text{MgCl}_2$  and  $\text{AlCl}_3$  are acidic, and there are some indications in the literature that polysulfides are unstable in acidic melts.<sup>178</sup> However, these speculations can only be verified by further experimentation.

It has been demonstrated experimentally that it is possible to produce high-purity aluminum and elemental sulfur with reasonably good current efficiency *via* the electrolysis of  $\text{Al}_2\text{S}_3$ . In  $\text{MgCl}_2$ - $\text{NaCl}$ - $\text{KCl}$  eutectic melt, the electrolysis is limited by the diffusion of aluminum ions and the limiting cathodic current density is about 300 mA/cm<sup>2</sup> at the saturation solubility of  $\text{Al}_2\text{S}_3$ . With the presence of  $\text{AlCl}_3$  in the eutectic, the limiting current becomes anodic, and higher current densities can be used for the electrolysis. Also, the presence of  $\text{AlCl}_3$  enhances the solubility of  $\text{Al}_2\text{S}_3$ . Higher concentrations of  $\text{Al}_2\text{S}_3$  permit much higher current densities. The use of higher current densities may be necessary for practical application if the operation is to be carried out under diffusion conditions. It has been found that,

within the current density range 0.2-1.2 A/cm<sup>2</sup>, the current efficiency (75-85%) of the electrolysis of 5 wt % Al<sub>2</sub>S<sub>3</sub> in MgCl<sub>2</sub>-NaCl-KCl eutectic/10 wt % AlCl<sub>3</sub> does not vary significantly with the current density. A fundamental understanding of secondary reactions such as back reactions is required to explain the trend in current efficiency.

It must be concluded that continued work on the research and the development of the electrolysis of Al<sub>2</sub>S<sub>3</sub> for the production of aluminum is necessary. It is recommended that the following areas be investigated:

- A laboratory study of the electrolysis of Al<sub>2</sub>S<sub>3</sub> in promising AlCl<sub>3</sub>-containing chloride electrolytes needs to be undertaken. Performance characteristics such as cell voltage, electrode overpotential, IR drop, and current efficiency should be studied as functions of controllable variables such as temperature, Al<sub>2</sub>S<sub>3</sub> concentration, electrode spacing, electrolysis time, and current density. Such studies are needed to select the most suitable solvent for the electrolysis and to optimize operating parameters. A comparative study of the electrolysis of Al<sub>2</sub>S<sub>3</sub> should be carried out in fluoride systems to evaluate the feasibility of these melts as electrolytes.

- A study of the chemistry of the selected electrolyte should be made. This study should be focused on the solubilities of Al<sub>2</sub>S<sub>3</sub>, aluminum metal, and sulfur and their interactions in the molten salt. The study will be helpful in explaining any loss in the current efficiency of the electrolysis.

- A study of the anode reaction needs to be undertaken. Conditions which result in the formation of sulfur halide compounds (*e.g.*, S<sub>2</sub>Cl<sub>2</sub>), the formation of any polysulfides, and anode corrosion (to form CS<sub>2</sub> for example) should be determined. Although anodic current efficiency measurements present considerable experimental difficulties (particularly in regard to ensuring that all the sulfur is collected for measurements), the determination of anodic efficiency should also be an important part of this study.

- The effects of impurities such as other sulfides, alumina, and silica on the electrolysis operation should be investigated.

- A laboratory-scale investigation of the continuous electrolysis of Al<sub>2</sub>S<sub>3</sub> in a bipolar cell should be carried out under the optimum conditions defined by the above studies. Such a study is needed for economic and technical assessment of the electrolysis process.

#### ACKNOWLEDGMENTS

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