

The Evolution of Technology for Structural Materials over the Last 50 Years: Al, Mg, and Li

James W. Evans



Author's Note: This paper has been written in response to a request to review technological progress over the past 50 years on "... aluminum, magnesium, recycling, and alkali metals, ranging from key aspects of extractive processing to end product development" in approximately eight printed pages. I hope that I can be excused for failing to compress all that time and all subjects into these pages and the time available for preparation! Accordingly the following is biased toward areas of which I am least ignorant; the result has been an emphasis on aluminum, particularly on how it is produced. That emphasis might anyway be appropriate in view of the membership of the Light Metals Division of TMS. Magnesium receives coverage (and here I have been greatly helped by others through the literature or e-mail correspondence) while lithium, the only alkali metal that I think of as a material, receives brief mention.

ALUMINUM

The Significance of Aluminum

The world's production of aluminum has grown, almost without interruption, since early in the last century, as illustrated in Figure 1. Primary production is the reduction of aluminum oxide (alumina) to metal. How various regions of the world contribute to that production is illustrated in Figure 2.

North America continues to be the major primary producer of aluminum but its position has slipped in recent years as growth in production in other regions, particularly Asia, has occurred. Much of North American primary production is now in Canada, rather than the United States, as illustrated in Figure 3. This figure shows that the United States was a net exporter of aluminum in 1991 whereas imports have now grown to the point where net imports have exceeded primary production for the past few years. Also shown in this figure is the contribution of "secondary production" (production from melting scrap) to the nation's metal supply. In 1990 the United States boasted 23 smelters³ but by 2003 that number had diminished to 14.⁴

The form in which products are

shipped to customers is shown in Figure 4a while Figure 4b illustrates the use to which sectors of the North American economy are putting aluminum.

Transportation is an important market for aluminum products (aircraft structural materials, automobile engine components and body parts for automobiles and light trucks designed to reduce vehicle weight and improve mileage). For example, the 2007 Toyota *Camry's* new aluminum engine is 25 kg (27%) lighter than its predecessor.⁶ And the 2007 Jaguar *XK* has a "... bonded and riveted aluminum monocoque body structure..." that is "significantly lighter and stiffer... than the steel model it replaces."⁷ Containers and packaging are also important aluminum markets, with almost 100 billion beverage cans shipped by U.S. producers last year.⁵

The Technology of Aluminum Production

Space limitations preclude any introductory descriptions of the Bayer process or Hall-Héroult cells ("pots"). It is

assumed that the reader has some knowledge of this technology and can acquire more background from texts by K. Grjotheim et al.⁸ or Grjotheim and B.J. Welch.⁹

Technological advancement in the production of aluminum over the past half century can be roughly categorized into evolutionary and revolutionary changes. Examples of the former can be seen in an excellent 1999 article "Aluminum: Approaching the New Millennium" by H.A. Øye et al.¹⁰ from which Table I is taken. [An earlier article in the same vein is that of Grjotheim, Kvannd, and Zhuxian¹¹ "Key Improvements to Hall-Héroult since the End of World War II."] It is seen that in the last half of the last century the direct current (d.c.) through a typical cell increased by a factor of about five, with more than a corresponding increase in cell productivity, bringing economies of scale such as more production per operator. More electricity is now consumed in producing aluminum around the world than is consumed by France¹² and the high cost

Table I. Comparison of 1948 and 1998 Hall-Héroult Cells¹⁰

Parameters	1948	1998
Current Rating (kA)	50–60	300–325
Al Production (kg Al/day)	385	2,475
Unit Energy (d.c. kWh/kg Al)	18.5–19.0	12.9–13.5
Anodic Current Density (A/cm ²)	1.2–1.3	0.8–0.85
Area of Cavity (m ²)	8	40–45
Nominal Anode Area (m ²)	4–5	38
Ratio of Area (Anode/Cavity)	~0.55	~0.9
Average Velocity of Flow in Cathode (cm/s)	10–15	4–6
Cathode Life (days)	600–800	2,500–3,000
Potroom Worker Hours (per tonne Al)	5–8	1.7
Interval for Al ₂ O ₃ Additions (minutes)	80–240	0.7–1.5
Emissions (kg/t Al)		
CO ₂ *	2.4	1.6
F	~30	<0.5
CF ₄	~1.5	0.05

* Including anode manufacture.

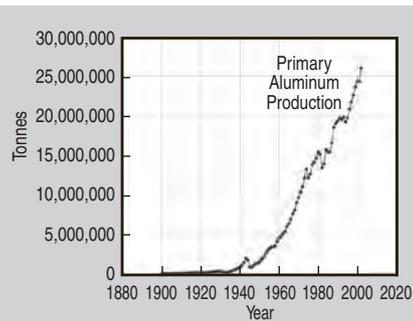


Figure 1. The primary production of aluminum.¹

of this energy has been a concern in aluminum electro-winning for decades. The evolution from 18.5–19 kWh/kg aluminum in 1948 to 12.9–13.5 kWh/kg in 1998 is seen in the table. A part of that improvement can be ascribed to a lower current per unit area of anode surface as delineated in the table. A further evolutionary improvement is the development of alumina feeding and control methods permitting more frequent alumina additions and thereby better control of the alumina content of the electrolyte. Finally, the increase in cathode life (before cells must be stopped and relined) from about 2 years in 1948 to 7–8 years in 1998 is notable.

In the same article the authors estimated the reduction in production cost arising from various technical improvements (Table II). Not surprisingly, the decrease in the cost of the electrical energy was foremost. Electrical energy cost continues to drive the search for lower power consumption around the world and, as expected, various regions report not very disparate power consumption. According to International Aluminium Institute (IAI) statistics, consumption ranged from 14.337 kWh/kg in Africa to 15.613 kWh/kg in North America.² These numbers include the d.c. power, rectification power, and normal smelter auxiliaries; the variation probably reflects the age of the smelters rather than other factors. Statistics such as these are intended not to reveal the performance of individual pot designs, smelters, or corporations and it is exceptional for these data to be available. Exceptions include articles by C. Vanvoren and colleagues on the Dunkirk smelter of Aluminium Pechiney,¹³ by S.C. Tandon and R.N. Prasad on Hindalco's smelter,¹⁴ and by D. Woodfield and coworkers on 35 years of improvement at the Anglesey Aluminium smelter.¹⁵

Results from this last paper are used here as clear demonstrations of evolution toward better technology. While approximately doubling the annual production of metal to 147,000 tons in 2006, Anglesey Aluminum was able to reduce the power consumption per kilogram of metal, as shown in Figure 5.

This significant improvement was in part achieved by reduction of cell voltage (Figure 6) and improved current efficiency (Figure 7). The improvements in cell voltage were partly due to the use of larger anodes, and therefore lower current densities, and partly due to lower cell temperatures (955°C in 2006), allowing the heat balance to be sustained at lower cell volts. Current efficiency (CE) improvements were partly due to changes in temperature and bath ratio (ratio of NaF to AlF₃ = 1.1–1.15 in 2006). The generally accepted explanation for current efficiency loss is the dissolution of a part of the aluminum metal produced and its transport to the anodes where it is re-oxidized chemically or electrochemically. Lower bath ratios inhibit this dissolution/transport.¹⁰ A readable account of how CEs can be precisely determined by the silver dilution technique is provided by G.P. Tarcy and K. Tørklep.¹⁶ These authors provide an equation for predicting CE as a function of aluminum solubility and percent alumina in the bath. They also report an overview of results from 1,128 Alcoa cells and 110 measurements at Elkem. These results show a distinct CE advantage for prebaked cells over Söderberg cells (a mean of 94.4% versus 90.5%). Söderberg cells would seem to be obsolete; in 2003 they accounted for 27.1% of world primary production (17.6% vertical stub Söderberg and 9.5% horizontal stub Söderberg) according to figures in a paper by R. Chase et al.¹⁷ As we shall see they accounted for a disproportionate amount of emissions. Bath

chemistry continues to be a well-studied topic and there is debate about the most basic questions, such as whether additions of lithium fluoride are beneficial or not. A good review of bath chemistry is that of H. Kvande.¹⁸

Evolutionary improvements continue; a well-known figure in the aluminum world, Barry Welch, provided figures for the improvement of CE through the mid 1980s in the *Hall-Héroult Centennial* volume.¹⁹ Those percentages were in the 70s for typical cells at the end of the 19th century, rising to the high 80s to 90% in the 1950s, with CE in the 90–95% range for cells in the 1980s. More recently he said,²⁰ “By use of good modern design, cell condition optimization, and extremely good process control and work practices, new technology can operate in the high 96% (even for significant periods exceeding 97%) current efficiencies in the first year or so of operation of the technologies. However, the performance usually deteriorates about 0.5–1% to give long-term efficiencies in the high 95% low 96% region for the best available technology.

Different smelters have different ways of calculating their CE, and this may introduce errors of typically ±1% in the reported values. Despite this it is evident that gains have been made through application of knowledge, fundamentals, design, and control.

The deterioration in CE is associated with deterioration in conditions of the cell (such as cathode lining and its partial coverage with a non-conducting layer—hence impacting current distribution) impacting the magnetic balance and bath flow conditions.

The gains in efficiency can be initially attributed to:

- Reduced average mass transfer coefficient at the metal pad interface by lowering turbulence
- Chemistry control where the ex-

Table II. Costs Savings Estimated by Øye et al. for Various Technical Improvements to Aluminum Electro-winning (1998 \$)

Technical Improvement	Cost Reduction (\$/kg Al)
Decreased Unit Energy (at \$0.03 kWh)	0.16
Labor Savings through More Efficient Productivity and Mechanization	0.13
Improved Electrolyte, Dry Scrubbing, and Fume Control	0.06
Automated Voltage, Alumina, and Anode-Effect Control	0.035
Increased Cathode Life and Optimization of Heat Balance	0.14–0.17

cess aluminum fluoride concentration now exceeds 10% but is less than 11.5%. Going above that value the impact of reducing metal solubility (and consequential operating temperature) further by adding aluminum fluoride is small whereas the stability of operation of the cell (by having good aluminum solubility and not forming sludge and muck, etc.) becomes a more dominant feature.

- Better alumina feeding control logic to ensure better alumina “solubility”

In some technologies, introduction of slotted anodes to direct the gas and hence the flow and mixing of the electrolyte have also enabled the current densities or line currents to be increased while maintaining CE. Essentially, then, the cells are operating at the limit of alumina solubility.

For cells with efficiencies above 95.5%, the main mode of loss in efficiency becomes short- or long-term short circuiting between the anode and the metal pad (the formation of spikes, protrusions, and bellies). This occurs when the cells are at low anode-cathode distance, and low superheats and the rate of melting of the freeze formed under newly set anodes is slow. The consequential redistribution of current results in changing magnetic fields with horizontal currents in localized zones and, because of the low density difference in metal and bath, much shorter intra-electrode distances. Thus, work practices

and control practices around them become contributing factors.

In other words, we are now away from simply looking at mass transfer theory from the metal pad to the deoxidizing zone, although this is still part of the efficiency loss. Having a low metal saturation solubility, as currently happens, gives a significant reduction in that parameter. Voltages of modern cells in operation are typically in the range 4.00 to 4.20—this voltage includes the external bus bars.

New technologies are generally designed and built to operate above 330 kA and at current densities up to 0.86 A/cm² (both anode and cathode).⁷

Several of the papers surveyed for this article have ascribed Hall-Héroult cell improvements partly to the success of mathematical modeling of cells. This topic is reviewed in a volume of the *Encyclopedia of Electrochemistry*,²¹ and space limitations preclude a repetition here. Recent models have mostly been concerned with the stability of the bath-metal interface; just one example is the work of A. Gusev and colleagues²² from which Figure 8 is taken. The model of a Rusal cell was tested against magnetic field measurements. The model shows that this cell is operated in a stable regime under normal working conditions (filled dark circles) but that reducing the anode-cathode distance (arrows), or reducing the metal depth at constant ACD, brings the cell to instability (the red colored region). This was confirmed by experiment. A paper with fine illustrations of

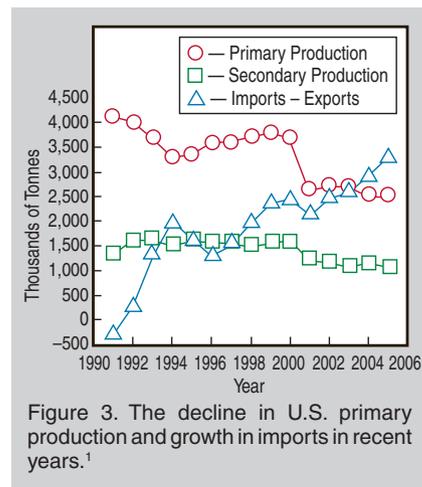


Figure 3. The decline in U.S. primary production and growth in imports in recent years.¹

many capabilities of modeling is that of M. Dupuis and collaborators on a (yet to be built) 500 kA cell.²³ Nowadays it is almost inconceivable to develop a new cell design without prior extensive mathematical modeling; capital costs (Table III, taken from L. Berrueta’s paper²⁴ shows some of these costs) are huge so that every effort must be made to avoid failure or even redesign.

Whatever one’s views on global warming, it is evident that climate change is here already as a political and therefore economic consideration. (For example, the governor of my state, a Republican, recently signed a bill, passed by the Democratic legislature, which mandates a reduction in the fraction of the state’s electricity supply generated from fossil fuels.) Therefore the aluminum industry has for several years curbed the emissions of fluorides from Hall-Héroult cells. Particularly notable are the emissions of the perfluorocarbons (PFCs) (tetrafluoromethane and hexafluoroethane); the IAI reports a kilogram of the former to have 6,500 times the global warming effect of a kilogram of CO₂.²⁵ These PFCs are primarily generated during anode effects which result from the alumina content of the electrolyte dropping to abnormally low levels. Avoidance of anode effects is therefore a matter of good control of alumina feeding to the cell and its rapid dissolution. The IAI has surveyed PFC emissions from smelters for some years and Figure 9 is taken from a recent paper of authors from that organization.²⁶ Clearly progress has been made in minimizing PFC emissions.

The industry’s past and future efforts to minimize electrical energy consumption also reap benefits in the reduction of greenhouse gas emission at the power

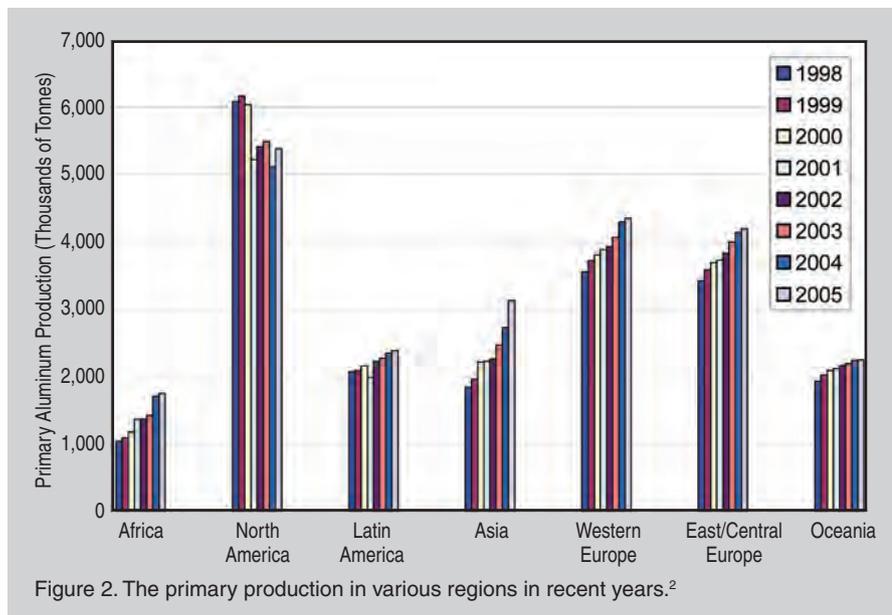


Figure 2. The primary production in various regions in recent years.²

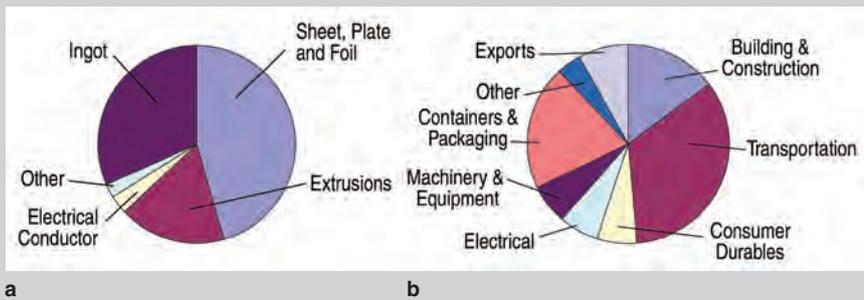


Figure 4. (a) Form of aluminum shipments (%) in North America, 2004; (b) end uses of aluminum in North America, 2004.⁵

cal heating. Carbothermic reduction is presently under development in a joint effort by Alcoa and Elkem.³⁴

Downstream Processing

There have been commensurate advances in the past 50 years in the casting of aluminum and its alloys, along with advances in rolling, extrusion, and other finishing operations. Figure 10, from P. Waite's paper,³⁵ is a schematic of the technology under discussion. This paper focuses on molten metal processing (between the potroom or melting furnace and the caster) and details the treatment of the metal to remove impurities. It also chronicles Alcan's interest in minimizing the use of chlorine fluxing to that end.

D.L. Stewart³⁶ has provided an overview of current melting technology and future trends while E. Rooy³⁷ has written an account of developments in casting and fabrication with an historical emphasis plus a glimpse of the future. The caster on the lower right of Figure 10 is a direct chill (DC) caster which is the commonly used device for producing sheet ingots and extrusion billet. W. Schneider³⁸ has reviewed the past, present, and future of DC casting in a paper containing many informative illustrations. In the paper by H.A. Øye and collaborators¹⁰ the growth of the size of DC cast sheet ingot is described. They report that a "giant" ingot in 1948 was 30 cm × 76 cm × 183 cm while a comparable ingot in 1999 would be 66 cm × 249 cm × 914 cm.

R.E. Sanders³⁹ has written on many aspects of technology innovation in aluminum products. The upper caster in Figure 10 is a twin roll caster which

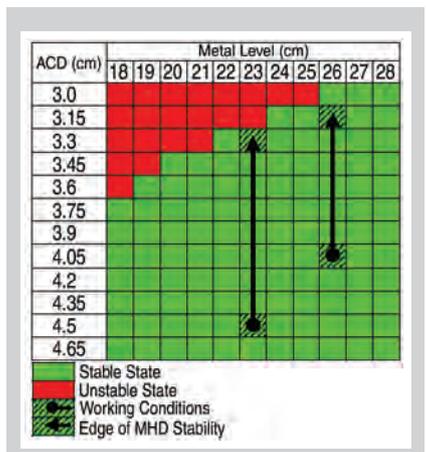


Figure 8. The stability/instability boundary determined by the mathematical modeling of Gusev and colleagues.

plant, depending on the extent to which that plant uses fossil fuels. However, an additional contribution to CO₂ emission is the consumption of the carbon anodes to produce this gas. This provides one of several incentives for the development of an inert anode. Work to this end through the late 1990s was summarized by J.W. Evans and D. Ziegler²¹ and included an effort at Alcoa during the 1980s to develop a cermet anode with a nickel ferrite/nickel oxide ceramic phase and a nickel or copper metallic phase. R.P. Pawlek²⁷ has provided an update on inert anodes with 64 references, mostly in the patent literature through 2002. There has recently been interest in metal-

lic inert anodes²⁸ including one advanced by V. de Nora.^{29,30} Of course research and development on carbon anodes continues and an account of future needs for anodes is that of W.K. Fischer and colleagues.³¹ In surveying needs through 2015, these authors provide projections of the countries where smelters will be built in the next decade.

The inert anode of the last paragraph would be a revolutionary change in aluminum extraction, eliminating, for example, Söderberg anodes or the pre-bake anode plants that have been adjuncts to potlines for more than a century. Another revolutionary development would be the advent of a wettable cathode material such as a titanium diboride coating that would provide an opportunity for a substantial reduction in ACD and thereby cell voltage. These too are described at greater length in Reference 21. A recent paper on TiB₂ is that of N. Feng et al.³² Even more revolutionary would be the near-room-temperature electrowinning of aluminum, as described in papers from R.G. Reddy's group,³³ using ionic liquids. These liquids are aprotic organic liquids with high conductivity that are capable of dissolving, for example, aluminum chloride. This forms an electrolyte from which solid aluminum can be electrowon in much the same way that copper or zinc are electrowon (in those cases from aqueous solutions). Finally, the carbothermic reduction of alumina should be mentioned. This technology would be as revolutionary to the aluminum industry as fusion would be to the nuclear power industry and has proved just as elusive over many decades. In its simplest form a device akin to the iron blast furnace would be used with carbon (coke) serving both as a reductant and a fuel. In reality vaporization of aluminum and its suboxide mandates the need for electri-

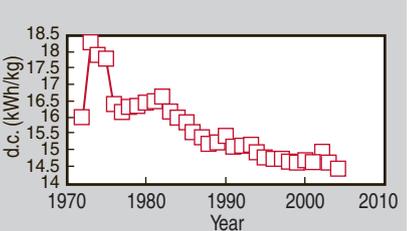


Figure 5. Electrical energy consumption per kilogram of aluminum reported by Woodfield et al.

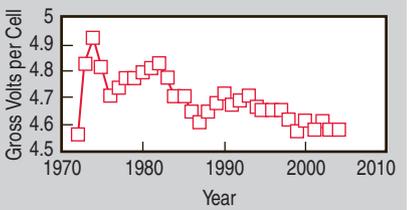


Figure 6. The improvement of cell voltage reported by Woodfield et al.

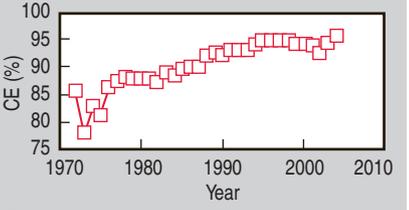


Figure 7. Improvement of current efficiency (CE) reported by Woodfield et al.

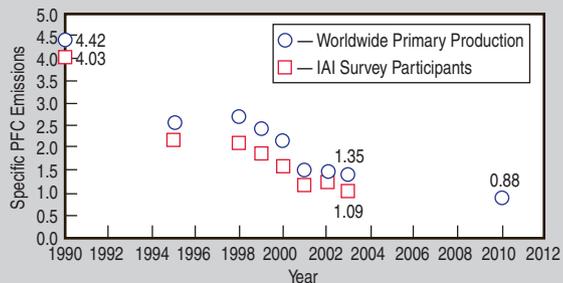


Figure 9. The PFC emissions as reported by the International Aluminium Institute and the IAI member companies' target for 2010.

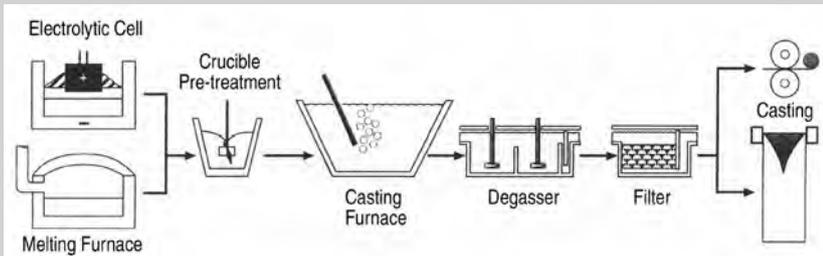


Figure 10. The sequence of molten metal processing steps (from *Light Metals 2002*, p. 842).

produces a continuous strip, 5–10 mm thick and suitable for rolling to thinner sheet, by solidifying the metal between two water-cooled steel rolls (Figure 11). Sanders reports (2001) that strip can now be produced in widths of more than 2.1 meters and that twin roll casters are the largest producers of continuously cast aluminum flat-rolled products with more than 260 casters in operation worldwide.

Just as in Hall-Héroult cell development, mathematical modeling has played a role in downstream processing. One example is the paper by V. Goutière et al.⁴⁰ on modeling a melting furnace; another is the work of A. Fjeld and others⁴¹ on the modeling of gas fluxing

Recycling of Aluminum

As Figure 3 shows, the secondary production of aluminum has been roughly half the primary production in recent years. The energy required to melt and process recycled aluminum is just 5% of that required for primary production.¹⁰ This is shown clearly in Figure 12 from the paper by T.A. Utigard.⁴² All the steps to the left of Clean/Alloy are eliminated in the case of secondary production. Therefore we may anticipate that recycling will remain a significant part of metal production in the future. (P.R. Bruggink and K.S. Martchek⁴³ predict a growth in the secondary to primary production ratio based on the model that they developed at Alcoa. They also examine the reduction in greenhouse gas emissions consequent

to this growth.) Much of this recycled aluminum is made up of used beverage cans. Although the rate of recycling of such cans has diminished recently⁵ (Figure 13), even in 2005, 52% of aluminum cans produced in the United States were recycled (down from a peak of 67.9 in 1992). Recycle rates in Europe have tended to be lower, for example 35% in 1995¹⁰ when the U.S. recycling rate was 62.2%. Two very recent articles on can recycling are those concerning a study in Fayette County, Kentucky, which is trying to find the causes of the recent drop in recycling evident in Figure 13.^{44,45} However, it is evident that this is still a work in progress.

The Future

It seems inevitable that the growth in aluminum production will continue as the world's two most populous nations expand their economies and environmental considerations drive the increasing use of aluminum in transportation. In developed countries, which typically have high electricity costs, the increased reliance on imported and recycled metal seems unavoidable. Thus aluminum production will be even more an international activity with the second "a" in Alcoa and the last three letters in Alcan becoming meaningless. The Hall-Héroult cell will continue to evolve with older plants, for example ones with Söderberg anodes, being phased out in favor of newer, larger cells in distant countries. It seems likely that there will be increased monitoring of cell param-

eters, particularly environmental ones, using modern instrumentation such as wireless devices.⁴⁶ At the revolutionary level, the success of inert anodes seems likely because of the possibility for the industry to reduce greenhouse gas emissions by their use. Wettable cathodes appear at first to be an easier materials challenge and one where energy savings would be the "low hanging fruit." However, large-scale projects spanning a couple of decades, involving TiB₂ and composites thereof, have failed to achieve widespread commercial acceptance. Even more revolutionary would be low-temperature electrowinning using ionic liquids and carbothermic reduction. The former is dependent on converting alumina into a species soluble in the liquid (e.g., aluminum chloride) and a radical conversion to technology similar to that of the copper industry, but both of these seem practical. Carbothermic reduction appears, to this author, to have a lower ratio of benefits to development costs and risks. Evolution in downstream processing is to be expected with further advancement in continuous casting, resulting in, for example, not just an increasing number of casters but increased strip width and casting speed. Advancement of DC cast-

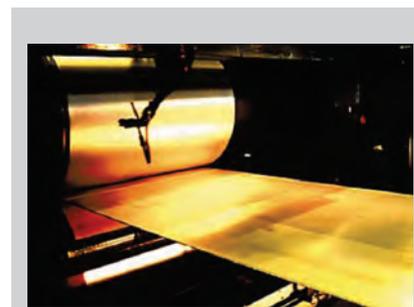


Figure 11. Aluminum strip emerging from a twin roll caster (from Sanders).

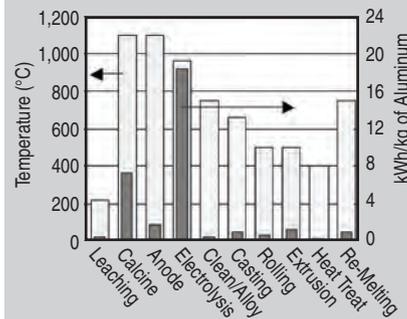


Figure 12. Temperatures and energy consumptions entailed in the various steps of primary and secondary aluminum production (from Utigard).

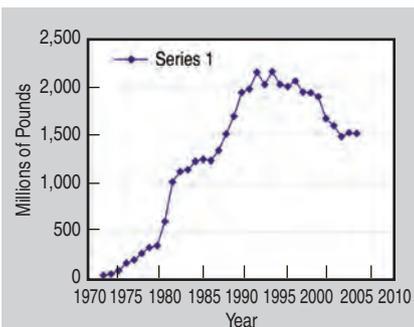


Figure 13. The weight of used aluminum beverage cans recycled in the United States each year (from Aluminum Association data).

ing has been significant over the past decade with large non-rectangular cross sections now being possible. Here, too, some increase in casting speed would be beneficial; the speed at which a DC caster operates is well below the speed at which a continuous slab caster operates in the steel industry.

MAGNESIUM

The Significance of Magnesium

The world's production of magnesium has also grown over much of the past century, as seen in Figure 14, although with more variability than seen for aluminum in Figure 1. (It is assumed in what follows that the statistics exclude magnesium produced in the Kroll process for immediate use in titanium production.) Part of that variability is linked to substantial variability in metal price. For example the U.S. Geological Survey¹ reports the value of a tonne of the metal (in \$1998) as peaking at \$5,860 in 1977, with \$4,930 in 1995 and \$2,320 in 2002. The *Metal Bulletin* year-end European free market price in 2005 was reported as \$1,650/tonne. Besides these price fluctuations the magnesium industry has met with substantial changes in the technology by which the metal is produced and in the location of that production. As recently as 1998, F.H.Froes and coauthors⁴⁷ declared "... currently the majority of production on a worldwide scale is by the electrolytic method." Now there has been a reversion to the older silicothermic reduction of magnesium oxide (the Pidgeon process and its variants); R. Harris and collaborators⁴⁸ are among those pointing to the near dominance of magnesium production by China (450 kt in 2005 versus 85 kt in 1998) and the sorry state of North American production (e.g.

U.S. production of 51 kt in 2005 versus 90 kt in 1998 and even higher production prior to that date). There are currently six electrolytic magnesium plants around the world (with one slated to close next year), plus another five producing magnesium solely for use in titanium production.⁴⁹

Magnesium continues to find use as an alloying element with aluminum and for die castings. Table IV, from International Magnesium Association statistics, shows the strong growth in the latter application. The breakdown of the magnesium castings market is shown in Figure 15 and the very substantial fraction represented by use in the automotive industry is apparent. A.A. Luo has given details of the uses to which the Big Three automakers in the United States are putting magnesium.⁵²

The Technology of Magnesium Production

Brown⁵³ has catalogued the major magnesium projects from 1950 through the end of the last century. F. Habashi⁵⁴ has provided an account, with a historical emphasis, of both the silicothermic and electrolytic routes to magnesium. Habashi's text⁵⁵ on amalgam and electrometallurgy has a good account of the electrolytic route. There are two variants of the latter which use either anhydrous magnesium chloride feed or a hydrated chloride feed. The hydrated chloride approach has the advantage of a simpler feed preparation but a cell where the graphite anodes are consumed at a high rate due to the inevitable presence of water in the electrolyte. The principal plant at which this hydrated chloride approach was exploited (Dow Chemical in Texas) is now closed so that this technology is given no further treatment here. The anhydrous chloride approach entails first preparation of solid magnesium oxychloride by processing

Table III. Investment Cost for a Potline of 240 V350 Cells Reported by Berrueta

Description	Cost (\$ Million)
Soil and Land Preparation	14.1
Potroom and Buildings	47.0
Pots	159.0
Pot Tending Equipment	27.7
Power Substation	30.7
Alumina Conveying and Storage System	31.2
Fume Treatment System	43.7
Compressed Air System	6.4
Electrical System	7.5
Bath Recycling System	9.9
Ladle Cleaning Shop	2.6
Casthouse	40.0
Paste Plant	30.0
Baking Furnace	50.0
Anode Rodding Shop	10.7
Pitch Terminal	2.3
Dock Facilities	40.0
Other Services (water, gas, etc.)	3.0
Freight of Imported Goods	24.9
Others	40.0
Contingency	31.0
TOTAL	651.7

brines containing magnesium chloride, the latter obtained, for example, by evaporation of sea water or natural brines. The oxychloride is then chlorinated in the presence of carbon to yield carbon monoxide and molten anhydrous magnesium chloride that is transferred to the electrolytic cells. This carbochlorination step is a crucial one and Harris et al. have provided a detailed examination of the technology (and alternative routes to anhydrous chlorides).⁴⁸

The original electrolytic cell used commercially with an anhydrous chloride feed was the I.G. Farben cell illustrated in Figure 16. The cell is sealed so as to capture the chlorine generated at the vertical graphite anodes and minimize oxidation of the liquid magnesium product. The cathodes are vertical steel sheets. The electrolyte, at 750–780°C, is

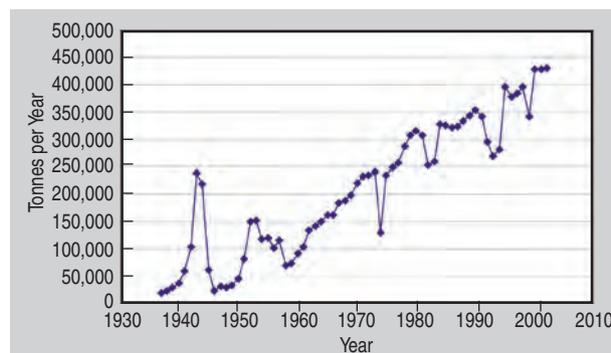


Figure 14. The world production of magnesium. Plotted from U.S. Geological Survey statistics.¹

Table IV. Major Uses of Magnesium. Prepared from IMA Statistics⁵⁰

Application	Tonnes 1996	Tonnes 2002
Aluminum Alloying	138,200	145,613
Desulfurization	39,600	57,385
Die Casting	72,300	127,803
Other	Balance	Balance
TOTAL	295,400	364,959

a molten mixture of chlorides of calcium, potassium, sodium, and magnesium with the addition of a small amount of calcium chloride. A distinctive feature of magnesium electrowinning, compared to aluminum electrowinning, is that the liquid metal produced is less dense than the electrolyte and consequently floats to the top of the cell. Therefore, the cell is designed to minimize contact of the chlorine from the anodes with metal from the cathodes which would cause reaction of the two; this separation is achieved by the partition walls seen projecting down from the top of the cell to part way between anodes and cathodes. Alternatives are less complicated designs where the metal and electrolyte flow into a separation chamber where molten magnesium rises to the surface and the electrolyte returns

to the electrolysis compartment.⁵⁶ Such is the Norsk Hydro cell seen in Figure 17. The gas lift caused by chlorine evolution on the anode provides the force to bring about the circulation of the electrolyte and magnesium.

R.L. Thayer and R. Neelamegghan⁵⁷ have written on the extensive modernizations made at one magnesium plant (U.S. Magnesium). No drawing of the cells is provided but, from the description: "These new electrolyzers, referred to as M cells, are large-scale, monopolar diaphragmless electrolyzers. These units utilize large electrodes, a reduced interelectrode distance (less than 30 mm), and channeled magnesium collection," it can be guessed that they bear similarity to the Norsk Hydro cell. These authors report a substantial energy saving (12.1–14.3 kWh/kg magnesium compared to 18.8–19.9 kWh/kg for an I.G. Farben cell). Table V,⁵⁸ taken from this paper, details the performance of the M cell compared to other cells. The introduction of the M cell and improvement in feed preparation, notably a third chlorination stage, resulted in a 20% reduction in overall production costs.

The silicothermic production starts with magnesium oxide or calcined dolomite (CaO·MgO). As practiced in the Pidgeon process the silicothermic reduction is a batch process where retorts are packed with magnesium oxide and ferrosilicon and then the retorts are externally heated to bring about the reduction reaction shown in Figure 18a.

The reduction is thermodynamically remarkable in that, at the reduction temperature (approximately 1,200°C) the free energy of reaction is positive (i.e., the reaction would not be expected to occur). However the reactor is run at low pressure, approximately 0.1 Pa, so that the magnesium vaporizes and leaves the reduction zone, achieving separa-

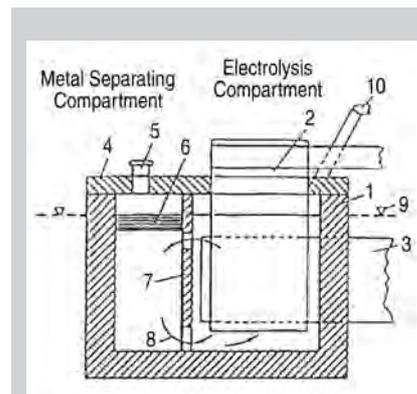


Figure 17. Norsk Hydro cell. 1 = refractory lining, 2 = graphite anode, 3 = steel cathode, 4 = refractory cover, 5 = metal outlet, 6 = metal, 7 = partition wall, 8 = return flow of electrolyte, 9 = electrolyte level, 10 = chlorine outlet.

tion from the other reaction products. The vaporized magnesium condenses at the mouth of the retort and, after reaction is completed, the condensed magnesium is removed from the retort which is then reloaded with briquetted feed for the next batch. Figure 18b is a photograph of retorts in a furnace in Nanjing, China.⁵⁸

An overview of the Pidgeon process in China has been provided by J.C. Zang and W. Ding.⁵⁹ The energy consumptions of an electrolytic and Pidgeon processes have been compared by S. Ramakrishnan and P. Koltun.⁶⁰ The electrolytic technology was a proposed one from Australian Magnesium Corporation at the heart of which was an Alcan multipolar cell. These authors conclude that, if all process energy expenditures are accounted for (e.g., including the energy for dolomite calcination), then the electrolytic technology is more energy efficient (174 MJ/kg Mg versus 284 MJ/kg for the Pidgeon process). Ramakrishnan, Koltun, and Tharumarajah⁶¹ subsequently studied the life cycle environmental impact of a magnesium automotive component, a converter housing, compared to the cost

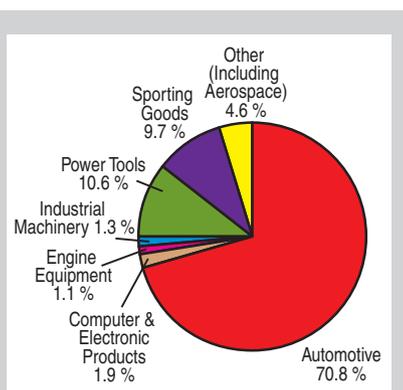


Figure 15. U.S. magnesium die casting market (from K. Jereza et al.)⁵¹

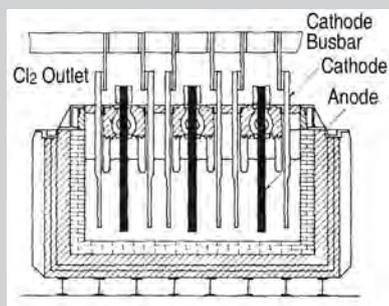


Figure 16. I.G. Farben magnesium cell (from Habashi.)⁵⁵

Table V. Comparison of Industrial DC Cells*

Company	Cell	Cell Type	Power Voltage	Unit Efficiency	Production
Norsk-Hydro	DLE	Monopolar	5.3 V	13.0 kwh/kg	>4.0 t/d
Alcan Int.	MP3	Multipolar	NA	10.5 kwh/kg	NA
MagCorp.	M-Cell	Monopolar	5.0 V	12.6 kwh/kg	2.8 t/d
AVISMA	Bottom entry	Monopolar	4.7 V	13.5 kwh/kg	0.7 t/d
UKTMP (Kaz)	Top entry	Monopolar	4.8 V	13.2 kwh/kg	1.8 t/d

*Competitor information was derived from published reports and the basis of evaluation in each category may be inconsistent.

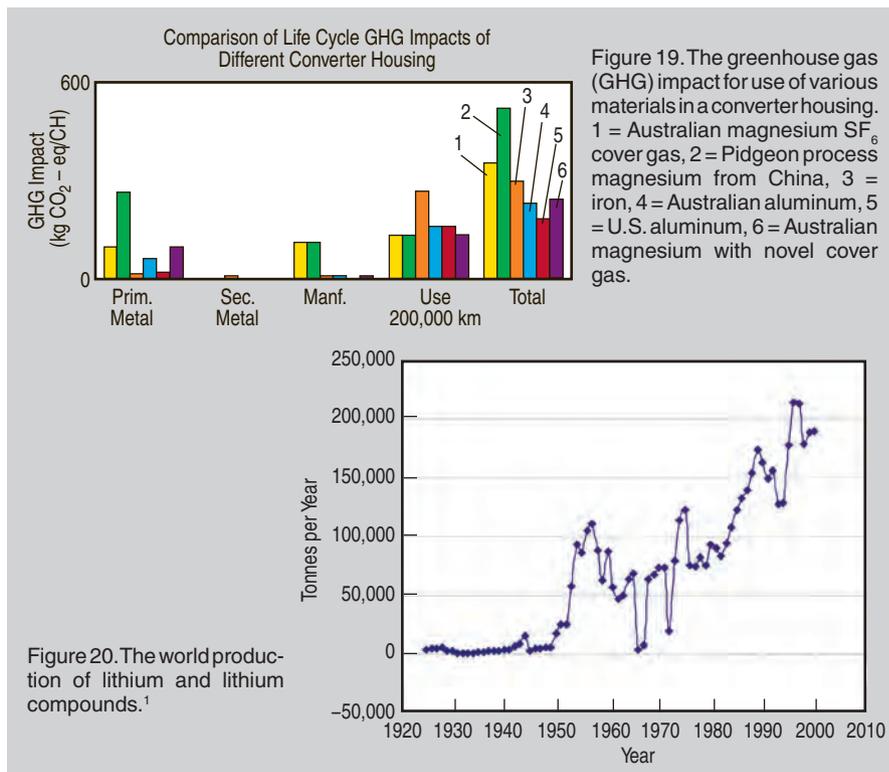
in other materials. Figure 19 is taken from their results and shows an advantage for electrolytic magnesium over Pidgeon process magnesium but a higher greenhouse gas emission level compared to a CH produced with the mix of primary and recycled aluminum existing in the United States. H. Xu et al. have recently compared the energy consumption of the Pidgeon and electrolytic processes arguing that the former need not necessarily suffer from a high energy consumption.⁶² They suggest modifications to the Pidgeon process, such as energy recovery from furnace off-gasses that might curtail energy consumption.

Recycling of magnesium scrap has been discussed by H. Antrekowitsch and coauthors,⁶³ among others, and A. Javaid and colleagues⁶⁴ have recently reviewed the literature on this topic.

The future of magnesium is hard to estimate because of the current anomalous situation where one nation has a near monopoly on production but appears to be using technology that is inefficient in terms of energy and environmental impact.

ALKALI METALS

The only alkali metal that should be considered a material, rather than a reagent, is lithium, which finds use in aluminum-lithium alloys. Such alloys



have a density advantage over other aluminum alloys and therefore find use in aerospace applications. Figure 20 gives the world production of lithium but these figures include production of lithium compounds for use other than the production of metals or alloys. The *Journal of the Electrochemical Society* provides an annual report on the electrolytic industries, for example the 2004

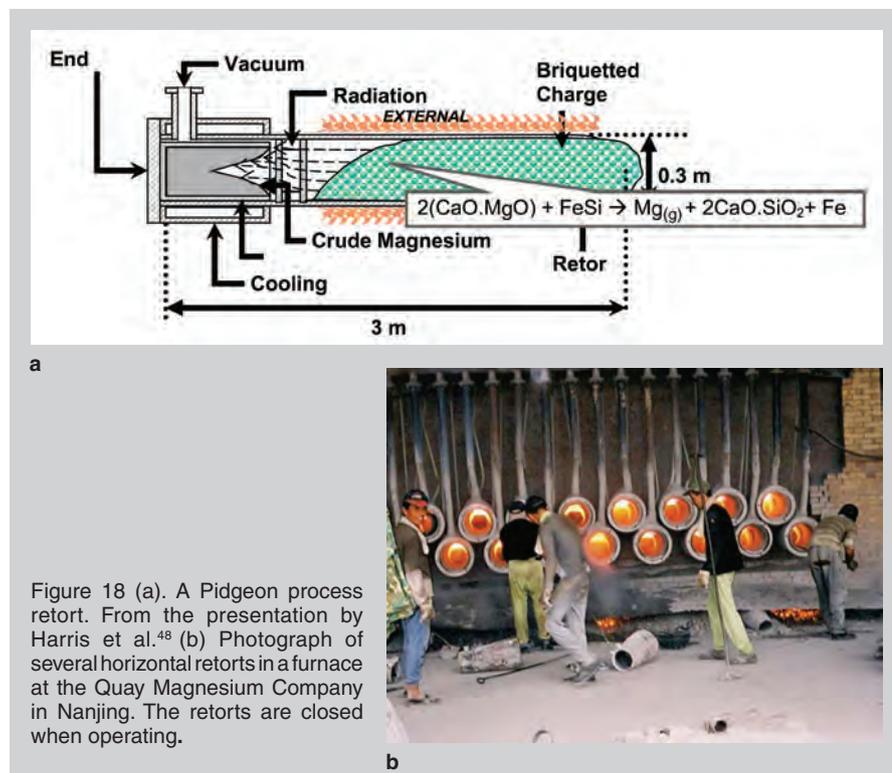
report⁶⁵ that is the latest available at the time of writing, and the interested reader is referred to those reports for information on alkali metals.

ACKNOWLEDGEMENT

The comments from Barry Welch and helpful suggestions from D. Ziegler of Alcoa, M. Earlam of Timet, and R. Neelamegghan of U.S. Magnesium are gratefully acknowledged. R. Harris of McGill University is thanked for a copy of his unpublished comprehensive examination of magnesium production.⁴⁸

References

1. USGS mineral data available at <http://minerals.usgs.gov/minerals/>.
2. From International Aluminium Institute statistics available at www.world-aluminium.org/iai/stats/index.asp.
3. P.A. Plunkert and E.D. Sehnke, *Aluminum, Bauxite and Alumina Annual Report* (Washington, DC: U.S. Bureau of Mines, 1991).
4. S.K. Das et al., *JOM*, 56 (8) (2004), p. 14.
5. Aluminum Association statistics at www.aluminum.org.
6. *Aluminum Now*, 8 (5) (Sept./Oct. 2006), p. 18.
7. M. Taylor, *San Francisco Chronicle* (27 October 2006).
8. K. Gjotheim et al., *Aluminium Electrolysis: The Chemistry of the Hall-Héroult Process* (Düsseldorf: Aluminium-Verlag, 1977).
9. K. Gjotheim and B.J. Welch, *Aluminum Smelter Technology* (Düsseldorf: Aluminium-Verlag, 1980).
10. H.A. Øye et al., *JOM*, 51 (2) (1999), p. 29.
11. K. Gjotheim et al., *JOM*, 47 (11) (1995), p. 32.
12. C. Carroll, "The Role of Technology in the Global Primary Aluminum Industry Today and in the Future" (Presentation at the TMS Annual Meeting, San Francisco, February 2005).
13. C. Vanvoren et al., *Light Metals 2003*, ed. P. Crepeau



(Warrendale, PA: TMS, 2003), p. 185.
 14. S.C. Tandon and R.N. Prasad, *Light Metals 2003*, ed. P. Crepeau (Warrendale, PA: TMS, 2003), p. 379.
 15. D. Woodfield et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 231.
 16. G.P. Tarcy and K. Torklep, *Light Metals 2005*, ed. H. Kvande (Warrendale, PA: TMS, 2005), p. 319.
 17. R. Chase, R. Gibson, and J. Marks, *Light Metals 2005*, ed. H. Kvande (Warrendale, PA: TMS, 2005), p. 279.
 18. H. Kvande, *JOM*, 46 (11) (1994), p. 22.
 19. B.J. Welch, *Hall-Héroult Centennial*, ed. W.S. Peterson and R. Miller (Warrendale, PA: The Metallurgical Society, 1986), p. 120.
 20. Barry J. Welch, private communication (October 2006).
 21. J.W. Evans and D. Ziegler, *Encyclopedia of Electrochemistry*, 5 (2006).
 22. A. Gusev et al., *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 467.
 23. M. Dupuis et al., *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 453.
 24. L. Berrueta, *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 223.
 25. International Aluminium Institute, World-Aluminium.org, www.world-aluminium.org/environment/climate/index.html.
 26. R. Chase et al., *Light Metals 2005*, ed. H. Kvande (Warrendale, PA: TMS, 2005), p. 279.
 27. R.P. Pawlek, *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 283.
 28. J. Yang et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 421.
 29. J. Antille et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 391.
 30. R. von Kaenel and V. De Nora, *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 403.
 31. W.K. Fischer et al., *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 579.

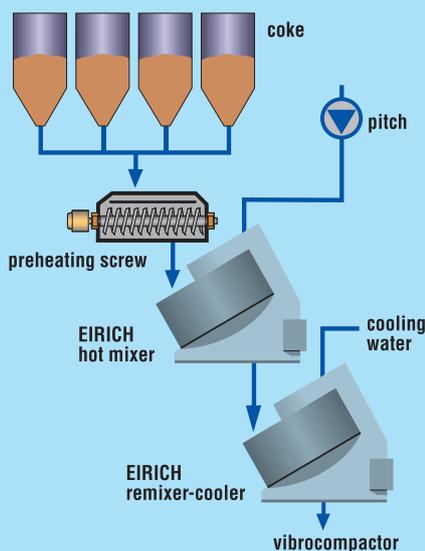
32. N. Feng et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 505.
 33. M. Zhang and R.G. Reddy, *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 451.6
 34. W. Choate and J. Green, *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 445.
 35. P. Waite, *Light Metals 2002*, ed. W. Schneider (Warrendale, PA: TMS, 2002), p. 841.
 36. D.L. Stewart, *Light Metals 2002*, ed. W. Schneider (Warrendale, PA: TMS, 2002), p. 719.
 37. E. Rooy, *Light Metals 2000*, ed. R.D. Peterson (Warrendale, PA: TMS, 2000), p. 33.
 38. W. Schneider, *Light Metals 2002*, ed. W. Schneider (Warrendale, PA: TMS, 2002), p. 953.
 39. R.E. Sanders, *JOM*, 53 (2) (2001), p. 21.
 40. V. Goutière et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 157.
 41. A. Fjeld, J.W. Evans, and C. Chesonis, *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 771.
 42. T.A. Utigard, *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 289.
 43. P.R. Bruggink and K.J. Martchek, *Light Metals 2004*, ed. A.T. Taberaux (Warrendale, PA: TMS, 2004), p. 907.
 44. S.K. Das and M. Hughes, *JOM*, 58 (8) (2006), p. 27.
 45. F.W. Morgan and M.V. Hughes, *JOM*, 58 (8) (2006), p. 32.
 46. M. Schneider et al., *Light Metals 2006*, ed. T.J. Galloway (Warrendale, PA: TMS, 2006), p. 331.
 47. F.H. Froes et al., *JOM*, 50 (9) (1998), p. 30.
 48. R. Harris et al. (Presentation at the International Symposium Magnesium Technology in the Global Age, Conference of Metallurgists, Montreal, October 2006).
 49. R. Neelamegghan, private communication (November 2006).
 50. International Magnesium Association, www.intlmg.org.

51. K. Jereza et al., *Magnesium Technology 2006*, ed. A.A. Luo et al. (Warrendale, PA: TMS, 2006), p. 89.
 52. A.A. Luo, *JOM*, 54 (2) (2002), p. 42.
 53. R.E. Brown, *Magnesium Technology 2000*, ed. H.I. Kaplan et al. (Warrendale, PA: TMS, 2000), p. 3.
 54. H. Habashi, *Magnesium Technology in the Global Age*, ed. M.O. Pekguleryuz and L.W.F. Mackenzie (Montreal, Canada: MetSocCIM, 2006), p. 31.
 55. F. Habashi, *Principles of Extractive Metallurgy; Amalgam and Electrometallurgy* (Sainte-Foy, Québec, Canada: Métallurgie Extractive Québec, 1998).
 56. O. Wallevik et al., *Magnesium Technology 2000*, ed. H.I. Kaplan et al. (Warrendale, PA: TMS, 2000), p. 13.
 57. R.L. Thayer and R. Neelamegghan, *JOM*, 53 (8) (2001), p. 15.
 58. Quay Magnesium, Sydney, NSW, Australia, www.quaymagnesium.com.
 59. J.C. Zang and W. Ding, *Magnesium Technology 2001*, ed. J. Hryn (Warrendale, PA: TMS, 2001), p. 7.
 60. S. Ramakrishnan and P. Koltun, *Magnesium Technology 2004*, ed. A.A. Luo (Warrendale, PA: TMS, 2004), p. 173.
 61. P. Koltun et al., *Magnesium Technology 2005*, ed. N.R. Neelamegghan et al. (Warrendale, PA: TMS, 2005), p. 43.
 62. H. Xu et al. (Presentation at the 63rd Annual World Magnesium Conference [IMA], Beijing, China, 21–24 May 2006).
 63. H. Antrekowitsch et al., *Magnesium Technology 2002*, ed. H.I. Kaplan (Warrendale, PA: TMS, 2002), p. 43.
 64. A. Javaid, *Magnesium Technology 2006*, ed. A.A. Luo et al. (Warrendale, PA: TMS, 2006), p. 7.
 65. V. Srinivasan et al., *J. Electrochem. Soc.*, 153, K1 (2006), p. 4.

James W. Evans with the Department of Materials Science and Engineering at the University of California at Berkeley. He can be reached at (510) 642-3807; e-mail evans@berkeley.edu.

EIRICH Carbon Technology

Continuous preparation of anode paste

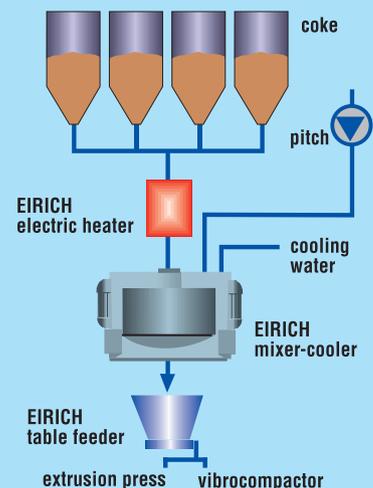


Your advantages:

- low investment costs
- low operating and maintenance costs
- optimum mixing and cooling conditions
- excellent paste quality

Visit us
at TMS 2007
Booth #223

Batch preparation of electrode + cathode paste



Eirich Machines, Inc.

4033 Ryan Road, Gurnee, IL 60031
 Phone: 847-336-2444, Fax: 847-336-0914

Email: eirichsales@eirichusa.com
 Web: www.eirichusa.com



EIRICH