Advances and Innovations in the Extraction of Aluminum and Magnesium

D.R. Sadoway

Department of Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139-4307, USA

Abstract Aluminum ranks second only to steel as the most common metal. All of the world's primary aluminum is produced by molten salt electrolysis. Magnesium ranks next to aluminum in the order of structural metals and is extracted by a number of electrochemical and thermochemical processes, all involving molten salts. This article reviews the current technologies for aluminum and magnesium extraction and assesses the prospects for change.

Introduction Aluminum and magnesium are both structural metals, and as such they lie in the shadow of steel which represents roughly 95% of all metal in use. Table 1 reports world production figures from 1996. Why is steel so dominant? Look at its price – mild steel averages about $0.45/kg. In Japan, they say that steel is cheaper than potatoes. Indeed, there are few items in our supermarket that sell for less than $0.45/kg. It is truly remarkable. Aluminum sells for about $1.75/kg, while the price of magnesium is in the vicinity of about $4/kg. The world steel industry is worth about a third of a trillion dollars a year, the world aluminum industry about $37 billion and the world magnesium industry about $1 billion. Aluminum and magnesium are global industries. Tables 2 and 3 show the countries that are major producers and report tonnage figures for 1996.

Table 1. Selected Properties of Structural Metals

	Fe	Al	Mg
prod^n (10^6 tpy[1]) [1-3]	752	21	0.35
price ($/kg)	0.45	1.75	4.25
sales (10^9 $)	338	37	1.50
abundance (%)	4.1	8.2	2.3
(rank)	4	3	7
$-\Delta_f G_{M_xO_y}$ (kJ/mol O_2) [4]	503	1055	1138
(kJ/g M)	6.7	29	23

Is there a scientific basis for metal prices? Table 1 shows that aluminum is more abundant in the earth's crust than either iron or magnesium. So relative abundance doesn't explain pricing. However, there is some correspondence between the prices of steel and aluminum and the free energies of formation of their oxides. Magnesium is the exception to this rule.

---

[1] All tonnages are reported in metric tons, *i.e.*, 1 tonnes = 1000 kg.

Table 2. Major Aluminum Producers		Table 3. Major Magnesium Producers	
$(10^3$ tpy)		$(10^3$ tpy)	
U.S.A.	3500	U.S.A.	143
Russia	2750	Canada	50
Canada	2300	China	40
China	2050	Norway	38
Australia	1450	Russia	35
Brazil	1200		
Norway	850		

Magnesium Chemistry [5] Magnesium is found in nature as a $MgCl_2 \cdot 12H_2O$ in seawater or brine. The strategy for reducing it to metal involves dehydration and purification of the dodecahydrate followed by molten salt electrolysis, the salient features of which are given in Table 4. In the electrolysis of anhydrous salt there is a central graphite anode on which chlorine evolves, and opposing mild steel cathodes on which magnesium is produced. Liquid metal and anode gas both rise. A ceramic spacer prevents the liquid magnesium from shorting between the cathode and the anode. The Dow cell uses a feed that contains roughly 2 moles of water per mole of $MgCl_2$. There is a tradeoff between complexity of dehydration operations and anode consumption rates. The Dow cell consumes about 0.1 kg of anode per kg of metal produced, a substantially higher rate than that of cells using anhydrous feed. Magnesium can also be produced by thermochemical means. The feed is derived from magnesite, and the reductant can be either a metal such as ferrosilicon or carbon. Two examples of contemporary metallothermic reduction technology are the Pidgeon (Canada) and the Magnetherm (France) processes.

Table 4. Magnesium Electrolysis

electrolyte: NaCl - KCl - $CaCl_2$

feed: $MgCl_2$

temperature: 740°C

anode: carbon

anodic reaction: $2\ Cl^- \rightleftharpoons Cl_2 + 2\ e^-$

cathode: mild steel

cathodic reaction: $Mg^{2+} + 2\ e^- \rightleftharpoons Mg$

overall cell reaction: $MgCl_2 \rightleftharpoons Mg + Cl_2$

standard potential: $E° = 2.5\ V$

As for new processes to produce magnesium, here are several new chemistries that are being proposed. In Quebec, Noranda plans to exploit serpentine (Mg_2SiO_4) tailings from asbestos mining. In some places, the magnesium content exceeds 24% -- this is a rich ore body. Magnesium oxide derived from serpentine will be chlorinated to form anhydrous magnesium chloride. This will be electrolyzed in Alcan cells which are fitted with vertically disposed bipolar electrodes [6]. In Australia there are large deposits of magnesite which is to be chlorinated and the magnesium chloride electrolyzed in Alcan cells [6]. It is a departure from current practice not

to extract magnesium metal from an oxide ore body by thermochemical means. Table 5 shows the announced expansion of magnesium smelting capacity.

Table 5. Announced Expansion of Magnesium Smelting Capacity

(10^3 tpy)

55	Israel, Dead Sea Works
58	Canada, Magnola
43	Canada, Norsk Hydro
90	Australia, Queensland Metals Corp.
50	Iceland, Icelandic Magnesium Co.
50	Jordan, Dead Sea
100	Congo, Congo Minerals/Ashurst Tech.

What are the challenges and opportunities for magnesium extraction? Well, certainly there is the need for new electrode materials. In the Dow cell carbon consumption rates are very high; hence, an inert anode would constitute an improvement there. There is a need also for a new process for preparing anhydrous magnesium chloride in a manner that is energy efficient and gives a product of high purity. Environmental concerns are high on the priority lists of metal producers. In cast house operations, a replacement for SF_6 shielding gas is sought.

What about radical innovation, *i.e.*, totally different reduction chemistry? Here is a short list of candidate chemistries, none of which is in practice: carbothermic reduction, electrolytic calciothermic, and electrolysis of the oxide in an oxide melt. These will be described later in connection with aluminum. Here, let us turn to the electrolysis of magnesium oxide from a melt of neodymium chloride [7]. Sharma at General Motors has conceived of a process that exploits the fact that magnesium oxide will dissolve in neodymium chloride to form neodymium oxychloride and magnesium chloride according to

$$2\,MgO + 2\,NdCl_3 \rightleftharpoons 2\,NdOCl + 2\,MgCl_2.$$
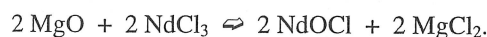
This obviates the need for carbochlorination of magnesium oxide in order to convert it to the chloride. Now generally speaking oxychlorides are to be avoided in chloride electrolysis because they precipitate out of solution causing sludging. But in this case the oxychloride remains soluble in the electrolyte. The cathodic reaction is magnesium deposition. At the anode a number of reactions is proposed, but the one that seems dominant at industrial current densities is the oxidation of oxygen accompanied by anode consumption to form CO_2. The process has been tested at the lab bench in the U.S.A. and in pilot cells in Australia, but there are still many unanswered questions. Under certain conditions neodymium codeposits with magnesium, reducing its purity. Sometimes chlorine evolution occurs at the anode. More research is needed to determine commercial viability.

Aluminum Chemistry [8,9] Aluminum metallurgy is less varied than that of magnesium. There is only one route from ore to metal: conversion of bauxite to alumina (Bayer process) followed by molten salt electrolysis (Hall-Héroult cell). Details are well documented in the literature. The main features are given in Table 6. Modern cells draw currents of 200 to 300 kA at approximately 4 V.

Table 6. Hall-Héroult electrolysis

electrolyte: Na_3AlF_6 - AlF_3 - CaF_2

feed: Al_2O_3

temperature: 970°C

anode: carbon

anodic reaction: $3\ O^{2-} + 1.5\ C \rightleftharpoons 1.5\ CO_2 + 6\ e^-$

cathode: carbon

cathodic reaction: $2\ Al^{3+} + 6\ e^- \rightleftharpoons 2\ Al$

overall reaction: $Al_2O_3 + 1.5\ C \rightleftharpoons 2\ Al + 1.5\ CO_2$

standard potential: $E° = 1.2\ V$

There have been many advances and innovations in the past 50 years. Automation and process control have been furthered by new sensor technologies allowing us to characterize bath chemistry, to follow alumina feeding, and even to manage the electromagnetic fields in the cell. In mathematical modeling, thanks to improvements in computational capability, we can now treat the physical properties of the melt as well as transport phenomena in the cell, *e.g.*, current distribution, thermal profile, position of sidewall ledge, to cite a few. Other changes include better energy utilization, *i.e.*, less energy per unit metal product (kWh/kg), and a reduction in harmful emissions. The undesirable by-products include so-called red mud (Bayer process), volatile organic compounds, particulates, and SO_2 (anode manufacture), and fluorides, perfluorocarbons, and spent potliner (Hall cell).

What are the challenges and opportunities for the future [10]? One thrust area is new electrode materials enabling the use of inert anodes and drained cathodes. At the moment we consume slightly less than 1/2 kg carbon per kg aluminum product. The emissions associated with consumable carbon anodes are cited above. Eliminating carbon from the Hall cell is by far the change that would have the greatest environmental impact. Based on the selection criteria enunciated by this author [11] inert anodes consisting of metal alloys consisting of a base metal (or metals) plus aluminum have been identified as the most promising materials [12]. Installing cathodes made of a material that is wetted by molten aluminum and positioning such cathodes above the floor of the cell would eliminate the need to maintain a deep pool of liquid metal on the bottom of the cell. The material showing the most promise is titanium diboride which has graduated from laboratory testing to installation in industrial cells for long-term performance assessment [13]. New electrolyte chemistry is also of interest. In particular, there has been growing interest in so-called low-ratio baths, *i.e.*, baths containing much greater amounts of AlF_3 ($\approx$ 40 wt % in excess of cryolite stoichiometry) than is currently the practice ($\approx$ 10 wt % in excess of cryolite stoichiometry). At such high levels of AlF_3 the liquidus temperature drops below 700°C, almost 300 K below the operating temperature of contemporary cells [14]. The hope is that operation at lower temperature will reduce the wear on cell components and perhaps even allow the sustained performance of inert anodes that have been found to be unworkable at 970°C. Indeed, it may well be that if low-ratio bath is to be used at all, the cell will need to be free of carbon anodes. Recent work by the author suggests that at 800°C electrolysis of low-ratio bath (B.R. = 0.56) on carbon anodes generates perfluorocarbons at normal operating voltage [15].

What about radical innovation, *i.e.*, totally different reduction chemistry? Here is a short list of candidate chemistries, none of which is in practice: carbothermic reduction, electrolytic

calciothermic, electrolysis of potassium aluminum sulfate, and electrolysis of the alumina in an oxide melt. Carbothermic reduction has been studied many times in the past but has never been shown to be economically viable [16, 17]. While it is thermodynamically possible to reduce alumina with carbon at temperatures exceeding 2100°C, there are other kinetic pathways and parasitic reactions that greatly reduce productivity. Calciothermic reduction involves *in situ* generation of calcium from a bath of calcium oxide and calcium chloride into which one adds aluminum oxide. At the cathode, the product of electrolysis is calcium metal which chemically reduces alumina present in the bath. At the anode we have the choice of either a consumable anode or a nonconsumable anode. The process can be viewed as calciothermic reduction of alumina combined with *in situ* generation of the calcium reductant. The electrolysis of potassium aluminum sulfate derived from tar sands has been proposed. Unfortunately, there is not enough information in the open literature at this time to allow a proper technical assessment of the process. Lastly, there is electrolysis of alumina from an all-oxide electrolyte. The concept is to avoid carbon and fluorine chemistries altogether and to break alumina into its constituent aluminum and oxygen. Obviously, there are major technical obstacles to overcome. However, if it can be shown to be viable, the process would be environmentally sound and long-term sustainable [18].

Summary and Conclusions What can be said in general about the metals industries? In the opinion of the author, environmental concerns will prompt a shift from thermochemical approaches to electrochemical approaches. We see evidence of this with the announced new magnesium smelters where ore bodies that historically were processed by metallothermic reduction are now being electrolyzed. If we couple this trend to carbon-free generation of electricity, the result will be "greener" metallurgy. The second point is that the transitional technologies will play an uncertain role. This is largely due to the fact that the metals industry is very conservative owing to the very high capital costs associated with technology. For example, it has been roughly 25 years since a major new technology for producing aluminum was installed: the Alcoa smelting process. There can be no denying that the Alcoa smelting process was an engineering achievement with its bipolar electrode array, fluoride-free electrolyte, and negligible carbon consumption rate. Yet the plant proved to be an economic failure and was ultimately closed, even though the electrolysis step was 30% more efficient than the Hall cell. So on the heels of such an experience the metals industry is going to be very loathe to make major changes. Even so, we recognize that attaining *sustainable metallurgy* requires major technological adjustment– a paradigm shift. The processes we have in place today have been around about a hundred years, and mounting environmental pressures are going to force change. The result is tension. Conservative management is afraid to spend money on risky technology, and impatient policy makers and government officials want to force dramatic changes in the emissions profile of the metals industry. This juxtaposition represents a great opportunity. Whether we consider incremental changes in current technology or radical innovation, the future looks bright for molten salts.

References

[1] *Iron & Steelmaker* 24 (13) (1997), p. 2.

[2] *Light Metal Age* 55 (1, 2) (1997), p. 8.

[3] U.S. Geological Survey, *Mineral Commodity Summaries*, February 1997.

[4] M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, 3rd edition, American Institute of Physics, New York, NY, 1985.

[5] G.J. Kipouros and D.R. Sadoway, "The Chemistry and Electrochemistry of Magnesium Production," in *Advances in Molten Salt Chemistry*, Vol. 6, G. Mamantov, C.B. Mamantov and J. Braunstein, editors, Elsevier, Amsterdam, 1987, pp. 127-209.

[6] O. Sivilotti, "Advances in electrolytic production of magnesium," in *Light Metals 1997 Métaux Légers*, C.M. Bickert and R.I.L. Guthrie, editors, CIM, Montreal, 1997, pp. 543-555.

[7] K.J. Cathro, R.L. Deutscher, and R.A. Sharma, *J. Appl. Electrochem.* 27 (4) (1997), p. 404.

[8] K. Grjotheim, C. Krohn, M. Malinoský, K. Matiašovský, and J. Thonstad, *Aluminium Electrolysis*, 2nd edition, Aluminium-Verlag, Düsseldorf, 1982.

[9] H.A. Øye, "Smelting of Magnesium and Aluminum," *Proceedings of the Elliott Symposium on Chemical Process Metallurgy*, P.J. Koros and G.R. St. Pierre, editors, ISS, Warrendale, PA, 1991, pp. 33-50.

[10] *Aluminum Industry: Industry/Government Partnerships for the Future*, The Aluminum Association, Inc., Washington, DC, March, 1996.

[11] D.R. Sadoway, "A Materials Systems Approach to Selection and Testing of Nonconsumable Anodes for the Hall Cell," *Light Metals 1990*, C.A. Bickert, editor, TMS, Warrendale PA, 1990, pp. 403-407.

[12] J.N. Hryn and D.R. Sadoway, "Cell Testing of Metal Anodes for Aluminum Electrolysis," *Light Metals 1993*, S.K. Das, editor, TMS, Warrendale PA, 1993, pp. 475-483.

[13] H. Zhang, V. de Nora, and J.A. Sekhar, *Materials Used in the Hall-Héroult Cell for Aluminum Production*, TMS, Warrendale PA, 1994, pp. 37-42.

[14] K. Grjotheim, H. Kvande, and B.J. Welch, "Low-melting Baths in Aluminium Electrolysis," *Light Metals 1986*, R.E. Miller, editor, TMS-AIME, Warrendale PA, 1986, pp. 417-423.

[15] S.S. Nissen and D.R. Sadoway, "Perfluorocarbon (PFC) Generation in Laboratory-Scale Aluminum Reduction Cells," *Light Metals, 1997*, R. Huglen, editor, TMS, Warrendale, PA, 1997, pp. 159-164.

[16] J.P. McGeer, "Alternate Methods for the Production of Aluminum Metal," *Proceedings of a conversazione on "The Production of Liquid Aluminum,"* E. Ozberk, D.W. Macmillan, and R.I.L. Guthrie, editors, TMS-CIM, Montreal, series 25-7, No. 2, 1986, pp. 125-139.

[17] K. Grjotheim and J.B. See, Minerals Sci. Engng. 11 (2) (1979), pp. 80-98.

[18] D.R. Sadoway, *J. Mater. Res.,* 10 (1995), pp. 487-492.

For correspondence, readers may contact the author at dsadoway@mit.edu (e-mail) or 617.253.5418 (fax).