MAGNESIUM FROM THE ELECTROLYTIC REDUCTION OF MAGNESIUM OXIDE

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CHAPTER I

INTRODUCTION

The direct electrolysis of magnesium oxide from an anhydrous melt offers attractive possibilities, provided a satisfactory melt can be found in which magnesium oxide is appreciably soluble. Theoretically magnesium oxide can be reduced electrolytically to the metal with the expenditure of less energy than is required by the electrolysis of magnesium chloride (38). Present methods of producing electrolytic magnesium entail the chlorination of the magnesium oxide to magnesium chloride which is subsequently electrolyzed to magnesium metal and chlorine. The conversion of the oxide to the chloride is a costly process. The direct electrolysis of the magnesium oxide would eliminate this intermediate process and thus reduce the cost of producing magnesium.

The principal impediment to the oxide process has been the lack of a satisfactory melt in which magnesium oxide is appreciably soluble. Magnesium was formerly produced commercially by the electrolysis of a fluoride melt containing magnesium oxide. The process failed to be competitive because of the high melting point of the fluoride electrolyte and because of the low solubility of magnesium oxide in the melt (1, 50). The magnesium oxide solubility was reported as 0.1 per cent at 950° C., the melting point of the electrolyte (1). Due to this low solubility there was a deficiency of magnesium oxide in contact with the anode and, as a result, fluorine accumulated on the anode. This interrupted normal functioning of the cell and gave rise to low current efficiencies.

Thus, before magnesium can be produced from magnesium oxide, it will be necessary to find a solvent that will dissolve appreciable quantities of magnesium oxide. Moreover, this solvent will need to satisfy the other requirements of an electrolyte--that is, be chemically inert to molten magnesium and contain no constituents that would deposit at the cathode to contaminate the magnesium product.

The object of this research was to find such a solvent and in so doing discover a new process for producing magnesium from magnesium oxide.

Accordingly, the research was conducted in three principal parts:

(1) Investigation of the solubility of magnesium oxide in various molten salts.

(2) Investigation of the chemical reactivity of molten magnesium with the more promising molten solvents.

(3) Electrolysis of magnesium oxide in those melts found to dissolve appreciable quantities of magnesium oxide and to be non-reactive with magnesium.

CHAPTER II

REVIEW OF THE LITERATURE

A. Historical Background of Magnesium Production

Magnesium was discovered in 1808 by the English chemist Sir Humphrey Davy. He reduced magnesium oxide to the metal with potassium vapor. In 1830, Bussy of France reduced magnesium chloride with potassium. Faraday, in 1833, prepared magnesium by electrolysis of fused anhydrous magnesium chloride. Later, in 1852, Bunsen of Germany developed an electrolytic cell for the electrolysis of the anhydrous chloride. In 1856, Deville and Caron successfully reduced the chloride with metallic sodium, but the magnesium produced was contaminated with sodium. They had little success in purifying the metal by distillation (11, 45, 50).

Most of the early investigations were merely for scientific purposes. It was not until 1859, when Bunsen called attention to the importance of magnesium in photography, that production of magnesium was attempted on a commercial scale. In 1863, in England, Sonstadt developed a process for the reduction of magnesium chloride with metallic sodium (68, 69). Based on Sonstadt's patents, the Magnesium Metal Company was organized to produce magnesium wire and ribbon for photography. This company had very little commercial success and the magnesium industry was of minor importance until about 1909, when an electrolytic process was developed in Germany to produce magnesium from the chloride. The source of the magnesium chloride was carnallite, which is a mixture of magnesium and potassium chlorides. The process was developed by using a modification of the Bunsen cell which was fed with carnallite. The early product was at first inferior, analyzing about 98 per cent magnesium, and was contaminated with chloride salts. At about the same time an English metal company attempted a similar process, but cheaper raw material and labor gave the Germans a world monopoly (1, 11, 45).

The earliest recorded commercial production of magnesium in America was by a company which operated from 1865 to 1892 in Boston, Massachusetts. The metal was made by using the process described in the Sonstadt patents and, as in England, the product was confined to wire and ribbon for photography (45).

During World War I, German magnesium was unavailable in this country, and as a result eight different companies produced magnesium during the period 1916 to 1917. The total American production reached 284,118 pounds. After the war only two of these companies remained, the Dow Chemical Company and the American Magnesium Corporation (1, 11, 16). In 1920 both companies were forced to close their plants because of the severe competition from the German chemical trust. In 1922 Congress passed a tariff which gave the entire American chemical industry a chance to compete and both companies then reopened their plants (51). However, in 1927 the American Magnesium Corporation discontinued production of magnesium and limited its activities to fabrication. The Dow Chemical Company remained the sole producer of magnesium in the United States until 1941 (1, 50).

Both the American Magnesium Corporation and the Dow Chemical Company used processes for manufacturing magnesium based upon electrolysis in a bath of fused salts. The American Magnesium Corporation used an electrolyte consisting of a fused mixture of magnesium fluoride, barium fluoride, and sodium fluoride to which calcined magnesite ($MgCO_3$) or magnesium oxide from dolomite ($MgCO_3 \cdot CaCO_3$) was added. This "oxide" process was characterized by low current and energy efficiencies. The Dow process (Midland, Michigan) treated brine pumped from deep wells to obtain a cell feed material corresponding to approximately 94 per cent magnesium chloride, 1 per cent magnesium oxide, and 2 per cent water, with the balance consisting of impurities. The electrolytic bath was composed of approximately 25 per cent magnesium chloride, 15 per cent calcium chloride, and 60 per cent sodium chloride. The temperature was maintained between 700 and 750° C. by controlled gas firing (11, 16, 45, 47).

In 1941 the United States government declared magnesium a strategic metal and at the same time began construction of magnesium plants. During the same year the Permanente Metals Corporation, in a privately owned plant, began manufacturing magnesium by the carbothermic process. Before the middle of 1943 there were 15 magnesium plants being operated by 11 different companies. The total rated annual capacity of the combined plants amounted to 293,000 short tons of magnesium. The peak production of magnesium was attained in 1943 when 184,078 short tons of primary magnesium were produced. The capacity to produce by the three processes utilized was approximately 72 per cent electrolytic ($MgCl_2$), 24 per cent ferrosilicon, and 4 per cent carbothermic (21, 27).

The ferrosilicon and the carbothermic processes were introduced during World War II. The carbothermic process employs carbon and heat at a high temperature (approximately 2000° C.) in vacuum to reduce magnesium oxide or magnesium oxide containing ores. This process is sometimes referred to as the "Hansgirg" process after the deceased Austrian scientist Dr. F. J. Hansgirg, who did most of the development work. In the ferrosilicon process, ferrosilicon is used to reduce calcined dolomite into magnesium leaving a residue of calcium silicate and iron (11, 21, 27).

By the end of 1945 only the Dow Chemical Company's Freeport, Texas, plant remained in operation, and Dow was again the single producer of magnesium in the United States. However, the Government retained six plants in stand-by condition, and these were reactivated in 1951 to meet the demand for magnesium during the Korean emergency (11, 21).

The six reactivated plants produced an additional 164,177 tons of magnesium before four of them were closed in 1953 and again placed in a stand-by condition. The Government contract with Dow to operate the Velasco plant (50 per cent owned by the Government and 50 per cent owned by Dow Chemical Company) was extended to 1956 and, subsequently, to 1957 (11). The sixth reactivated plant located at Canaan, Connecticut, (ferrosilicon magnesium process) began production of magnesium and calcium in 1953 for the atomic energy program (11). Dow again remains the only large commercial producer of magnesium in the United States.

However, a new company, Alabama Metallurgical, (formed by Brooks and Perkins, and Dominion Magnesium of Toronto) is building a 10,000 ton per year ferrosilicon plant at Selma, Alabama. The plant is to be completed by the end of 1957 (22).

The Dow process, particularly as developed for the sea water plants located in Texas at Freeport and Velasco, is the most economical method of producing magnesium in the United States (21). The market price in 1953 was only 26.6 cents per pound of magnesium from the Dow operated plants, whereas the average cost in the reactivated plants was 42.39 cents per pound of magnesium (11).

B. A Summary of Magnesium Production Technology

The problem of extracting magnesium from its ores has been resolved into two general methods: the electrolysis of fused magnesium compounds (usually chloride) and the thermal reduction of the oxide or carbonate (1). A discussion of the sources of magnesium and the technology of the variations of the general methods follows:

1. Sources of Magnesium

Magnesium constitutes 2.5 per cent of the earth's crust and is the sixth most plentiful element (11). It occurs in all parts of the world in sea water, natural brines, and a variety of minerals. The metal always exists in one of several combined forms, the more common of which are (1, 11, 27):

(1) Magnesium chloride ($MgCl_2$)--found in sea water, salt lakes, and underground brine and salt beds. One cubic mile of sea water contains approximately 12,000,000,000 pounds of magnesium as magnesium chloride.

(2) Magnesite ($MgCO_3$)--a common mineral widely distributed all over the world. Extensive deposits of magnesite are found in Nevada, Washington, and other parts of the United States.

(3) Dolomite ($CaCO_3 \cdot MgCO_3$)--widely distributed throughout the world and is used as the chief source of magnesium metal in England. This mineral frequently contains more calcium than magnesium, and, therefore, only part of the dolomite deposits are economical for magnesium metal extraction.

(4) Carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)--The mineral is found in the famous Stassfurt salt beds in Germany as well as in the United States and other parts of the world. Carnallite is the parent raw material of modern magnesium manufacture in Germany, although it does not have the importance that it once had.

(5) Brucite ($MgO \cdot H_2O$)--There is an important deposit in Quebec, Canada, where brucite occurs in nodular form embedded in a limestone matrix. Large deposits also occur in Gabbs, Nevada. The Nevada deposits were used as a source of magnesium metal at the Basic Magnesium, Inc., Plant, Henderson, Nevada, during World War II.

(6) Other minerals such as serpentine ($3MgO \cdot 2SiO_2 \cdot 2H_2O$), kierserite ($MgSO_4 \cdot H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$), olivine ($Mg_2SiO_4$), and enstatite ($MgSiO_3$) are of less importance as a source of metallic magnesium.

2. Electrolytic Processes

a. Electrolysis of Magnesium Chloride

Magnesium chloride for cell feed is obtained in a number of ways: from salines, brine wells, the reaction of magnesium hydroxide (from sea water or dolomite) with hydrochloric acid, and the reaction of magnesium oxide with carbon and chlorine (64). The Dow Chemical Company obtains magnesium chloride from sea water. An example of the manufacture of magnesium chloride from magnesium oxide, carbon, and chlorine is the Basic Magnesium process.

Dow Process.--The raw materials for the preparation of magnesium chloride from sea water are oyster shells, natural gas, and sea water (27). The oyster shells ($CaCO_3$) are burned to lime, slaked, and mixed with sea water to precipitate magnesium hydroxide. This magnesium hydroxide is filtered from the solution and treated with hydrochloric acid to form a magnesium chloride solution (50). Impurities are removed by filtration and the magnesium chloride solution is evaporated to $MgCl_2 \cdot 6H_2O$. This salt is easily dehydrated to $MgCl_2 \cdot 2H_2O$, which may be heated in an atmosphere of either hydrochloric acid or ammonium chloride to produce $MgCl_2 \cdot 1\frac{1}{2}H_2O$ (11). Dehydration is completed in the electrolytic cell where the magnesium chloride is decomposed into magnesium metal and chlorine. The chlorine is reacted with natural gas to produce additional hydrogen chloride which is recycled to produce magnesium chloride from the magnesium hydroxide (11).

The electrolysis is carried out in steel pots approximately 6 feet deep, 5 feet wide, and 11 feet long, which hold the 10 tons of molten salts and conduct the current to the internal cathodes (1). The cell operates at about 6.3 volts, with a current efficiency of 75 to 80 per cent and a power requirement of 8 d.c. kilowatt-hours per pound of magnesium (1). The cell is externally heated so as to maintain the bath temperature at 700° C. The external heating lowers the power requirement and permits flexibility in the cell voltage (1). The purity of the metal produced is about 99.9 per cent. The main disadvantage of the process is the cost of purifying and dehydrating the magnesium chloride (1).

Basic Magnesium Process.--This process was used by Basic Magnesium, Inc., at Henderson, Nevada, during World War II. A modification of the process is now being used in Norway. In the Basic Magnesium process magnesium carbonate or brucite ($MgO \cdot H_2O$) was calcined to the oxide. In Norway the magnesium oxide is obtained by a sea-water process.

The oxide is mixed with coal, peat moss, and a binder and chlorinated by an atmosphere of chlorine at about 850° C. in an electrically heated furnace (64). Molten anhydrous magnesium chloride is produced as shown by the reactions:

$$MgO + C + Cl_2 \overset{850^\circ\ C.}{=} MgCl_2(liq.) + CO$$

$$2\ MgO + C + 2\ Cl_2 \overset{850^\circ\ C.}{=} 2\ MgCl_2(liq.) + CO_2$$

The molten magnesium chloride is transferred to the cells without allowing it to cool (1).

Electrolysis of the magnesium chloride is carried out in a ceramic lined, rectangular cell. Other salts are added to the magnesium chloride to increase the conductivity and to lower the melting point of the bath (25). The cell does not require external heating for the influx of 20,000 amperes is enough to maintain the temperature required. The electrodes consist of a carbon anode and an iron cathode (1). Since the cell feed is absolutely anhydrous, there is not the anode consumption that exists in the Dow cell. Chlorine from the anode is removed and circulated back to the chlorinators (1). Magnesium is extracted at the cathode and removed by hand ladling (same as from the Dow cell). The efficiency of the electrolysis is well over 85 per cent (1). The electric power consumption is 8 to 9 kilowatt-hours per pound of magnesium produced.

This electrolysis process is known as the M.E.L. (Magnesium Elektron Ltd.) process and is used in England (1) and in Norway (70). The M.E.L. process was developed by the I. G. Farbeindustrie A. G. during the period of 1924 to 1929 (1). A similar process is being used in Russia and France (50).

It is reported that the energy requirement (per pound of magnesium) of the M.E.L. cell is greater than that of the Dow cell (11).

b. Oxide Process

The oxide process attempts to electrolyze magnesium oxide in fluoride melts in the same manner as the aluminum process electrolyzes alumina in cryolite (6). Magnesium oxide is only slightly soluble in the fluoride melts (0.1 per cent), whereas alumina is soluble to approximately 10 per cent in cryolite (53, 70). Even so, the oxide process was employed by the American Magnesium Corporation for several years prior to 1927 (1). In the process, dead-burned (high temperature calcination) magnesite is fed into an electrolyte consisting of a fused mixture of equal parts of magnesium and barium fluorides with enough sodium fluoride to reduce the melting point below 950° C. (1). Magnesium is removed at an iron cathode and carbon oxides are evolved at the carbon anode. The metal is refined by distillation to produce a metal of 99.9 per cent purity. About 1.7 pounds of magnesium oxide yields 1 pound of magnesium (1).

Power requirements of the oxide process are from 14 to 25 kilowatt-hours per pound of magnesium metal. The cell operates at 9 to 16 volts and at 9,000 to 16,000 amperes (current density of less than 40 amperes per square inch). The current efficiency is 50 to 60 per cent, and energy efficiency is 10 to 20 per cent (1).

One of the difficulties encountered in the process was the anode effect which interrupted normal functioning of the cell. This was attributed to a deficiency of magnesium oxide in contact with the anode and, as a result, accumulation of fluorine on the anode (16). The high melting point of the fluoride electrolyte and a low current efficiency were the most serious defects of the oxide process (1, 50).

Many attempts have been made to eliminate the difficulties encountered (4, 24, 25, 28, 29, 39, 55, 56, 62, 63). However, no method has been revealed which would encourage another attempt to electrolyze magnesium oxide in fluoride melts on an industrial scale (6).

Harvey, in 1925, compared the oxide and chloride processes, stating that the oxide process had lower cost for raw materials and labor but required more power and subsequent refining of the product. He also emphasized the difficulties in the chloride process due to the hygroscopic nature of the electrolyte and the fact that even traces of the chloride in the metal greatly increased the rate of corrosion, whereas metal from the oxide process was non-corroding (32).

3. Thermal Reduction Processes

Considerable attention has been directed toward the technical development of the thermal processes which dispense with the complicated pre-treatment of the raw materials required for the electrolytic processes (6, 11). These processes differ from each other mainly in the reducing agent used. Since the reducing reactions with the magnesium-containing raw materials take place above the boiling point of magnesium, the metal can be separated from the residue by distillation (6).

a. Carbon Reduction of Magnesium Oxide (Carbothermic)

The reduction of magnesium oxide by carbon takes place in accordance with the reaction

$$MgO + C = Mg + CO.$$

At atmospheric pressure and at temperatures above 2,000° C., the reaction is directed to the right while at lower temperatures magnesium vapor reacts with carbon monoxide to form magnesium oxide and carbon (6). It is the reversal of the reaction that has been one of the major problems in the carbothermic reduction of magnesium (1).

There are three general methods by which reversal of the reaction may be partly prevented (1):

(1) The reduction products may be chilled very rapidly to a temperature (below 200° C.) at which the rate of reaction is negligible.

(2) The activity of the gaseous products may be reduced by dilution with an inert gas.

(3) The magnesium vapor may be removed from the carbon monoxide atmosphere by absorbing it in another molten metal (such as lead).

The first method successfully used to prevent the reverse reaction was shock cooling of the vapors in a stream of cool hydrogen. This method was developed by Dr. F. J. Hansgirg in Austria. The first pilot plant to use this process was built and operated at Rodenthein, Austria, by the Austro-American Magnesite Company. It has been reported that this pilot plant had an explosion in 1939 and has been abandoned (1). Later, large scale plants designed after the pilot plant were built at Konan, Korea, and at Swansea, Wales (50). In this country, the Permanente Metals Corporation produced magnesium by the carbothermic process during World War II (11).

Instead of hydrogen, the Permanente process uses natural gas for cooling the reduction products (11). The use of natural gas has a great advantage over hydrogen in that no subsequent purification is necessary (1). Also, the hot exhaust gas could be used for fuel.

There is one distinct disadvantage in the use of this method. Magnesium dust is pyrophoric when exposed to air; consequently, it must be stored in an inert atmosphere until distilled. Only the inert gases, hydrogen, methane, and other hydrocarbon vapors are non-reactive to magnesium (1). In addition to this hazard, the magnesium dust which is produced must be briquetted with oil, vacuum distilled, and remelted to obtain a pure product. Also, the process, in general, consists of a series of batch operations (11).

The United States Bureau of Mines has done a great deal of research work toward improving the carbothermic process, but they have met with little success (11, 16). Their last pilot plant at Dearborn, Michigan, burned before all of the research had been completed (11). The Bureau discontinued its carbothermic research in June, 1954 (11).

It is interesting to note that the Russians have published basic research work on the carbothermic process as late as 1955 (30).

b. Silicon (Ferrosilicon) Reduction of Magnesium Oxide

The most efficient of the thermic processes employed during World War II is often referred to as the ferrosilicon or Pidgeon process, named for Dr. L. M. Pidgeon who placed the first pilot plant in operation (1938 in Canada) (11). In this process silicon (combined with iron) instead of carbon is used to reduce magnesium oxide (27). The process entails mixing powdered ferrosilicon with calcined dolomite containing about 14 per cent magnesium. This mixture is pressed into small pellets and charged into a tubular steel retort, one end of which is located in a fuel-fired furnace. The retort is put under vacuum and heated to about

2200° F. As the charge heats the following reaction takes place:

$$FeSi + 2\ MgO \cdot CaO = 2\ Mg(vapor) + SiO_2 + Fe \cdot 2CaO$$

The magnesium vapor condenses in a crystalline form at the cool end of the retort (27). These crystals are remelted and cast into ingot form (6).

Six ferrosilicon plants were operated in the United States during World War II (11) as well as one in Canada (1).

The disadvantages of the ferrosilicon process are the batch type operation, the high cost of ferrosilicon (16 cents per pound), and the frequent interruption of operation due to leaking or collapsing retorts.

c. Calcium Carbide Reduction of Magnesium Oxide

This operation is conducted in closed retorts under a vacuum at a temperature high enough to volatilize the magnesium without evolving carbon monoxide (1100° C. with a vacuum of 0.1 mm. of mercury) (50). The reaction is shown by the equation

$$MgO + CaC_2 = CaO + 2\ C + Mg.$$

This process has been commercially operated in England and Australia using gas-fired retorts and yielding magnesium of well over 99.9 per cent purity (21). The cost is high because it requires a minimum of three pounds of carbide to produce one pound of magnesium. Some 300 retorts are required to produce 1,000 tons of magnesium per year (50). This is a considerable installation for a relatively small production (50).

d. Aluminum Reduction of Magnesium Oxide

The reaction is

$$3\ MgO + 2\ Al = Al_2O_3 + 3\ Mg.$$

Like the other thermal processes the operation is carried out at a high temperature (1100 to 1350° C.) in vacuum (73). This process is unsatisfactory because of the high cost of aluminum. However, the aluminum process was used in England during the second World War when magnesium was needed urgently (50).

e. Other Patented Processes Which Have Not Been Used Commercially

(1) Reduction of $MgCl_2$ with hydrogen (17, 18).

(2) Reduction of MgF_2 with CaC_2 (2).

(3) Reduction of MgS with CaC_2 (26).

(4) Reduction of MgO with Al_4C_3 (74).

(5) Reduction of MgO with CH_4 (47).

(6) Reduction of MgO with NO (35).

(7) Reduction of MgO with SiC (48).

(8) Reduction of MgO with $CaSi_2$ (14).

(9) Reduction of MgO with SiO_2 and C (59).

(10) Reduction of magnesium silicates with Al (31).

C. Theoretical Basis for Direct Electrolysis of Magnesium Oxide

The decomposition potential of magnesium chloride and the equilibrium reaction potential of magnesium oxide with carbon have been determined theoretically by K. K. Kelley (38). The following relationships have been developed for the reaction

$$MgCl_2(liq.) = Mg(liq.) + Cl_2:$$

$$\Delta H = 148{,}620 - 6.42\ T + 0.28 \times 10^{-3}T^2$$

$$\Delta F^o = 148{,}620 - 14.79\ T \log T - 0.14 \times 10^{-3}T^2 - 77.47\ T$$

where H = Heat of reaction, cal. per mole

T = °K

F^o = Free energy of reaction, cal. per mole

Values computed from these equations are listed in Table I (38).

TABLE I

Energy Requirements for the Decomposition of Magnesium Chloride

T, °K.	ΔH, Cal./Mole	ΔF^o, Cal./Mole	Decomposition Potential Volts
987	142,560	115,600	2.51
1000	142,480	115,380	2.50
1050	142,190	114,040	2.47
1100	141,900	112,720	2.44
1150	141,610	111,400	2.42
1200	141,320	110,100	2.39
1250	141,030	108,820	2.36
1300	140,750	107,540	2.33

The decomposition potentials in the last column are related to the free energy by the equation

$$\Delta F^o = 46,132 \text{ E.}$$

The potential figures are for pure magnesium chloride. Addition of other salts would lower the activity of the magnesium chloride and cause a rise in the decomposition potential (38).

The reaction

$$MgO + C = Mg(liq.) + CO$$

occurs in the direct electrolysis of magnesium oxide in a fused salt bath--that is, a fused salt bath containing a carbon anode into which solid magnesium oxide is fed. The heat of reaction and free energy of reaction can be determined from

$$\Delta H = 120,950 - 0.97 T - 0.51 \times 10^{-3}T^2 - 4.177 \times 10^5T^{-1}$$

and

$$\Delta F^{o} = 120{,}950 + 2.23\ T \log T + 0.51 \times 10^{-3} T^{2} - 2.088 \times 10^{5} T^{-1} - 57.79\ T.$$

Values calculated from these equations are listed in Table II (38).

TABLE II

Energy Requirements for the Electrolysis of Magnesium Oxide in the Presence of Carbon

T, °K.	ΔH, Cal./Mole	ΔF°, Cal./Mole	Equilibrium Reaction Potential, Volts
1000	119,050	70,150	1.52
1100	118,890	65,270	1.41
1200	118,700	60,400	1.31
1300	118,510	55,530	1.20

Comparison of ΔH values of Tables I and II shows that magnesium theoretically may be recovered, with the formation of carbon monoxide from the direct electrolysis of magnesium oxide in the presence of carbon by the expenditure of about 16 per cent less energy than is required in the electrolysis of the chloride alone. Also, the free-energy requirements and reaction potentials are lower than in the electrolysis of magnesium chloride (38). Investigations by the Bureau of Mines have shown that the back e.m.f. of a fused chloride cell fed with solid magnesium oxide and carbon actually corresponds almost exactly to the appropriate value interpolated from Table II (38).

D. Economic and Practical Considerations

The direct electrolysis of magnesium oxide has the following inherent advantages:

(1) The process does not depend upon the sale or utilization of by-products to meet economic competition from other processes (43).

(2) Magnesium oxide is cheaper than magnesium chloride and contains a larger weight percentage of magnesium (32).

(3) High grade magnesium oxide can be purchased in large quantities in the open market, whereas magnesium chloride in dependable quantities can be obtained only from the Dow Chemical Company. Duplication of the Dow process for producing magnesium chloride would require quite a large capital investment. A limited supply of magnesium chloride is now available from the Kroll process--titanium and zirconium chloride reduction with magnesium metal. This supply is dependent upon the demand for titanium and zirconium.

(4) Magnesium oxide is easier to handle than anhydrous magnesium chloride and plant labor cost would be lower (32).

(5) Carbon oxides produced at the anode would be less corrosive to a plant than hot chlorine and hydrogen chloride gases produced in the magnesium chloride process.

A cost analysis on the oxide electrolysis process was made by the Boulder City Experimental Station of the U. S. Bureau of Mines in 1942 (15). The analysis was based on data from the pilot plant electrolysis of magnesium oxide in a molten magnesium chloride bath (p. 21). For a 10-ton per day magnesium plant, the costs are shown in Table III (15).

TABLE III

Cost Analysis of Magnesium Oxide Electrolysis

Cost Factor	Cost of Magnesium Cents/Pound
Magnesium Oxide	1.37
Chlorination	0.545
Cell Power	3.125
Carbon Anode	1.60
Cell Labor	2.40
Cell Room Repair Maintenance	0.25
Plant Administration	0.50
Depreciation and Amortization	1.00
Miscellaneous Cost	1.00
Total	11.79

The power consumption which was 10.5 kilowatt-hours per pound of magnesium could be reduced if the anode effect due to low solubility could be avoided (42). Labor, power, and material costs have risen since this analysis was made. But if the above total cost of producing a pound of magnesium were double, there would still remain a considerable profit margin between the production cost of 23.6 cents per pound and the present market price of 36 cents per pound of magnesium.

E. Previous Investigations

1. Bureau of Mines Pilot Plant

During the course of exploratory tests on electrolytic and electrothermic processes, it was found by the Bureau of Mines that fused magnesium chloride would dissolve appreciable quantities of magnesium oxide in the presence of small amounts of boric oxide (43). With the magnesium chloride saturated with boric oxide (0.03 per cent B_2O_3 at 750° C. and 0.17 per cent at 815° C.) the solubilities of magnesium oxide were reported as 1.7 per cent at 750° C. and 2.85 per cent at 815° C. (67). The use of this solution in an electrolytic cell employing a graphite anode and a steel cathode caused the deposition of magnesium at the cathode and the evolution of carbon oxides at the anode with only small amounts of chlorine. The original results were sufficiently encouraging so that further investigations were made on an enlarged scale (8,000 amp. pilot cell). In the large scale experiments it was found that the addition of boric oxide to the electrolyte resulted in dispersion of the magnesium in the cell with constantly decreasing current efficiency (43). Similar results have been reported by other investigators (65). It is now generally accepted that the boric oxide also acts as a dispersing agent on magnesium oxide in the magnesium chloride melts and that the reported solubilities of 1.7 to 2.85 per cent do not represent true solubilities but suspensions of magnesium oxide in the melt (70). However, it was found that up to 0.5 per cent of magnesium oxide is soluble in magnesium chloride melts containing no boric oxide and development work was continued (43). Approximately four years of work were directed toward this project during the period of

1941 to 1945. The 8,000 ampere pilot cell operation was characterized by sludge formation and subsequent loss of current efficiency (42, 43). A 10,000 ampere cell was constructed; but it became necessary to discontinue the project in the interest of other more urgent work, and the cell was not operated but was stored at the Boulder City Station (11).

The starting electrolyte actually consisted of magnesium oxide, magnesium chloride, calcium chloride, potassium chloride, and sodium chloride in varied proportions. The additives were necessary to adjust the conductivity, density, and viscosity of the melt (43).

It has been reported that magnesium oxide has a stabilizing effect on magnesium emulsions that sometimes form in melts of magnesium chloride, potassium chloride, and carnallites ($MgCl_2 \cdot KCl$) (40). This effect possibly could be a reason why the work at the Bureau met with such little success, although the basic difficulty of the process was the low solubility of the magnesium oxide in the electrolyte (44).

Several patents have been issued on the electrolysis of magnesium oxide in magnesium chloride melts over the period of 1936 to 1939--three in Britain and two in Japan (36, 37, 43, 72, 76).

2. Chlorination of Magnesium Oxide Within the Electrolytic Cell

It is generally accepted that magnesium oxide is not directly separated by electrolysis in molten baths of magnesium chloride, magnesium fluoride, or other halide salts within which the magnesium oxide is only slightly soluble. But that the magnesium chloride, for example, is separated into magnesium at the cathode and chlorine at the carbon anode. The chlorine reacts with the magnesium oxide and the carbon anode as follows:

$$Cl_2 + MgO + C = MgCl_2 + CO.$$

The magnesium chloride thus formed is electrolytically decomposed and the process is repeated (43).

It follows that the magnesium oxide and carbon must be in intimate contact at the anode for the chlorination reaction to occur. The following schemes have been proposed for accomplishing this:

(1) The Bureau of Mines tried suspensions of magnesium oxide and carbon in molten chlorides (10). In short tests with a magnesium chloride melt and a liquid lead cathode, covering a wide range of current density temperature and alloy composition, anodic and cathodic current efficiencies approaching 100 per cent were obtained and 95 to 99 per cent of the chlorine generated reacted with the suspended magnesium oxide and carbon to form magnesium chloride and carbon oxides. In longer tests a sludge of magnesium oxide mixed with graphite formed on the surface of the lead cathode. Molten aluminum cathodes gave similar results.

(2) A Japanese patent describes a means of forming an anode of magnesium oxide, graphite, pitch, and tar. The electrolyte containing magnesium chloride and potassium chloride is electrolyzed with this anode and a carbon cathode to give magnesium on the carbon cathode. The chlorine evolved at the anode reacts with the magnesium oxide of the anode to form magnesium chloride and the concentration of magnesium chloride in the electrolyte remains

unchanged during the electrolysis (19, 20). A disadvantage of this method is the considerable increase in the ohmic resistance of the anode (50).

(3) A similar method is used in the Japanese Suzuki cell. This cell has a cylindrical compartment surrounding the anode which is made of refractory material through which the magnesium chloride melt can percolate. The compartment forms a hopper into which the magnesium oxide-carbon mixture is fed. The mixture is heated by the fused electrolyte and converted to magnesium chloride by a current of hot gaseous chlorine which is liberated at the anode (50, 71). As in the above mentioned method, there is considerable increase in the ohmic resistance of the anode (50). A French patent proposes a similar cell arrangement in a bath of molten fluorides (49).

3. Solubility and Electrolysis of Magnesium Oxide in Various Molten Solvents

Others have investigated the solubility of magnesium oxide in various melts. Most of these investigations were directed toward finding a solvent suitable for a cell bath in which magnesium oxide could be reduced electrolytically. Many of the published solubility values were not in agreement. A discussion of these investigations in chronological order follows:

1908--Beck reported the solubility of magnesium oxide in a melt of 40 per cent sodium fluoride and 60 per cent potassium fluoride to be 11.4 per cent at 677° C. (7, 66). In 1943 the Bureau of Mines attempted to repeat Beck's work and found a solubility of only 0.5 per cent (66).

1925--Ruff and Busch reported that the solubility of magnesium oxide in lithium fluoride-calcium fluoride-magnesium fluoride melts is small over a large temperature range (62). However, they reported that good yields of magnesium were obtained at 725 to 775° C. with a current density of 1,000 amp./sq. dm.

1925--Ilínskii and Antipine on the basis of cooling curve studies reported that the solubility of magnesium oxide exceeded 10 per cent at 753° C. or above in an eutectic melt of 53 per cent magnesium fluoride and 47 per cent lithium fluoride. They also found that magnesium could be electrolyzed from the melt (66). When the Bureau of Mines checked this work in 1943, they found a solubility of only 0.4 per cent (66).

1927--Grube worked out the phase diagram for the magnesium fluoride-barium fluoride-sodium fluoride system (28). He found three ternary eutectics and two compounds--$BaF_2 \cdot MgF_2$ and $NaF \cdot MgF_2$. The composition of the lowest melting eutectic was 32 per cent sodium fluoride, 18 per cent magnesium fluoride, and 50 per cent barium fluoride, and it melted at

750° C. He reported the solubility of magnesium oxide in the melts to be approximately 1 per cent at temperatures just above the melting point. He found the metal deposited by electrolysis to consist of a mixture of sodium and magnesium, or magnesium alone, depending on the composition of the melt (28, 66).

1930--Grube and Henne worked out the phase diagram for mixtures of sodium fluoride, magnesium fluoride, and calcium fluoride (29). Eutectics were found at 740° C. containing 50 per cent sodium fluoride, 30 per cent calcium fluoride, and 20 per cent sodium fluoride, and at 894° C. containing 19 per cent sodium fluoride, 41 per cent calcium fluoride, and 40 per cent magnesium fluoride. A melt containing 40 per cent of the latter eutectic with 60 per cent barium fluoride was electrolyzed at 765° C. with addition of 3 per cent magnesium oxide at a current density of 450 amp./sq. dm. and gave 54.5 per cent current yield of magnesium and 10.1 per cent of sodium. Another mixture containing 36 per cent magnesium fluoride, 8 per cent sodium fluoride, and 56 per cent barium fluoride, to which was added 5 per cent magnesium oxide, was electrolyzed at 850° C. with a current density of 150 to 300 amp./sq. dm. to yield a 98 to 99 per cent pure magnesium metal (29). The amount of magnesium oxide added to the electrolyte probably did not represent the solubility of the magnesium oxide.

1935--Solubility of magnesium oxide in systems of barium fluoride-magnesium fluoride-sodium fluoride and calcium fluoride-magnesium fluoride-sodium fluoride were investigated by Povlov and Ovanova (55). They found that the solubility does not exceed 0.2 per cent. Electrolysis of magnesium from these solutions was difficult because of frequent occurrence of the anode effect (high voltage) (55, 56).

1941--Berent and co-workers conducted experiments which indicated that fused cryolite (Na_3AlF_6) dissolved 10 to 12 per cent magnesium oxide (8). Others have reported similar solubilities in cryolite (33). Berent's work showed that the addition of magnesium fluoride decreases the solubility of magnesium oxide in the cryolite. At 5 per cent magnesium oxide and 13 per cent magnesium fluoride the melting point of the ternary system was 902° C. The system of 8 per cent magnesium oxide and 3 per cent magnesium fluoride had the lowest melting point of 890° C. (8). In electrolysis experiments to determine the decomposition potential of magnesium oxide in molten cryolite, Mergaut, in 1955, found that only aluminum was deposited on the cathode (46). Others have recently investigated the physical state of magnesium oxide in molten cryolite-magnesium oxide systems and found that the magnesium oxide was ionized in the melt (60, 61).

1943--In connection with the pilot plant work on a process in which magnesium oxide was converted to the metal in a molten chloride bath (43), the Bureau of Mines performed a series of solubility studies on the system of magnesium chloride-magnesium oxide-boric oxide and on the systems of magnesium oxide in alkali and alkaline earth fluorides and chlorides (66, 67). The results of this work are summarized in Table IV.

The experimental procedure used was essentially as follows: weighed amounts of materials, totaling about 45 grams, together with 20 grams of lead-magnesium alloy, were sealed into steel bombs. Several bombs were placed in a cylindrical steel chamber and covered with a lead-magnesium alloy containing about 3 per cent magnesium. The chamber was sealed tightly by welding a steel cover to the top. After being rotated for one hour at the temperature at which the solubility was to be determined, the chamber was permitted to stand in an upright position for at least 35 hours at the desired temperature. At the end of this time it was withdrawn from the furnace and cooled rapidly, the bombs were removed, and samples were taken for analysis. The samples were analyzed by various wet laboratory methods

TABLE IV (66, 67)

Solubility of Magnesium Oxide in Alkali and Alkaline Earth Fluorides and Chlorides at 870° C.

No.	Composition of Solvent--Weight Per Cent													Solubility MgO Per Cent
	$MgCl_2$	KCl	NaCl	$CaCl_2$	$BaCl_2$	LiCl	MgF_2	KF	NaF	CaF_2	LiF	BaF_2	B_2O_3	
(1)								26.2	73.8					0.65
(2)								48.9	51.1					0.50
(3)								51.1	48.9					0.40
(4)								60.0	40.0					0.50
(5)								73.4	26.6					0.75
(6)								74.8	25.2					0.35
(7)			7.6					43.5	48.9					0.45
(8)			7.6					48.9	43.5					0.40
(9)								13.6			86.4			0.15
(10)							55.0				45.0			0.30
(11)							53.0				47.0			0.40
(12)							35.0				65.0			0.15
(13)							45.0		55.0					0.25
(14)							45.0		55.0					0.35
(15)							45.0		55.0					0.75
(16)							40.0	60.0						0.75
(17)	30.0						70.0							0.50
(18)	30.0						70.0							0.50
(19)	10.5						36.8				52.7			0.20
(20)	10.5						52.7				36.8			0.25
(21)	20.0						60.0				20.0			0.25
(22)	26.9						62.6				10.5			0.20
(23)	21.9						65.6				12.5			0.30
(24)	10.5						68.4				21.1			0.55
(25)	23.7						71.3				5.0			0.80
(26)	15.8						73.7				10.5			0.40
(27)	7.6						43.5	16.3			32.6			0.90
(28)	10.5						68.5		21.0					0.35

TABLE IV (Continued)

	Composition of Solvent--Weight Per Cent													Solubility MgO
No.	$MgCl_2$	KCl	NaCl	$CaCl_2$	$BaCl_2$	LiCl	MgF_2	KF	NaF	CaF_2	LiF	BaF_2	B_2O_3	Per Cent
(29)	7.6						43.5		16.3		32.6			0.80
(30)	26.8						62.6			10.5				0.40
(31)	15.8						73.7			10.5				0.30
(32)	10.5						36.9					52.6		0.35
(33)	100.0													0.60
(34)				100.0										0.096
(35)	31.6			68.4										0.17
(36)	58.0			42.0										0.37
(37)	31.6				68.4									0.20
(38)	58.0				42.0									0.36
(39)		100.0												0.11
(40)	31.6	68.4												0.080
(41)						100.0								0.090
(42)	31.6					68.4								0.19
(43)	58.0					42.0								0.29
(44)			100.0											0.096
(45)	31.6		68.4											0.14
(46)	99.6												0.4	0.92
(47)	99.4												0.6	1.25
(48)	99.2												0.8	1.60
(49)	99.0												1.0	1.94
(50)	98.6												1.4	2.60
(51)	98.0												2.0	3.63
(52)	97.7												2.3	4.14
(53)	78.4		21.1										0.5	0.84*
(54)	57.4		42.1										0.5	0.50*
(55)	78.3			21.1									0.6	0.52*
(56)	57.3			42.1									0.6	0.52*

* At 815° C. instead of 870° C.

which were developed at the Bureau for these specific studies (67).

It will be noted from Table IV that the only solubilities of any magnitude are those of magnesium oxide in chloride melts containing boric oxide. As was discussed earlier these are probably not true solubilities but suspensions of magnesium oxide in the melt due to the dispersing action of the boric oxide (70). Also, there is some question as to whether the Bureau's method of rapidly cooling the melt prevented loss of some magnesium oxide from solution (42, 70). It is of interest to note the inconsistency in the magnesium oxide solubility values for Solvent Nos. 13, 14 and 15 in Table IV.

1948--Lux studied the system of magnesium sulphate-magnesium oxide-eutectic (Na_2SO_4 - K_2SO_4) at 950° C. (44). The solubility of magnesium oxide was 0.0066 mole per cent (44).

1949--Bauxitbanya was issued a Hungarian patent on a process for the electrolytic separation of magnesium oxide in salt mixtures containing 30 to 70 per cent sodium chloride, 30 to 70 per cent calcium chloride, 1 to 5 per cent ammonium chloride, and 2 to 10 per cent ammonium fluoride (5). The patent states that the temperature of the molten material should be 450 to 650° C. if solid magnesium is to be deposited on the cathode. For liquid deposition it should be between 650 and 700° C. A melt containing 45 per cent sodium chloride, 45 per cent calcium chloride, 7 per cent magnesium oxide, 2 per cent magnesium chloride, and 1 per cent ammonium fluoride was electrolyzed at an anode current density of 1.25 amp./sq. cm., 0.4 amp., and 7 volts. The product contained 96.93 per cent magnesium, 2.50 per cent sodium, and 0.57 per cent other ingredients. Likewise, a melt containing 43.5 per cent sodium chloride, 43.5 per cent calcium chloride, 3 per cent ammonium fluoride, and 10 per cent magnesium oxide was electrolyzed as above, and the product contained 98.1 per cent magnesium (5).

CHAPTER III

SOLUBILITY OF MAGNESIUM OXIDE IN MOLTEN SALTS

Because of the relatively low decomposition potential and the relative ease with which magnesium oxide can be produced from raw materials, the direct electrolysis of magnesium oxide in molten salts would appear to offer attractive possibilities, provided a satisfactory melt could be found in which magnesium oxide is appreciably soluble. Comparatively little information has been published on the solubility of magnesium oxide in molten salts. Accordingly, experiments were conducted to determine approximately the solubility of magnesium oxide in a variety of salt melts.

A. Apparatus and Method

In order to investigate a large number of solvents it was desirable to develop a method of determining magnesium oxide solubilities that would not vary with each solvent. The Aluminum Laboratories Limited developed a method for determining the liquidus curves for the binary system cryolite-alumina (53) which could be adapted to magnesium oxide systems. The method consisted of directing a beam of light through a clear melt of known cryolite-alumina composition and, as the melt cooled, observing with a telescope the first appearance of crystals. This method with modifications was used for the magnesium oxide solubility determinations.

1. Description of Apparatus

The molten solvent was contained in a 10 per cent rhodium-platinum crucible, which fitted inside a type 84 Multiple Unit, Hevi Duty electric furnace. See Figures 1 and 2 and Plate I. Dimensions of the furnace chamber were 3 in. i.d. by 3-1/2 in. deep. The crucible dimensions were 2-3/8 in. o.d. top, 2 in. o.d. bottom, and 2-1/2 in. deep. The crucible was supported in the furnace by a silica triangle formed by three 1/4 in. o.d. by 2 in. silica rods. The platinum, 10 per cent rhodium-platinum thermocouple was in a 1/4 in. protection tube, also of 10 per cent rhodium-platinum, because of its greater rigidity. The light beam from a type 42-44-85, Bausch and Lomb arc lamp was directed into the molten solvent, and the melt was observed through an Eberbach telescope with a magnification of 20 diameters.

The apparatus also included a variable speed stirring motor, a Model 141P, 0-1000° C., Wheelco pyrometer with automatic cold junction compensator that was calibrated for use with the above thermocouple, and a steel reflector for directing the light beam from the arc lamp into the furnace.

2. Method

A 100 gram sample of solvent was prepared and heated in the platinum crucible to a temperature at which a clear melt was obtained. Then the liquidus temperature of the solvent was determined by slowly cooling the melt while observing through the telescope the appearance of crystals. The temperature at which the first crystals began to form was recorded as the liquidus temperature of the solvent. Supersaturation was minimized by seeding the cooling melt with a few particles of

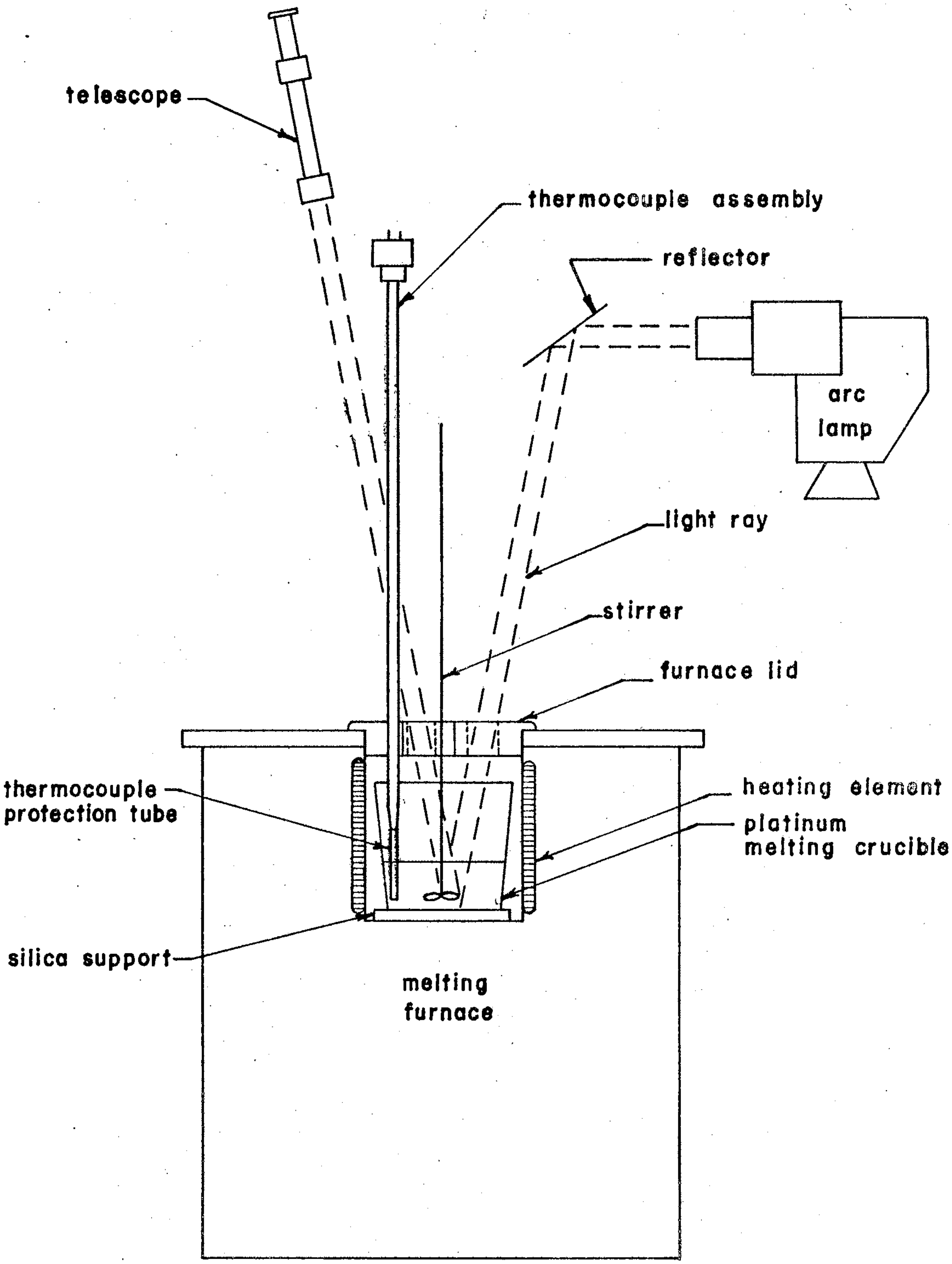
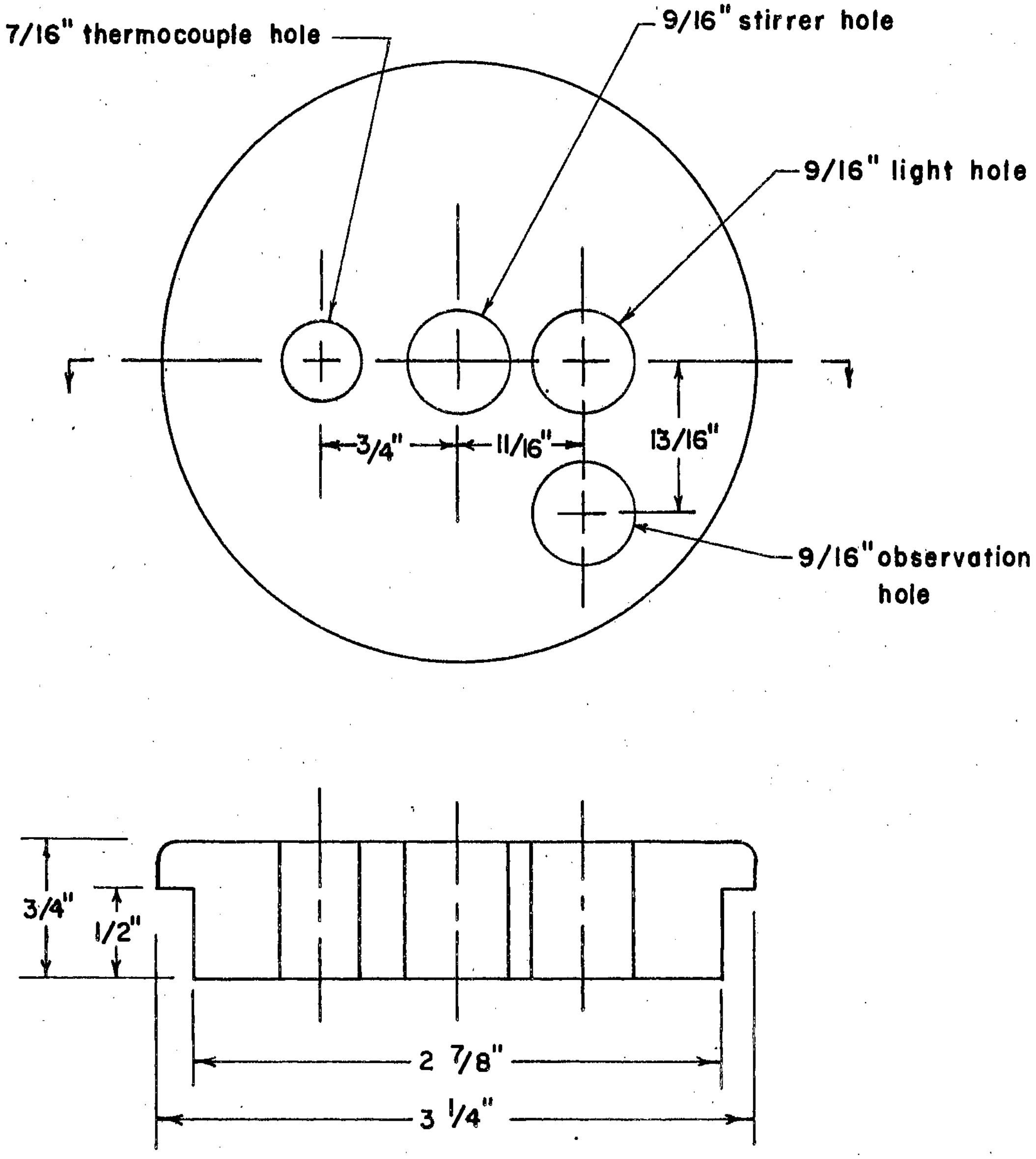


Figure 1

Solubility Apparatus



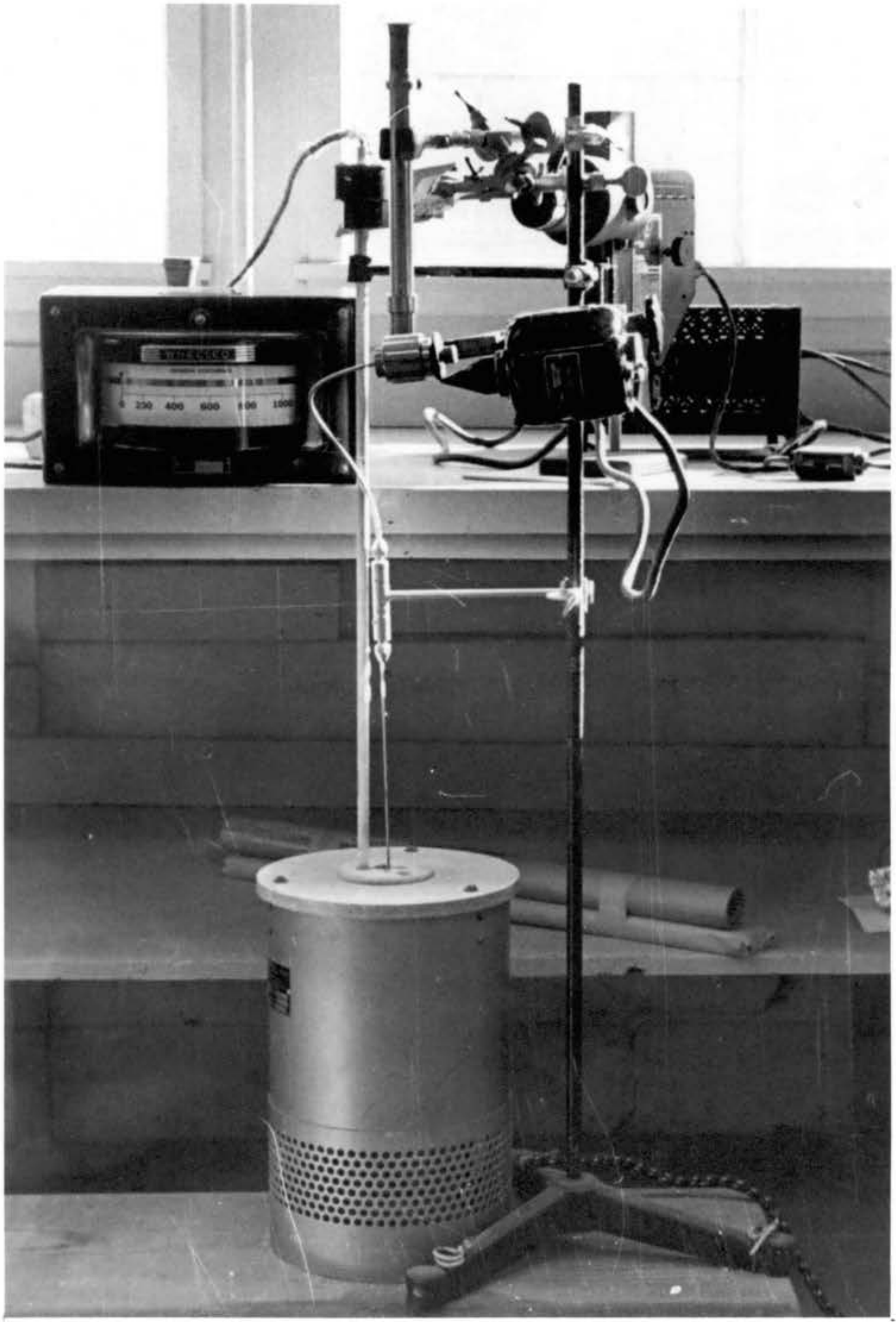
Scale — full
Material — transirte

Figure 2

Furnace Lid

Plate I

Solubility Apparatus



magnesium oxide. The melt was stirred gently and continuously during the liquidus determination.

A small amount of magnesium oxide from a weighed portion was added to the solvent. The temperature of the melt was increased until the melt was again clear. Then the melt was slowly cooled and the liquidus temperature of the system was determined in the same manner as the liquidus temperature of the solvent was determined. Again supersaturation was minimized by seeding with a few particles of magnesium oxide. The liquidus temperature and the magnesium oxide content of the system were recorded. Additional magnesium oxide was added and again the liquidus temperature determined. Thus by repeating this procedure for each magnesium oxide addition a temperature-magnesium oxide solubility relationship was obtained for the desired temperature range. This range included the approximate temperatures from the liquidus temperature of the solvent to the temperature at which fuming occurred. All liquidus temperatures were established by duplicate determinations.

The thermocouple was initially calibrated and regularly checked at the freezing point of reagent-grade sodium chloride which was taken to be 801° C. Reproducibility of the liquidus temperatures was within 5° C. The limit of error in the temperatures recorded was estimated to be 10° C.

With the exception of the cryolite the solvent constituents and magnesium oxide used in the solubility determinations were anhydrous reagent-grade chemicals. The cryolite was taken from selected natural lump and had the following analysis as determined by Aluminum Laboratories Limited (52):

Loss on ignition at 700° C.	0.13%
Fe	0.006%
Si	0.007%
Ca	0.01%
Mg	Not detected
Pb	0.01%
K	0.030%
Li	0.007%
Freezing point	1009° C. ± 1° C.

The accuracy of the solubility method and technique was checked by determining the solubility of aluminum oxide in cryolite. This system was chosen because the solubility of aluminum oxide in cryolite has been established at 10 wt. per cent at 963° C. (53). Using this method and technique, exact agreement with the published value was obtained.

B. Results

The results of the solubility study are summarized in Tables V and VI and in Figures 3 and 4.

In Table V the solubility of magnesium oxide is often recorded as a maximum value. As an example, the solubility of magnesium oxide in the first listed solvent is recorded as "<0.05." This is to be interpreted to mean that the solubility lies between 0 and 0.05 wt. per cent. More accurate determinations were not necessary for the purposes of this study because these solubilities were negligible. Any solvent dissolving less than 0.5 per cent magnesium oxide would not make a suitable electrolytic bath (see Chapter II, Review of the Literature).

It was found that magnesium oxide is appreciably soluble in molten mixtures of cryolite and sodium chloride. As a means of finding the optimum cryolite content, the solubilities of magnesium oxide in binary mixtures of cryolite and sodium chloride were determined as functions of composition and temperature. The solubilities are tabulated in

TABLE V

Solubility of Magnesium Oxide in Various Solvents

	Composition of Solvent	Wt. %	Liquidus Temp. of MgO Free Solvent °C.	MgO Solubility Wt. %	Temp. at which MgO Solubility Was Determined °C.
(1)	BaF	50.0	750	<0.05	940
	NaF	32.0			
	MgF_2	18.0			
(2)	BaF	60.0	Solvent not completely miscible @ 970° C.		
	CaF_2	16.4			
	MgF_2	16.0			
	NaF	7.6			
(3)	$CaCl_2$	100.0	772	0.05	870
(4)	$CaCl_2$	99.0	772*	<0.18	870
	B_2O_3	1.0			
(5)	$CaCl_2$	59.8	845	<0.05	870
	KCl	40.2			
(6)	$CaCl_2$	59.7	845*	<0.05	870
	KCl	40.1			
	B_2O_3	0.2			
(7)	$CaCl_2$	59.6	845*	<0.05	870
	KCl	40.1		0.10	920
	B_2O_3	0.2			
	NH_4BF_4	0.1**			
(8)	$CaCl_2$	79.7	603	0.10	853
	LiCl	20.3			
(9)	$CaCl_2$	60.0	499	<0.10	850
	LiCl	40.0			
(10)	$CaCl_2$	59.95	499*	0.10	850
	LiCl	39.95			
	NH_4BF_4	0.10**			
(11)	$CaCl_2$	59.9	499*	<0.20	850
	LiCl	39.9			
	NH_4BF_4	0.2**			

TABLE V (Continued)

Composition of Solvent		Wt. %	Liquidus Temp. of MgO Free Solvent °C.	MgO Solubility Wt. %	Temp. at which MgO Solubility Was Determined °C.
(12)	Cryolite	60.0	882	3.16	920
	NaF	40.0		4.20	962
(13)	KF	100.0	880*	<0.04	890
(14)	KF	99.9	880*	<0.04	890
	KBF_4	0.1			
(15)	KF	60.0	768	0.1-0.2	870
	NaF	40.0			
(16)	KF	67.4	740*	<0.1	870
	NaF	32.6			
(17)	KF	74.1	740	0.1	870
	NaF	25.9			
(18)	KCl	100.0	774	<0.05	900
(19)	KCl	56.0	372	<0.05	678
	LiCl	44.0			
(20)	KBr	100.0	730	<0.05	890
(21)	LiCl	100.0	615	<0.05	688
(22)	LiCl	66.5	563	<0.05	718
	NaCl	33.5			
(23)	MgF_2	70.2	655	2.0	708
	$NaPO_3$	29.8		3.9	795
				4.8	880
(24)	MgF_2	53.0	Solvent not completely miscible @ 970° C.		
	LiF	47.0			
(25)	$MgCl_2$	100.0	Hydrolyzed with moisture in the atmosphere and resulting MgO was not miscible.		
(26)	NaF	69.6	960*	<0.05	975
	MgF_2	30.4			

TABLE V (Continued)

	Composition of Solvent	Wt. %	Liquidus Temp. of MgO Free Solvent °C.	MgO Solubility Wt. %	Temp. at which MgO Solubility Was Determined °C.
(27)	NaF CaF_2	52.3 47.7	830	0.05	935
(28)	NaCl	100.0	801	<0.05	900
(29)	NaCl Cryolite			See Table VI	
(30)	NaCl $CaCl_2$ NH_4F	48.3 48.3 3.4***	670*	<0.05	890
(31)	NaBr	100.0	745	0.04	780
(32)	$SrCl_2$	100.0	870	<0.05	900

* Approximate liquidus temperature.

** Fuming was noted which was probably due to the decomposition of NH_4BF_4.

*** Loss of some NH_4F as the mixture was melted.

TABLE VI

Solubility of Magnesium Oxide in Mixtures of Cryolite and Sodium Chloride

Cryolite Wt. %	NaCl Wt. %	MgO Added to Mixture Wt. %	Liquidus Temp. of Mixture °C.
80.0	20.0	0	920
		2.94	920
		3.40	910
		3.85	910
		4.30	925
		4.77	935
		5.20	960
70.0	30.0	0	880
		2.37	838
		2.94	830
		4.00	920
68.5	31.5	0	740
		0.52	790
		1.05	835
60.0	40.0	0	848
		2.56	820
		3.15	880
50.0	50.0	0	802
		0.94	795
		1.25	790
		1.95	810
		2.55	870

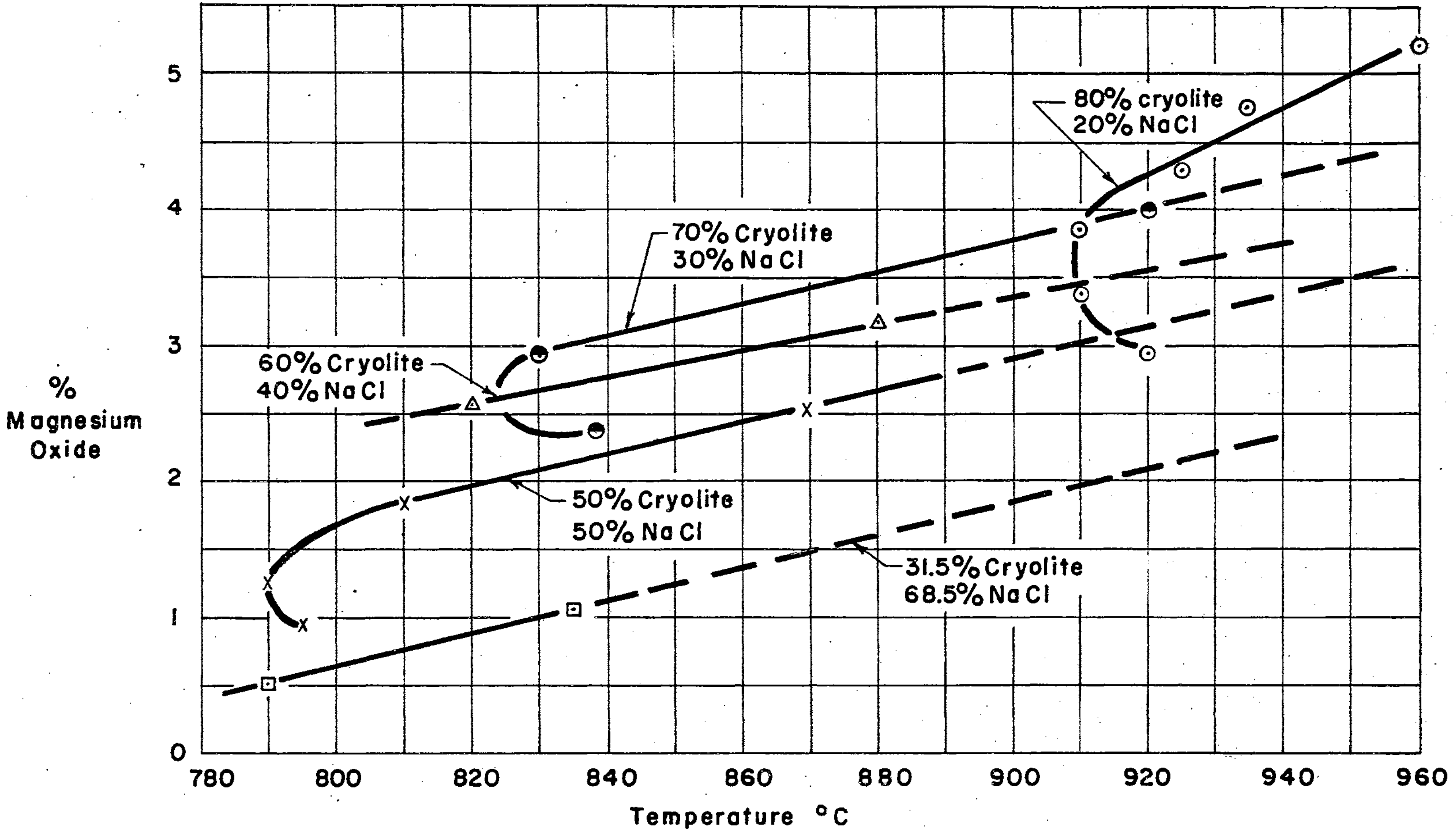


Figure 3

Solubility of Magnesium Oxide in Mixtures of Sodium Chloride and Cryolite
as a Function of Temperature

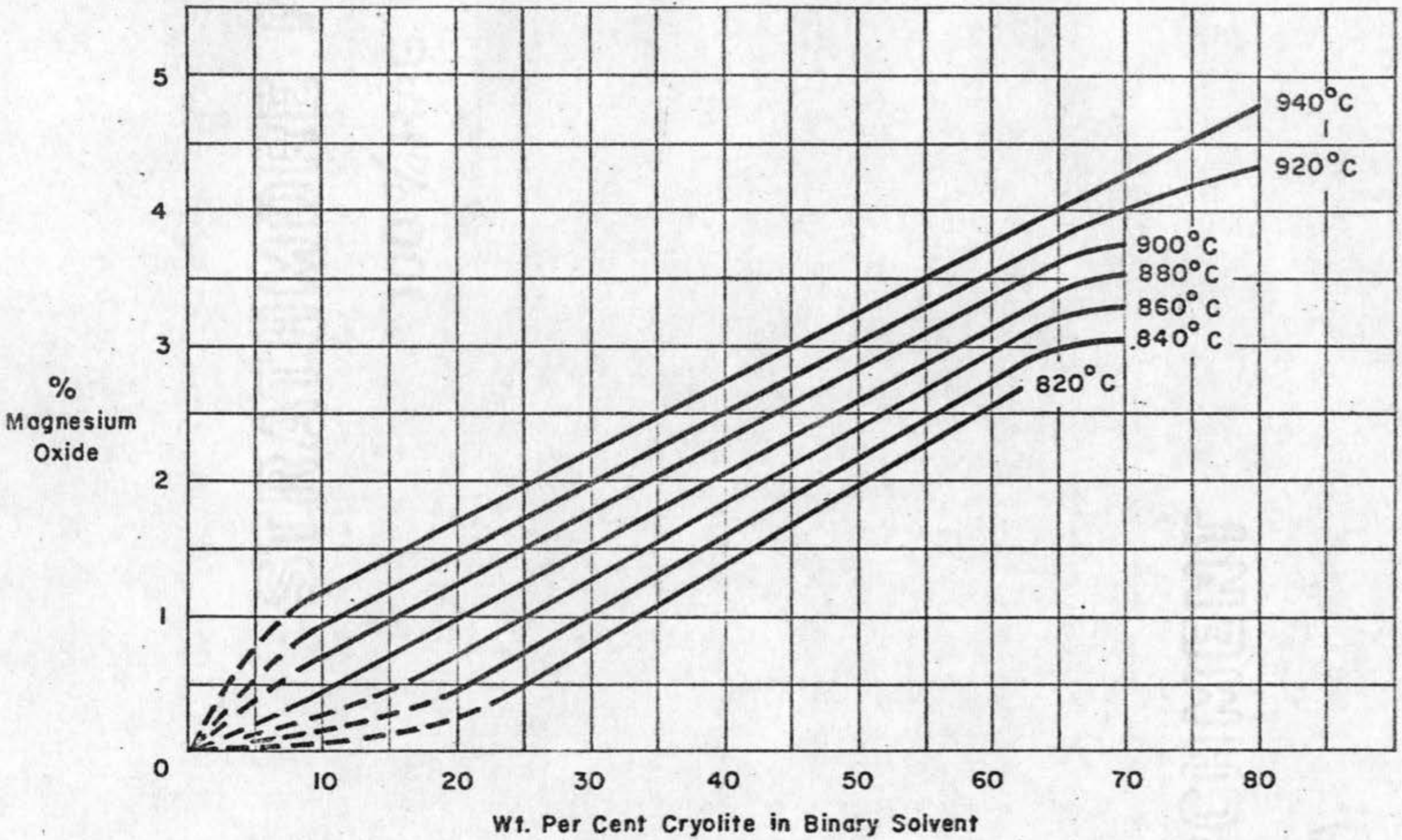


Figure 4

Solubility of Magnesium Oxide in Mixtures of Sodium Chloride and Cryolite as a Function of Composition

Table VI. The tabulated values are plotted in Figures 3 and 4. In Figure 3 liquidus curves are plotted for five cryolite-sodium chloride-magnesium oxide mixtures. The first addition of magnesium oxide lowers the liquidus temperature of the system. Specifically, for the 50 per cent cryolite-50 per cent sodium chloride mixture, the addition of 1.25 wt. per cent magnesium oxide lowers the liquidus temperature from 802° C. to 790° C. As the liquidus curve is drawn, this 790° C. is a minimum liquidus temperature. Upon further additions of magnesium oxide the liquidus temperature increases. Figure 4 is a cross plot of the portions of the curves for which the liquidus temperature increases with increasing magnesium oxide content.

C. Discussion of Results

The high solubilities reported by Beck (7, 66), and Grube (28), and Bauxitbánya (5) were not found in this study. Beck reported the solubility of magnesium oxide in a melt of 60 per cent potassium fluoride and 40 per cent sodium fluoride to be 11.4 per cent at 677° C. The Bureau of Mines found a solubility of only 0.5 per cent at 870° C. (66). This study shows a maximum of 0.2 per cent at 870° C. (Solvent No. 15, Table V). Grube reported the solubility of magnesium oxide in a melt of 50 per cent barium fluoride, 32 per cent sodium fluoride, and 18 per cent magnesium fluoride to be 1 per cent at approximately 750° C. From this study a solubility of less than 0.05 per cent is indicated (Solvent No. 1, Table V). Bauxitbánya reported the solubility of magnesium oxide in a melt of 48.3 per cent sodium chloride, 48.3 per cent calcium chloride, and 3.4 per cent ammonium fluoride to be 10 per cent. A maximum solubility of 0.05 per cent at 890° C. was found using the visual solubility method (Solvent No. 30, Table V).

Beck determined the solubility of magnesium oxide in the fluoride melt by use of blind cell liquidus determinations (7). The blind cell liquidus determinations rely upon the precipitation of relatively large amounts of magnesium oxide at the liquidus temperature. The latent heat of this precipitation causes a point of inflection on the time-cooling temperature curve which is taken as the liquidus temperature. In many systems the precipitation is slight at the liquidus temperature and heavy precipitation does not occur until the temperature has dropped considerably below the visually observed liquidus temperature. This could account for the large difference between the value of 11.4 per cent at 677° C. reported by Beck and the value of 0.1 to 0.2 per cent at 870° C. found in this study.

The latter value is less but of the same order of magnitude as the value of 0.5 per cent at 870° C. reported by the Bureau of Mines. As was discussed earlier, the Bureau of Mines' value might have included some magnesium oxide in suspension which could account for the difference between the two values. Moreover, solubility values for magnesium oxide in other solvents investigated are in similar agreement with the Bureau of Mines' work.

Of the solvents investigated only those containing cryolite or sodium metaphosphate ($NaPO_3$) dissolved appreciable quantities of magnesium oxide. The others show little or no promise as solvents. A 60 per cent cryolite-40 per cent sodium chloride melt dissolves 3.15 per cent magnesium oxide at 880° C. The 60 per cent cryolite-40 per cent sodium fluoride melt dissolves 4.2 per cent magnesium oxide at 962° C.

A sodium metaphosphate-magnesium fluoride melt dissolves 4.8 per cent magnesium oxide at 880° C. The maximum solubility in any of the remaining solvents is 0.2 per cent.

It was assumed in these solubility determinations that magnesium oxide precipitated at the liquidus temperature. In the event that some of the solvent constituents precipitated at the liquidus temperature, the reported magnesium oxide solubilities would be less than the actual values.

The limit of error in the liquidus temperature readings was estimated to be 10° C.

A possible source of error in the results would be compositional changes due to evaporation of the melt during the time period required to melt the solvent and to determine the magnesium oxide solubility. To minimize such error, the temperature of the system was held below the temperature at which fuming could be detected. Also, there could have been minor compositional changes in some of the melts due to reaction between constituents of the melt and the platinum crucible and/or the constituents of the atmosphere.

CHAPTER IV

REACTION OF METALLIC MAGNESIUM WITH SOLVENTS CONTAINING CRYOLITE OR SODIUM METAPHOSPHATE

In addition to dissolving magnesium oxide the electrolytic bath should be chemically inert to molten magnesium. Consequently experiments were conducted to determine if melts containing sodium metaphosphate and melts containing cryolite were reactive with molten magnesium.

A. Experimental Procedure

In these experiments 1/8 in. cubes of metallic magnesium were introduced into the molten solvents. The metal and solvent were kept molten for an 8-hour period before being solidified and cooled. Upon cooling, the solid mixture was crushed and visually examined.

B. Results

A molten mixture of 70.2 per cent magnesium fluoride and 29.8 per cent sodium metaphosphate reacted with the magnesium metal. An odor like that of phosphine resulted from this reaction. An examination of the contents of the melt indicated that all of the magnesium had reacted. No metallic magnesium remained.

The magnesium was relatively unaffected in melts containing cryolite and sodium chloride. No chemical change was observed. However, since magnesium and aluminum have similar appearances, it was possible that the metallic magnesium had reduced some of the aluminum fluoride from the cryolite to metallic aluminum. Consequently, a spot test was performed on the metal with a 0.5 per cent silver nitrate solution to determine whether the surface of the metal was aluminum or magnesium. The silver nitrate solution turned black on the surface of the metal, indicating that the metal was magnesium and not aluminum (58).

C. Discussion of Results

The cryolite-sodium chloride melts were non-reactive with magnesium and dissolved appreciable quantities of magnesium oxide. Thus these melts appeared attractive as electrolytic baths for the electrolysis of magnesium oxide.

The sodium metaphosphate melts dissolved appreciable quantities of magnesium oxide, but since the melts were found to be reactive with magnesium it would be unlikely that this melt could be electrolyzed to produce free magnesium metal. However, it is possible that electrolysis of magnesium oxide could be accomplished with the use of an inert molten cathode. This cathode would be chemically inert to both the electrolytic bath and the magnesium and it would dissolve the deposited metallic magnesium. The magnesium subsequently could be recovered from the cathode material by distillation or by electrolysis.

CHAPTER V

ELECTROLYSIS OF MAGNESIUM OXIDE

It was found that magnesium oxide is appreciably soluble in cryolite-sodium chloride and in cryolite-sodium fluoride melts. It was also found that cryolite is reasonably inert to molten magnesium at temperatures to 845° C. Sodium chloride and sodium fluoride are known to be chemically inert to molten magnesium (6, 27). Experiments were conducted to determine if magnesium oxide could be reduced electrolytically to the metal in these cryolite containing melts.

A. Electrolytic Cell and Auxiliary Equipment

1. Description of Equipment

Figures 5 and 6 show the two interior arrangements of the electrolytic cell used in the experiments. The cell consisted of a 4 in. i.d. by 6 in., No. 600101, Eclipse Fuel Engineering Company pressed steel pot. The cell held approximately 1,500 grams of the molten salts.

The pot served as the cathode in the initial cell. Figure 5 shows this arrangement. In this cell, referred to as cell A, a clay diaphragm was employed to separate the anode and cathode products. The diaphragm was in the shape of a hollow truncated cone. The interior of the cone formed the anode compartment. A transite cover supported the diaphragm in the cell. The diaphragm was manufactured by the Frankhoma Pottery Company, Sapulpa, Oklahoma, from clay with a high magnesium silicate

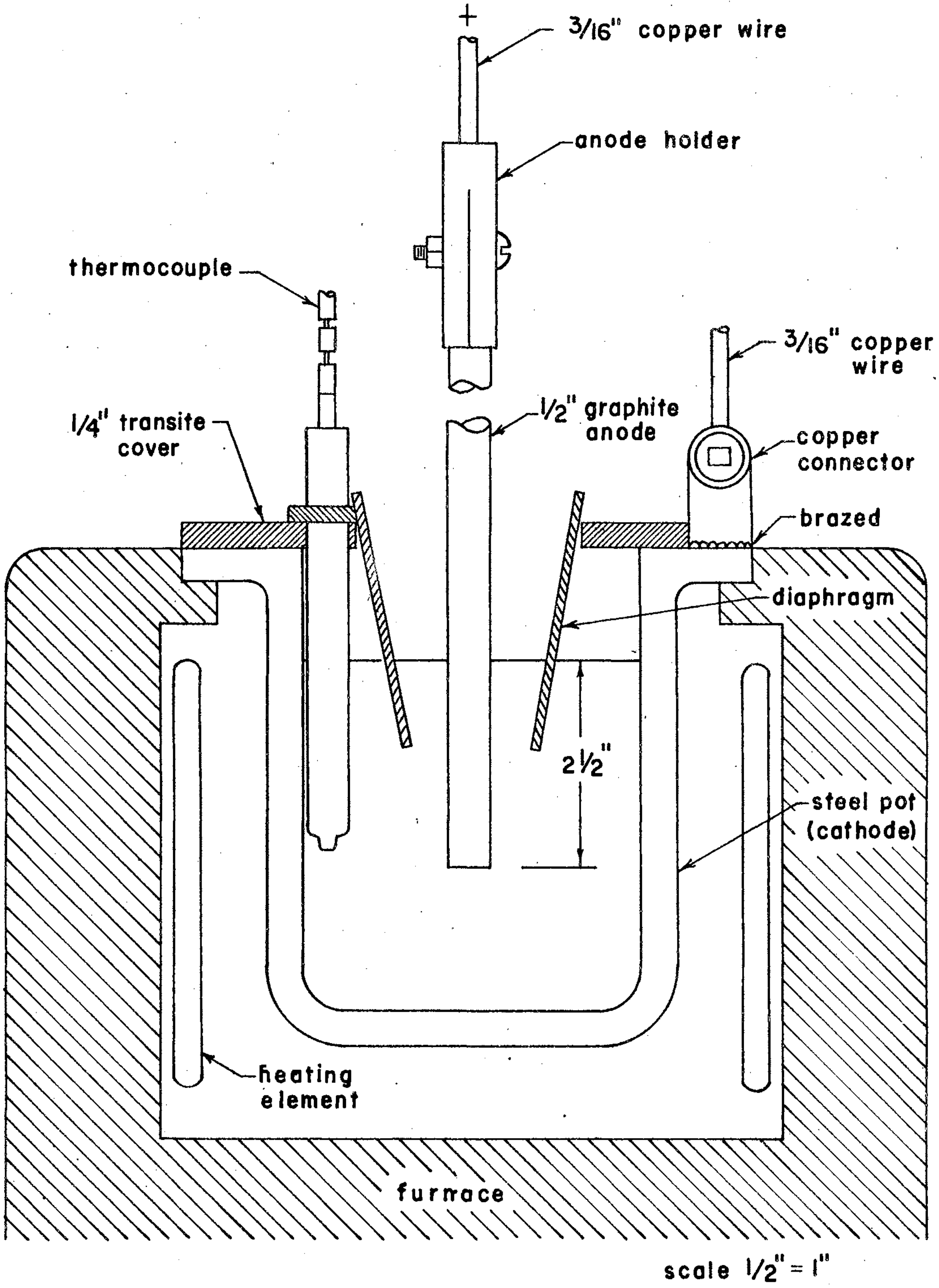


Figure 5
Electrolytic Cell A

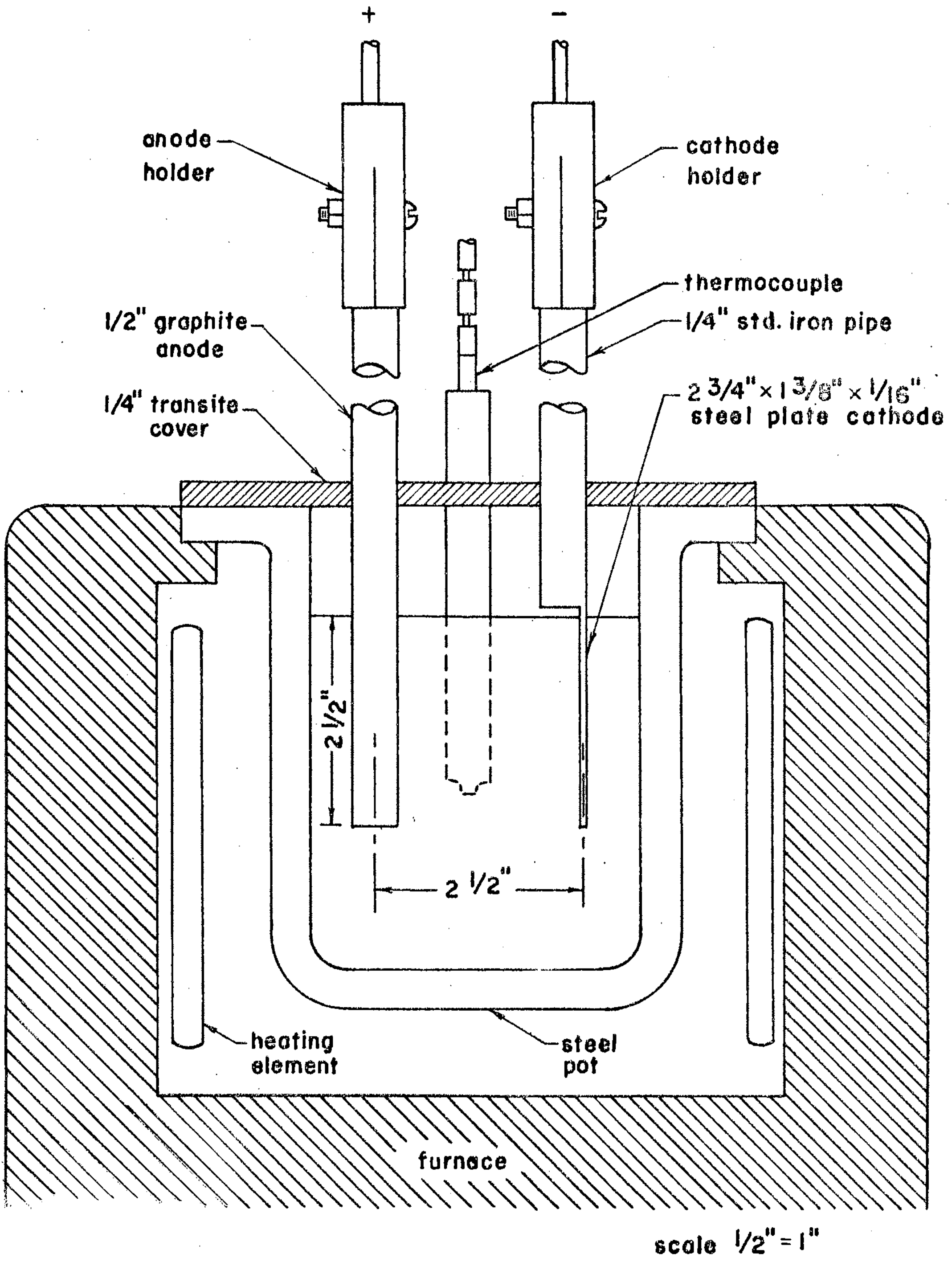


Figure 6

Electrolytic Cell B

content. A chromel-alumel thermocouple was suspended in the cell from the transite cell cover. This thermocouple was protected by a 1/2 in. o.d. iron sheath. The thermocouple was calibrated with a 0-2500° F., type MM-701 A, Claud S. Gorden Company pyrometer. The transite cover also served to thermally insulate the top of the cell and to exclude air from the cathode compartment.

Figure 6 shows the second cell arrangement that was used. In this cell, referred to as cell B, the cathode was an iron plate immerged in the cell bath. The same anode was used. However, the anode was not suspended in the center of this cell but to one side as shown in Figure 6. The clay diaphragm was not used. Otherwise, the cell construction was the same.

Power for electrolysis was supplied by means of a selenium oxide rectifier, style 8347, 0.97KVA, primary voltage 115, secondary voltage 19.5, Cathodic Equipment Company, Tulsa, Oklahoma. The control panel of this rectifier is shown in Plate II. The direct current output and corresponding voltage were read from meters built into the rectifier control panel.

Ventilation of the cell was provided by means of an exhaust fan set in a sheet iron duct (see Plate III).

The cell was electrically heated by a Lindberg CR-5 laboratory pot furnace. The furnace was supplied with a built-in transformer and relay, chromel-alumel thermocouple, and an automatic control. A Lindberg Model 292 automatic controlling pyrometer and temperature measuring system was used. The furnace and electrolytic cell assembly are shown in Plate III.

Plate II

Rectifier

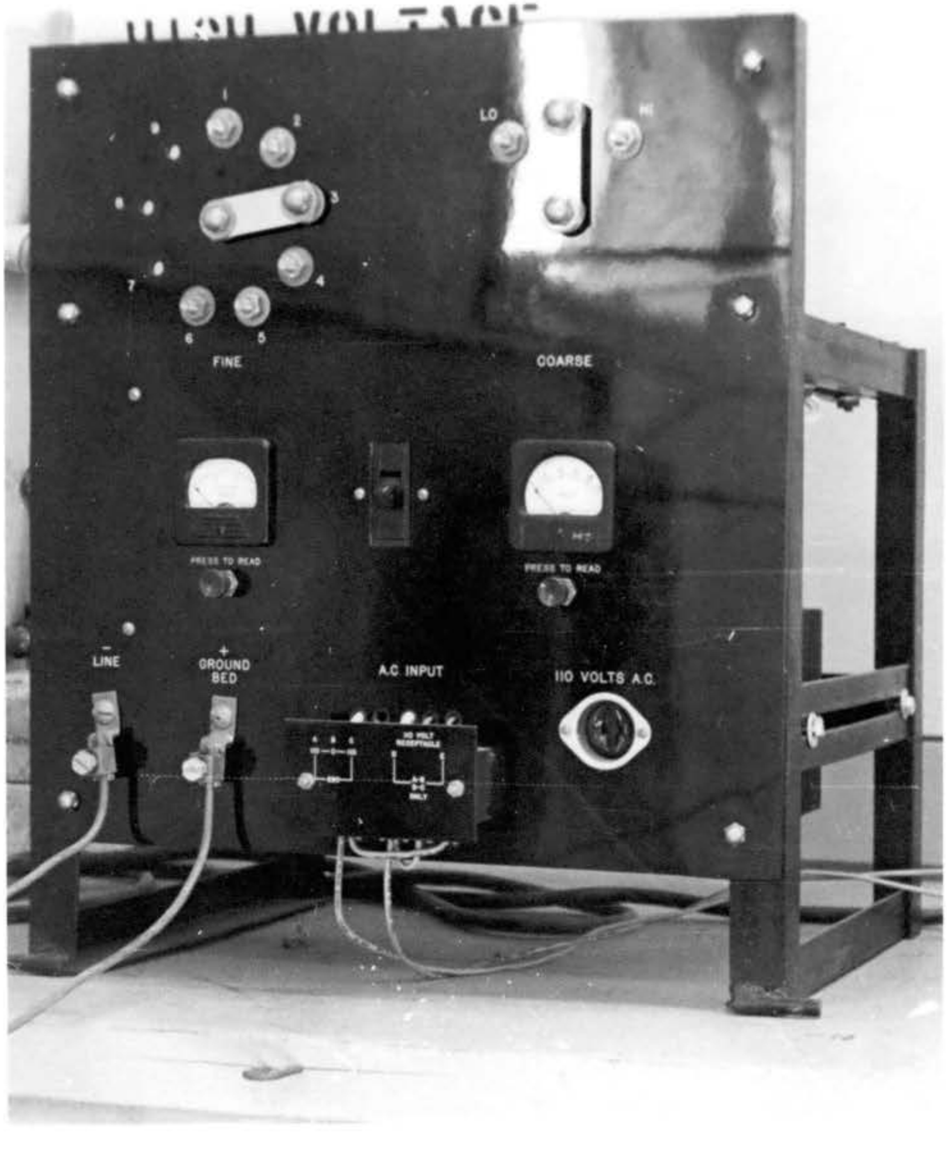


Plate III

Furnace and Electrolytic Cell Assembly

2. Preliminary Tests

The cell bath thermocouple was calibrated at the freezing point of reagent-grade sodium chloride. The thermocouple in the furnace setting was checked with the cell bath thermocouple. This was done by inserting the cell bath thermocouple adjacent to the furnace setting thermocouple in the hot furnace.

Using cell A, primary magnesium was produced from a cell bath of 25 per cent magnesium chloride, 15 per cent calcium chloride, and 60 per cent sodium chloride. The purpose of this test was to evaluate the operation of the cell and to gain experience in electrolytic cell operation. The Dow Chemical Company electrolyzes from a bath of this composition to commercially produce magnesium (27). The electrolysis was performed at 6 volts, 1300° F., and at an average anode current density of 6.4 amperes per sq. in. (25 total amperes). Chlorine gases were evolved at the anode and metallic magnesium formed around the periphery of the pot. This metal floated to the surface of the melt in the form of small spheres. Approximately 15 grams of magnesium were produced from this test.

B. Electrolysis of Mixtures of Cryolite and Sodium Chloride Containing Magnesium Oxide

1. Experimental Procedure

The 1,500 gram cell electrolyte was made up by weight from finely ground cryolite and sodium chloride. To this was added 50 grams of magnesium oxide. These three components were thoroughly mixed and placed in the cell. In the initial experiments a 60 per cent cryolite-40 per cent sodium chloride mixture was used because it exhibited the optimum characteristics of magnesium oxide solubility and liquidus temperature (see Figures 3 and 4). The mixture was melted and stirred vigorously for 5 to 10 minutes at approximately 1500° F. to insure that equilibrium conditions were approached. The anode and cathode were placed in position and the electrolysis was started. Oxides of carbon formed at the anode and metal deposited on the cathode. The cell voltage, cell current, furnace setting temperature, and cell bath temperature were recorded. Other factors, such as the distance between anode and cathode, and depth of anode and cathode immersion in the melt, were not varied during an experiment or from experiment to experiment.

With the exception of the cryolite, all chemicals used in the electrolysis experiments were reagent-grade. The cryolite was taken from selected natural lump that was obtained from the Pennsylvania Salt Company. The cryolite analysis is given in Chapter III.

2. Results

In the first experiment the steel pot was used as the cathode. The cell bath consisted of 60 per cent cryolite-40 per cent sodium chloride. The electrolysis was conducted at 5 to 6 volts, 18 to 37 amperes, and a cell bath temperature of 1500 to 1540° F. for six hours. During this period gas could be seen evolving at the carbon anode as well as around the periphery of the pot. The gas evolving around the periphery of the pot or cathode apparently was hydrogen from the electrolysis of the water content of the salts. Considerable necking down of the graphite anode was noted to have occurred below the surface of the melt. This was due to the reaction of the oxygen and carbon at the anode. The resulting carbon oxides came off as odorless gases. No halogens--that is, chlorine from the sodium chloride or fluorine from the cryolite--could be detected in the anode gases.

At various intervals in the experiment, the anode effect occurred. The anode effect was characterized by the formation of an insulating gas film between the anode and the molten electrolyte and a resultant large increase in cell resistance. The current passed through the film in many small arcs. Normal operation was restored by stirring the melt with a carbon rod. It is probable that the magnesium oxide content of the melt was reduced by electrolysis, thus causing the anode effect. By stirring in additional magnesium oxide which had gravitated to the bottom of the cell, the amount of magnesium oxide in solution was increased and the anode effect eliminated. An excess of solid magnesium oxide was maintained in the cell at all times.

At the conclusion of the electrolysis, the cell was removed from the furnace setting for cooling. As soon as the contents of the cell were solidified and cooled, they were removed from the cell with a hammer and cold chisel. The purpose of this crude procedure was to locate the position of any metal that had been produced by the electrolysis. Upon examining the contents of the solidified melt, small metallic particles were noted. Larger quantities of the metal were deposited around the periphery or walls of the pot. This metal was deposited in thickness of approximately 1/32 in. and covered the wall of the pot below the melt.

Qualitative spectrographic analysis of the metal indicated that the metal consisted of magnesium, aluminum, and iron. The spectral lines of sodium were not observed. A wet analysis of the metal using a gravimetric method indicated a magnesium content of 10.1 per cent with the remainder being mostly aluminum (see Appendix for analytic procedure). The conditions of this experiment are shown in Table VII, experiment No. 1.

A second experiment was conducted at a lower voltage and temperature. Samples of the metal produced in this experiment were removed from the pot periphery and analyzed by two chemistry students under the direction of Dr. S. R. Wood of the Oklahoma State University Chemistry Department. The two independent values obtained for the magnesium content were 5.96 and 5.75 per cent. The 5.85 per cent listed in Table VII is an average of these reported values.

Similar electrolysis experiments were subsequently performed at various conditions of temperature, cell bath composition, cathode composition, anode current density, and voltage in an attempt to increase the magnesium content of the metal deposited on the cathode. In these experiments an iron plate or graphite rod was used as a cathode. It was found that by using an iron plate as the cathode and thereby increasing the current density, the metal was deposited on the cathode in larger droplets. The cathode could be removed from the melt at intervals and the metal droplets scraped from the cathode while the metal was still molten. It was not necessary to solidify and cool the cell bath to examine the cathode as before, using the iron pot as the cathode. The results and conditions of these experiments are also shown in Table VII.

Experiments Nos. 3, 4, 5, and 6 were performed in consecutive order without changing the cell bath. Experiments Nos. 3, 4, and 5 were to evaluate the effects of voltage on the magnesium content of the deposited metal. The purpose of experiment No. 6 was to evaluate the effects of decreasing the aluminum ion content of the melt. Experiment Nos. 7

TABLE VII

Electrolysis of Mixtures of Cryolite and Sodium Chloride Containing Magnesium Oxide

Expt. No.	Cell Bath Composition	Cell Temp. °F.	Cell Voltage Volts	Cell Current Amperes	Duration of Experiment Hours	Average Anode Current Density Amp./sq.in.	Cathode Material	Per Cent Magnesium in Aluminum Base Alloy
1	60% Cryolite-40% NaCl	1500-1540	5.0-6.0	18-37	9	7.2	Steel Pot 0.05-0.15% C	10.1**
2	" "	1460-1510	4.5-5.0	13-24	3	4.6	"	5.85**
3	" "	1450-1525	4.75	12.5-15	3.5	4.3	Steel Plate 0.05-0.15% C	2.4*
4	" "	1525-1540	6.0-6.2	24-28	2	6.6	"	10.1*
5	" "	1500-1525	7.5	30-35	1	8.4	"	0.55*
6	" "	1475-1500	5.5-5.75	13-17	7	3.5	"	0.09*
7	31.5% Cryolite-68.5% NaCl	1480-1510	5.0-5.2	21	1.5	5.3	"	5.5*
8	" "	1375-1380	4.5-5.5	14-35	2	6.8	"	0.04*
9	60% Cryolite-40% NaCl	1490	4.8-5.0	17-22	0.2	5.0	Graphite Rod	Only sodium produced on the cathode
10	" "	1500	4.5-4.8	20-37	2	7.5	Iron Plate 3.5% C (approx.)	0.3*
11	" "	1500-1525	4.5	17-22	1.5	5.8	"	0.16*
12	" "	1500-1540	4.5-5.0	16-22	1	5.2	Steel Plate 1.2-1.3% C	0.73*
13	" "	1500-1515	6.5-6.8	25-30	2	6.6	Iron Plate 3.5% C (approx.)	0.08*

* ASTM "8-hydroxyquinoline" volumetric analysis method.
** Ammonium phosphate gravimetric analysis method.

and 8 were to evaluate the effects of decreasing the cryolite composition of the cell bath. In addition, experiment No. 8 was for the purpose of evaluating the effects of low temperature electrolysis. In experiment No. 8 the magnesium oxide solubility was so low that halogen odors were detected in the anode gases. This low magnesium oxide solubility was due to the low temperatures (1375 to 1380° F.) at which the electrolysis experiment was performed.

Experiments Nos. 1 through 8 were performed using an iron cathode with 0.05 to 0.15 per cent carbon. By changing the cathode material to graphite, it was found that only metallic sodium deposited (experiment No. 9). This sodium rapidly attacked the 1/2 in. graphite rod. After a short period of time the portion of the cathode below the surface of the melt was eroded away. Some of the sodium floated to the surface of the melt where it burned with a bright yellow light. Bits of this burning metal were taken from the melt and extinguished by plunging it into granular sodium chloride. The cooled metal reacted violently with water and at times burst into flame. This reaction indicated that the metal was largely metallic sodium.

To evaluate the effects of the carbon content of the cathode on the magnesium content of metal deposited on the cathode, experiments Nos. 10, 11, 12, and 13 were conducted. These were conducted using iron cathode plates containing different amounts of carbon. The effect of increasing the carbon content of the iron was to decrease the magnesium content of the produced metal.

In experiment No. 10 sodium and aluminum base metal formed independently on the cathode. The aluminum base metal was formed as small spheres and the sodium was formed as platelets.

All of the aluminum base alloys, with the exception of experiments Nos. 1 and 2, were analyzed using the ASTM "8-hydroxyquinoline" method for determining the magnesium content of aluminum alloys (3). Alloys of known composition were first analyzed to perfect the technique before analyzing the unknown metal samples. Qualitative spectrographic analyses of several of the metal samples were run to determine which elements were present. This information was helpful in subsequent "wet" analyses.

The anode current densities listed in Table VII were approximated by dividing the arithmetic average current reading by the anode surface immersed in the melt at the start of an experiment.

It was found that contamination of the melt with iron from the iron pot could be held negligible by conducting the initial electrolysis with the pot as the cathode. A layer of aluminum-magnesium alloy was built up on the inner surface of the pot which minimized iron contamination of the melt in subsequent electrolysis operations.

3. Discussion of Results

The maximum amount of magnesium in any of the aluminum base alloys was 10.1 per cent. An alloy with this magnesium content was produced in cell A (experiment No. 1, Table VII) and in cell B (experiment No. 4, Table VII). The approximate conditions for producing this alloy were:

Cell bath composition	60% Cryolite-40% NaCl
Cell bath temperature	1525 to 1540° F.
Cell voltage	6 volts
Anode current density	6.6 to 7.2 amp./sq.in.
Cathode material	Low carbon steel

Since iron is quite soluble in aluminum, a molten aluminum alloy would make a better cathode. In these experiments the iron cathode was coated with the aluminum alloy in the initial part of the electrolysis. Effectively the aluminum-magnesium alloy was the cathode material in the latter part of the electrolysis. The aluminum industry now employs a molten aluminum cathode in producing aluminum from the electrolysis of cryolite containing aluminum oxide.

In order to increase the magnesium content of the produced metal it appears necessary to increase the magnesium ion content of the cryolite melt. This could be done by adding magnesium fluoride to the melt. However, Berent and coworkers found that the addition of magnesium fluoride to cryolite-magnesium oxide melts decreased the solubility of magnesium oxide (8). Decreasing the aluminum ion content of a cryolite-magnesium oxide melt by electrolysis is essentially increasing the magnesium fluoride content of the melt. The effect of decreasing the aluminum ion content of the cell bath is shown by the results of experiment No. 6, Table VII. The magnesium content of the produced metal was only 0.09 per cent.

Attempts were made to prepare melts of cryolite and magnesium chloride. This would be a seemingly logical way to increase the magnesium ion concentration of the melt. However, these mixtures were found to be chemically unstable at molten temperatures. Upon melting 50 grams of magnesium chloride with 50 grams of cryolite, extensive fuming occurred at approximately 750° C. The fuming was so extensive that visual observation of the melt was almost impossible. The cooled melt was light pink in color.

Other investigators have found that only aluminum was produced by the electrolysis of cryolite-magnesium oxide melts (46). The addition of sodium chloride to the cryolite lowered the liquidus temperature and the aluminum ion concentration of the resulting melts. The lowering of the liquidus temperature allowed the electrolysis to be carried out at a correspondingly lower temperature. Apparently this was a factor which caused the magnesium to be co-deposited with the aluminum.

It has been generally accepted that magnesium oxide was not decomposed directly by electrolysis in molten baths containing magnesium halides, within which magnesium oxide was only slightly soluble; but that the magnesium halide was separated into magnesium at the cathode and halogen at the anode. The halogen reacted with the dissolved magnesium oxide and carbon anode to form carbon monoxide and additional magnesium halide (43). Complete conversion was not obtained in these reactions and halogen was always present in the anode gases. In the electrolysis of a 60 per cent cryolite-40 per cent sodium chloride mixture containing magnesium oxide, halogen odors were not detected in the anode gases. This suggests that for the first time magnesium oxide was directly electrolyzed to magnesium and oxygen.

C. Electrolysis of a Mixture of Cryolite and Sodium Fluoride Containing Magnesium Oxide

1. Experimental Procedure

The 1,500 gram cell electrolyte was made up by weight from 900 grams of finely ground cryolite and 600 grams of sodium fluoride. To this was added 50 grams of magnesium oxide. These three components were thoroughly mixed and placed in cell B. The 60 per cent cryolite-40 per cent sodium fluoride mixture was used because it forms the eutectic with a minimum liquidus temperature. The liquidus temperature of this mixture was 882° C. The ternary mixture was melted and stirred in the electrolytic cell for 5 to 10 minutes at approximately 1600° F. to insure that equilibrium conditions were approached. The graphite anode and iron cathode were placed in position and the electrolysis was started. The flow of current was too high with the graphite anode immersed to a depth of 2-1/2 in. in the cell bath. Consequently, an anode immersion depth of 1-1/4 in. was used in these experiments. Otherwise the experimental procedure was the same as that used in the electrolysis of mixtures of cryolite and sodium chloride containing magnesium oxide.

2. Results

Two electrolysis experiments were conducted--one at a voltage range of 5.1 to 5.5 volts and the second at a voltage range of 6.5 to 6.9 volts. No magnesium was produced in either experiment. The results and conditions of these experiments are shown in Table VIII.

3. Discussion of Results

The results of the two experiments show that magnesium was not codeposited with the aluminum at the cathode. Consequently further experiments were not conducted.

The basic differences between the electrolysis of this melt and the electrolysis of the 60 per cent cryolite-40 per cent sodium chloride melt were the liquidus temperatures and the fluoride ion concentrations. It was necessary to conduct the cryolite-sodium fluoride electrolysis experiments at a temperature approximately 100° F. above that of the cryolite-sodium chloride experiments because of the higher liquidus temperature of the cryolite-sodium fluoride melt. In the cryolite-sodium fluoride melt the fluoride ion was substituted for the chloride ion of the cryolite-sodium chloride melt. Either one or both of these

TABLE VIII

Electrolysis of a Mixture of Cryolite and Sodium Fluoride Containing Magnesium Oxide

Expt. No.	Cell Bath Composition	Cell Temp. °F.	Cell Voltage Volts	Cell Current Amperes	Duration of Experiment Hours	Average Anode Current Density Amp./sq.in.	Cathode Material	Per Cent Magnesium in Aluminum Base Alloy*
1	60% Cryolite-40% NaF	1610-1640	5.1-5.5	22-30	1	14.2	Steel Plate 0.05-0.15% C	None Detected
2	" "	1580-1640	6.5-6.9	16-25	1.5	8.8	"	<0.01

* ASTM "8-hydroxyquinoline" volumetric analysis method.

differences might have prevented the deposition of magnesium on the cathode.

D. Economic Evaluation of the Electrolysis of a Mixture of Cryolite and Sodium Chloride Containing Magnesium and Aluminum Oxides

The largest single use of magnesium is as an alloying element in the production of aluminum base alloys (23). Approximately 21 per cent of the 1953 magnesium production of 50,240 tons was alloyed with aluminum (11). The maximum amount of magnesium in commercial aluminum alloys is 10 per cent (9). In view of these statistics the production of a master aluminum alloy containing 10 per cent magnesium could be an economical method of producing magnesium for the aluminum industry. Such an alloy could be produced by the electrolysis of a mixture of cryolite and sodium chloride containing magnesium and aluminum oxides. An aluminum alloy containing 10 per cent magnesium was produced from a cryolite-sodium chloride melt containing magnesium oxide. To make the process continuous it would be necessary to add sufficient aluminum oxide to maintain the aluminum ion concentration of the melt. In the continuous production of the aluminum-magnesium alloy the oxides of magnesium and aluminum would be added to the melt in a proportion to maintain the initial composition of the cell bath.

The preparation of an accurate cost analysis of this process would require an extensive evaluation of such parameters as current efficiency, cell bath losses, etc. These could be evaluated accurately only from a continuous pilot scale operation. The current efficiency, for example, depends heavily upon the electrolytic cell design. Nevertheless, an attempt was made to evaluate the process by assuming some of the costs to be comparable to the costs of similar processes.

In Table IX the costs are tabulated for producing a 10 per cent magnesium-90 per cent aluminum alloy. A 100 ton per day alloy plant was assumed. The method for arriving at each cost factor is shown in the following paragraphs:

Power

Current efficiency of the electrolysis of aluminum oxide dissolved in a molten cryolite bath is 80 to 90 per cent. The corresponding power requirement is 9 to 10 kilowatt-hours per pound of aluminum (34). A cost analysis, by the Bureau of Mines, of the magnesium oxide electrolysis process was made using a power consumption of 10.5 kilowatt-hours per pound of magnesium (15). Thus an over-all cell power requirement of 10 kilowatt-hours per pound of aluminum-magnesium alloy appears to be a reasonable assumption. Power costs range from 0.2 to 0.7 cents per kilowatt-hour for a 100 ton reduction plant. An average cost of 0.45 cents per kilowatt-hour was used in the cost analysis. Therefore, the cost per pound of alloy would be 4.5 cents.

Carbon Anode

In the aluminum oxide electrolytic reduction process the carbon consumption is 0.4 to 0.6 lb. per pound of aluminum (34). An average of 0.5 lb. of carbon per pound of aluminum was assumed. There are theoretically 0.89 lb. of oxygen removed at the anode per pound of aluminum deposited at the cathode. Similarly there would be 0.66 lb. of oxygen removed per pound

TABLE IX

Costs of Producing a 10 Per Cent Magnesium-90 Per Cent Aluminum Alloy by the Electrolysis of a Cryolite-Sodium Chloride-Magnesium Oxide-Aluminum Oxide Melt

	Cost of Aluminum		Cost of Magnesium		Cost of Alloy
Cost Factor	Cents per 0.9 lb.	Cents per lb.	Cents per 0.1 lb.	Cents per lb.	Cents per lb.
Power	4.050	4.50	0.450	4.50	4.500
Carbon Anode	0.900	1.00	0.074	0.74	0.974
Magnesium Oxide			0.680	6.80	0.680
Aluminum Oxide	5.450	6.05			5.450
Cryolite	0.411	0.46	0.046	0.46	0.457
Sodium Chloride	0.018	0.02	0.002	0.02	0.020
Cell Labor	3.600	4.00	0.400	4.00	4.000
Cell Room Repair Maintenance	0.450	0.50	0.050	0.50	0.500
Plant Administration	0.900	1.00	0.100	1.00	1.000
Depreciation and Amortization	2.070	2.30	0.230	2.30	2.300
Total	17.849	19.83	2.032	20.32	19.881

of magnesium. Hence $0.5 \times \frac{0.66}{0.89}$ or 0.37 lb. of carbon would be consumed per pound of magnesium produced. The price of carbon electrodes is in the range of 2 cents per pound of carbon.

The carbon costs per 0.9 lb. of aluminum would be: $0.9 \times 0.5 \times 2.0 = 0.9$ cents.

The carbon costs per 0.1 lb. of magnesium would be: $0.1 \times 0.37 \times 2.0 = 0.074$ cents.

Total cost per pound of alloy would be 0.974 cents.

Magnesium Oxide

The price of high purity magnesium oxide is 4.1 cents per pound. Therefore, the cost per 0.1 pounds of magnesium is: $0.1 \times 4.1 \times \frac{40.3}{24.3} = 0.68$ cents.

Aluminum Oxide

The market price of aluminum oxide is 3.2 cents per pound (57). The cost per 0.9 pound of aluminum is given by: $0.9 \times 3.2 \times \frac{102.0}{54.0} = 5.45$ cents.

Cryolite and Sodium Chloride

In the aluminum oxide electrolytic reduction process, a total of about 0.05 pounds of cryolite and aluminum fluoride are added per pound of aluminum (34). Assuming an equal make-up of cryolite and sodium chloride for the alloy process, it would be necessary to add 0.05×0.60 or 0.03 pounds of cryolite and 0.02 pounds of sodium chloride per pound of alloy. The current price of cryolite is 15.25 cents per pound and the price of sodium chloride is

1.00 cents per pound (57). Thus the cost of cryolite would be approximately 15.25 x 0.03 or 0.457 cents per pound of alloy.

The cost of sodium chloride would be 1.00 x 0.02 or 0.02 cents per pound of alloy.

Cell Labor

The Bureau of Mines estimated the cell labor costs of the magnesium oxide electrolysis process to be 2.40 cents per pound of magnesium (15). Cost figures from nine government-owned aluminum plants show cell labor cost of 1.0 to 2.6 cents per pound of aluminum (9). These are costs during the years 1942-1945. Since this time period, labor costs for industrial workers have approximately doubled (75). Accordingly, the cell labor cost was estimated to be 4.0 cents per pound of alloy.

Cell Room Repair Maintenance

Since repair maintenance consists mainly of labor, the Bureau of Mines' estimate of 0.25 cents per pound of magnesium (15) was doubled. A value of 0.50 cents per pound of alloy was used.

Plant Administration

Administration costs are generally maintained proportional to labor costs. Again the Bureau of Mines' estimate of 0.50 cents per pound of magnesium (15) was doubled. A value of 1.0 cents per pound of alloy was used.

Depreciation and Amortization

Construction cost indices have increased by a factor of 2.3 since 1942 (12, 13). Therefore, the Bureau of Mines' value of 1.0 cents per pound of magnesium (15) was multiplied by 2.3. The costs were estimated to be 2.30 cents per pound of alloy.

The sum of the costs of producing magnesium by this process (shown in Table IX) is approximately 20.3 cents per pound. This does not include transportation costs or miscellaneous expenses for such items as property taxes, insurance, and rentals. Magnesium ingot is currently selling for 36 cents per pound (57). The margin of 15.7 cents per pound of magnesium indicates that the alloy process may be economically attractive. The total cost of producing aluminum is shown in Table IX to be 19.83 cents per pound. This cost appears to be in agreement with the current price of 25 cents per pound of aluminum (57).

CHAPTER VI

SUMMARY AND CONCLUSIONS

The purpose of this research was to find an electrolyte in which magnesium oxide is appreciably soluble and from which magnesium oxide can be reduced electrolytically.

Accordingly, experiments were conducted to determine approximately the solubility of magnesium oxide in a variety of molten salts. The experimental method consisted of directing a beam of light through a clear melt of known solvent-magnesium oxide composition and, as the melt cooled, observing with a telescope the first appearance of crystals. The magnesium oxide content of the system was recorded as being soluble at the temperature at which the first crystals began to form.

Of the numerous solvents investigated only those containing cryolite or sodium metaphosphate were found to dissolve appreciable quantities of magnesium oxide. A 60 per cent cryolite-40 per cent sodium chloride melt dissolved 3.15 per cent magnesium oxide at 880° C.; whereas, a 60 per cent cryolite-40 per cent sodium fluoride melt dissolved 4.2 per cent magnesium oxide at 962° C. A 70.2 per cent sodium metaphosphate-29.8 per cent magnesium fluoride melt dissolved 4.8 per cent magnesium oxide at 880° C. The maximum solubility of magnesium oxide in any of the other solvents investigated was 0.2 per cent.

It was found that the sodium metaphosphate melt was chemically reactive with metallic magnesium. The cryolite-sodium chloride melts were found to be non-reactive with magnesium. Thus, the cryolite melts appeared promising as electrolytes for the electrolysis of magnesium oxide.

Mixtures of cryolite and sodium chloride containing magnesium oxide were electrolyzed in a series of experiments. These experiments were conducted at various conditions of voltage, current density, cell bath composition, temperature, and cathode composition. An alloy of aluminum and magnesium was deposited on the cathode. The magnesium content of the alloy varied from 0.09 to 10.1 per cent, depending on the conditions of the electrolysis.

Similar electrolysis experiments were conducted in which a mixture of cryolite and sodium fluoride containing magnesium oxide was electrolyzed. The results of these experiments show that magnesium was not co-deposited with the aluminum at the cathode.

The largest single use of magnesium is as an alloying element in the production of certain aluminum base alloys. Moreover, the maximum amount of magnesium in commercial aluminum alloys is 10 per cent. In view of these statistics the production of a master aluminum alloy containing 10 per cent magnesium could be an economical process for producing magnesium for the aluminum industry. This process would consist of electrolyzing a mixture of cryolite and sodium chloride containing oxides of magnesium and aluminum. In a continuous process the oxides of magnesium and aluminum would be added in a proportion to maintain the initial composition of the cell bath.

A cost analysis was made of such a process. This analysis indicated that the alloy process may be economically attractive.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

Several suggestions for future study arose during the course of this investigation. These suggestions are listed below:

(1) Delineate the liquidus diagram for the system magnesium oxide, sodium metaphosphate, sodium fluoride, and magnesium fluoride.

While investigating the solubility of magnesium oxide in mixtures of sodium metaphosphate, sodium fluoride, and magnesium fluoride, a clear glass was produced. The approximate composition of the mixture was 8.7 per cent magnesium oxide, 64.1 per cent sodium metaphosphate, 4.0 per cent sodium fluoride, and 23.2 per cent magnesium fluoride. This glass was optically clear, colorless, hard, and resistant to breaking.

(2) Investigate the properties of the glass or glasses made from mixtures of magnesium oxide, sodium metaphosphate, sodium fluoride, and magnesium fluoride.

There is a possibility that this glass will have some commercial applications.

(3) Investigate the effect of the composition of the cathode on the composition of the material deposited on the cathode.

In the electrolysis of molten mixtures of cryolite and sodium chloride containing magnesium oxide, it was found that sodium was deposited on a carbon cathode and an alloy of magnesium and aluminum was deposited on an iron cathode. It is quite possible that other materials will also affect the composition of the deposited metal. For example, a molten aluminum cathode or molten magnesium cathode might change considerably the composition of the deposited metal.

(4) Design, construct, and operate an electrolytic cell of pilot scale for reducing oxides of aluminum and magnesium dissolved in mixtures of cryolite and sodium chloride.

The purpose of such work would be to obtain operational data on factors such as current efficiency, method of introducing cell feed, method of product removal, method of sludge removal, consumption of carbon, effect of impurities in the feed upon the purity of the alloy product, etc. Different cell designs would be tested.

(5) Conduct a search for a material that would make a suitable molten cathode for the electrolysis of magnesium oxide dissolved in a melt containing sodium metaphosphate. If such a cathode material is found, electrolyze the melt and subsequently investigate methods of separating the magnesium from the cathode material.

A melt containing sodium metaphosphate dissolves appreciable quantities of magnesium oxide, but the melt is not inert to molten metallic magnesium. It is possible that the electrolytic reduction of magnesium oxide could be accomplished with the use of an inert molten cathode. Such a cathode would be chemically inert to both the electrolytic bath and the magnesium. It would also be a requirement that the cathode material dissolve the deposited metallic magnesium. The magnesium could be subsequently removed from the cathode material by distillation, solvent extraction, or electrolysis.

(6) Review some important systems whose liquidus curves have been determined by the cooling temperature vs. time relationship and check by the visual method used in the solubility study of Chapter III.

The blind cell liquidus determinations rely upon the precipitation of relatively large amounts of material at the liquidus temperature. The latent heat of this precipitation causes a point of inflection on the time-cooling temperature curve. This point of inflection is taken as the liquidus temperature. In many systems the precipitation is slight at the liquidus temperature and heavy precipitation does not occur until the temperature has dropped considerably below the visually observed liquidus temperature.

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APPENDIX

GRAVIMETRIC ANALYSIS OF A MAGNESIUM-ALUMINUM ALLOY

The analytical procedure followed in analyzing the metal sample from electrolysis experiment No. 1 of Table VI, Chapter V, was not completely standard. For this reason, the procedure is recorded herein.

Procedure and Results

A weighed portion of the metal sample was treated with HCl and filtered. The filtrate was diluted to 100.00 ml. The residue was placed in a platinum crucible, where the paper was burned off. The residue was weighed as HCl insoluble material.

Two 10.00 ml. aliquots were taken from the filtrate. The iron content was determined by oxidizing the iron to Fe^{+++} with Br_2, boiling off the excess Br_2, adding excess KI, and titrating the liberated I_2 with 0.01085 N $Na_2S_2O_3$ solution. The iron content was determined by the relationship

$$\% \text{ Fe} = 0.01085 \times (\text{ml. of } Na_2SO_3) \times \frac{0.05585}{2} \times \frac{100}{0.6016} \times 10.$$

Samples from the above titrations were treated with HNO_3, evaporated to dryness, dissolved in HCl, made basic with NH_4OH, filtered, washed twice with boiling 3% NH_4Cl solution, dissolved in dilute HCl, reprecipitated, filtered, and washed twice with boiling 3% NH_4Cl solution. The residues were dried, ignited, cooled, and weighed as

$Al_2O_3 + Fe_2O_3$. The weight of Fe_2O_3 in this mixture was determined by the relationship

$$\text{Wt. } Fe_2O_3 = (\text{ml. of } Na_2SO_3 \text{ from above titration}) \times \frac{0.01085}{2} \times \frac{0.05585}{2} \times \frac{159.7}{111.70}.$$

The weight of Al_2O_3 was calculated by taking the difference between the total weight of the above residue and the weight of the Fe_2O_3. The weight per cent of aluminum was found by the equation

$$\%\ Al = \text{wt. } Al_2O_3 \times 0.5291 \times \frac{100}{0.6016} \times 10.$$

Filtrates from above were retained for Mg determination. These filtrates were treated with HNO_3, evaporated to dryness, dissolved in dilute HCl and boiled. A 15 ml. portion of 3% $(NH_4)_2\ HPO_4$ solution was added to each filtrate. These were cooled with ice water. Two drops of methyl red solution were added and each solution was neutralized with NH_4OH; 4 ml. of excess NH_4OH were added. After 4 hours the solutions were filtered into two previously weighed filtering crucibles, dried with ether, and then weighed. The magnesium content was calculated from the equation

$$\%\ Mg = (\text{wt. of } Mg(NH_4)PO_4) \times 0.1771 \times \frac{100}{0.6016} \times 10.$$

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