# Market Dynamics, Recycling and Recovery of Magnesium from Aluminum Alloy Scrap

A.J. Gesing and S.K. Das

**Abstract** This paper provides an overview of North American markets for magnesium and aluminum alloys along with life cycle material flow diagrams. Additionally, we review the production processes of magnesium and its alloys from various magnesium-bearing raw materials, including scrap. The main focus of the paper is on the collection, recycling and processing of post- and pre-consumer metal scrap containing magnesium. We discuss the latest status and economic analysis of RE-12<sup>TM</sup>, a scrap-based process for recovering magnesium from aluminum alloys and its potential application to can sheet, automotive (body and closure sheets) and aluminum foundry markets.

**Keywords** Magnesium recycling  $\cdot$  Aluminum recycling  $\cdot$  Magnesium electrorefining  $\cdot$  Market economics  $\cdot$  RE-12<sup>TM</sup> electrorefining process

### Introduction

# Aluminum and Magnesium Production and the Scrap Industry

Primary aluminum is produced exclusively from bauxite ore through refining to alumina (Bayer process) and electrowinning to primary Al metal melt (Hall-Héroult process). The energy cost of the electrowinning step is 13–15 kWh/kg, and a total mine-to-metal melt energy cost of nearly 56 kWh/kg. Primary magnesium metal can be produced by several methods. The two leading methods are silicothermic reduction of calcined magnesite (the Pidgeon process), and electrowinning of MgCl<sub>2</sub> that can be produced from seawater, lake salt deposits, or by carbo-chlorination of MgO-containing oxide ores. The Pidgeon process, which is practiced mostly in China using highly environmentally and energy inefficient

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technologies, currently dominates the prime Mg market producing Mg at the lowest dollar cost with a total mine-to-metal melt energy cost of over 100 kWh/kg.

Aluminum metal recycling is an integral part of the global material recovery and recycling system that supplies the material needs of the industry and society from the growing urban mine at a small fraction of the capital and energy cost that it takes to mine and process raw materials. Recycled Al alloys contain Mg as one of the alloying elements. Hence Al recycling also manages to recycle a large proportion of Mg metal units contained in these Al alloys. This recycling system is critically important to achieving a sustainable society and economy. A magnesium-based alloy recycling system is still in its infancy with only new Mg die-casting scrap being thoroughly collected and closed-loop recycled. The small proportion of magnesium-alloy scrap in machine shops makes it inconvenient to source-segregate Mg cut-offs and machining chips by alloy. The small proportion of magnesium alloys in consumer products makes it more profitable to leave it in the Al scrap then to separate it as a Mg-scrap product. In cases where old scrap Mg alloy mix is separated from light metal scrap, it is typically consumed as a desulfurizing agent for steel production.

New scrap is produced during material production and product fabrication, while old scrap is a post-consumer material. While most new scrap can be segregated at source by alloy for recycling to a composition-compatible alloy, it is often not practical to separate clippings, machining chips and turnings in large machine shops. As a result, these items constitute a major mixed-new-scrap category that is of low value and is downgraded to low-grade Al foundry alloys, where it is used after chlorinating the magnesium content out of the aluminum alloy scrap melt. The magnesium content of aluminum scrap destined for Al foundry alloys ends up as Mg-chloride contaminant of chlorination dross to be disposed of as salt-contaminated waste.

Old aluminum scrap is gathered through well-established collection systems for end-of-life vehicles, building demolition waste, food packaging, electrical and electronic waste and other metals collected by scrap yards. In any collection system, Al is not collected separately from other materials. Aluminum cans and rigid foil are recovered from food packaging by sorting in municipal recycling facilities (MRFs). At scrap yards there is a certain amount of manual sorting and grouping by International Scrap Recycling Institute (ISRI) categories, but these separate scrap by parent metal and generic source and shape, but not by alloy.

Old Al Sheet, a mixed-alloy category that groups old wrought Al alloys, is among the largest of the Al categories. The remaining scrap (from vehicles, machinery and building demolition residue) is shredded and then mechanically separated into ferromagnetic metals, non-magnetic metals and non-metals. Aluminum and magnesium contents are recovered together from non-magnetic metals by density separation and eddy current rotor cleanup and are almost exclusively used in secondary aluminum foundry alloys.

Pre-sorting and pre-cleaning is an integral part of the global material recycling system. With new scrap the best practice is to maintain and track alloy segregation at source. With old scrap, currently, density-based physical separation methods produce a Mg- and Al-containing light alloy mixture as a single shredded fraction sold to secondary Al smelters. In the USA over 35,000 tons annually of Mg ends up as a contaminant in the Al foundry alloy melt to be chlorinated out to a specification of <0.1% Mg. This amounts to ~50% of primary Mg production in the USA. <u>There is, therefore, a need for Mg recovery.</u> A practical way of recovering Mg from Al melt is to electrorefine. A Mg electrorefiner uses Mg-contaminated Al alloy melt as an anode electrolytically oxidizing the Mg and transporting it as a Mg halide through a halide electrolyte to deposit Mg in a cathode metal melt. The resulting Mg product is pure enough to be used as a Mg alloying element in batching prime Al alloys.

## Commercial Significance—Mg Recovery from Al Scrap Is Important Now

The processing of scrap has gained importance during the last 15 years.

With escalating energy costs for these very energy-intensive light metals, recycling saves energy costs as it requires only <5% of energy compared to Al or Mg production from ore.

As the primary aluminum and magnesium industry has largely left the USA for the cheaper electrical energy and environmental cost regions of the world (such as the Middle East in case of aluminum, and China for both aluminum and magnesium), US fabrication plants are paying a much higher price for imported primary aluminum and magnesium. These imports also lead to large trade deficits and may even have national security implications.

Public perception has moved towards sustainability and using recycle-friendly products and against landfills.

At the same time the demand for structural corrosion-resistant prime alloys that use Mg as an alloying element is increasing in the transportation marketplace for the construction of cars, trucks, busses, trains, boats, ships and aircraft. In the past, the supply of Mg in light-metal mixed-alloy scrap was insufficient to justify process development and operating economics. Going forward, Mg supply from scrap is steadily increasing, providing economic justification for Mg recovery and recycling.

### Magnesium Recovery Potential

There is almost three million tons of Al scrap recycled annually in North America, which can produce about 45,000 tons of Mg content in primary-quality recycled Al–Mg and Mg–Al products.

The amount of 45 kt of recovered Mg is transformational when compared to the total US primary Mg production capacity of only 60 kt. It is estimated that 28 kt of

Mg, contained in the 2140 kt of domestically generated Al scrap, leaves US shores —only to return as more value-added products.

The lower cost of magnesium recovery from scrap will reduce imports of Mg and Al to the USA. Commercial implementation of a magnesium recovery process will help reduce the export of Al and Mg scrap and develop an aluminum-scrap-based Al and Mg industry in the USA. Subsequently, successful commercialization of a magnesium recovery process will also lower costs, energy and emissions of Al–Mg alloy production, thereby expanding the use of both Al and Mg in their major usage sectors of aerospace and automotive industries.

### Magnesium and Aluminum Scrap North American Materials Flow

A detail discussion of aluminum and magnesium material flow including scrap is described in a recent TMS presentation [1]. Figure 1 illustrating Mg unit flows the importance of metal scrap to the Mg production system. Metal scrap supplies  $\sim 100$  kt of the Mg content. Most of the Mg units are in the form of Al scrap. The opportunity for a new RE-12<sup>TM</sup> Mg electrorefining process (described below) is the 45 kt of Mg chlorinated out of Al foundry melts and Mg in consumable products that are currently lost to the system.

Figure 2, which illustrates Al unit flows in North America, underlines that even in the well-established Al recycling system, North America still exports and



Fig. 1 North American Mg unit flow diagram based on 2012 USGS and USEPA data [1]



Fig. 2 North American Al unit flow diagram based on 2012 USGS and USEPA data [1]

landfills more Al scrap (nearly 5000 kt) than it imports as Al prime (3700 kt). An amount of 1537 kt of new Al alloy scrap and 1696 kt of old Al scrap provide potential raw material for the RE-12<sup>TM</sup> electrorefining process feed.

### Current State-of-the-Art and Available Technology

Current aluminum refining uses chlorination with a gas mixture or reactive salts and transfers reactive alloying elements (Mg, Li, Na, Ca, Sr, and Rare Earths (RE)) from secondary Al foundry alloy into dross for disposal typically as salt-contaminated wastes. This practice is both costly and hazardous as it takes extensive time, leads to melt losses of both Mg and Al, and uses highly toxic chlorine gas. Chloride byproducts in the dross again go into a difficult-to-dispose salt-contaminated waste. At present there are no industrial processes that recover Mg and other reactive elements from Al or Mg alloys for production of primary-quality alloys.

Hoopes [2, 3] invented the electrolytic three-layer refining process for Al in 1925. Bowman [4] and Dewing [5] proposed such a three-layer refining process for recovery of Li from Al-Li melt in 1989. Other literature, by Das, Gesing and Fray [6–9] suggests improvements to the molten salt electrolyte Al refining cells.

### Need for a New Technology

At present there are no industrial processes that recover Mg from Al–Mg alloy scrap for the production of primary-quality alloys. In 2013 SINTEF at the Norwegian University of Science and Technology (NTNU) held an International Al Recycling Workshop of 30 internationally recognized Al recycling experts in Trondheim, Norway. These experts (including Dr. Adam Gesing, a co-author of this paper) assigned highest priority to the development of a non-chlorine environmentally friendly process for removal and recovery Mg from Mg-bearing Al scrap [10].

### New Technology—Re-12<sup>™</sup> Electrorefining Process

The project to recover Mg from Al alloy melted scrap for recycling by Mg electrorefining was funded by the United States Department of Energy Advanced Research Project Agency (ARPA-E) [11].

This RE-12<sup>™</sup> technology, which builds on the electrochemistry of the industrially established Hoopes process for the production of five-nine (99.999%) pure Al, has been designed to transfer >90% of the Mg from secondary Al melt to the refined product. Electrorefining selectively transfers Mg to the Mg–Al alloy floating top layer. The cathodic product would be alloyed to the desired Mg–Al or Al–Mg alloy composition by diluting it with primary-grade Al and adding other specified alloying elements. The anode product is the starting Al alloy with Mg content reduced to the specificaction level.

Calculations of metal-electrolyte melt phase diagrams, predicted product compositions, electrolyte chemical stability and physical properties (such as density, viscosity, electrical conductivity, cell construction materials, vapor pressure and superheat) were made using commerciality available thermodynamic modelling FactSage software and databases [12] leading to electrolyte selection for the RE-12<sup>TM</sup> process.

This project experimentally demonstrated that the Mg recovery electrolyzer can produce refined product with 99.9% of Mg plus Al. There is no commercial need to produce Al-free Mg product since the target market for Mg is alloying of Al. Even for use in Mg-based alloys, Al content of the refined product is not a problem since most commercial Mg-based alloys contain >4% Al. A schematic flow sheet of the process along with a depicted commercial set up are described in Figs. 3 and 4.

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## **Experimental and Analytical Results**

Three recently published papers [13–15] describe the process details, laboratory-scale experimental results and product marketability, and economic analysis of the RE-12<sup>TM</sup> process. These results and analyses combine to give an experimental proof-of-concept. This RE-12<sup>TM</sup> process is a patent-pending [16] and trademark-pending [17] route for a Mg recovery for recycling from Al alloy melts.

The theoretical minimum energy requirements along with production costs, emissions and processing energy needed for the current magnesium producing (from Pidgeon and electrolysis) technologies have been extracted from the ARPA-e FOA document [18]. Comparable numbers for the RE-12<sup>™</sup> process have been experimentally demonstrated in laboratory electrorefining cells as shown in Table 1.

## Markets for RE-12<sup>TM</sup> Process Implementation

RE-12<sup>™</sup> electrorefiner is typically integrated with Al remelting furnace in a secondary smelter remelting Al scrap. There are three major market opportunities.

Current and target Mg metal reduction processes	Domestic production cost (\$/kg Mg)	Emissions (kg CO <sub>2</sub> / kg Mg)	Processing energy ore to metal (kWh/kg Mg)	Theoretical minimum energy (kWh/kg Mg)	
Mg-silicothermic	\$2.50	37	102	5.8	
Mg-electrolytic	\$3.31	6.9	43.6	5.8	
Mg reduction— ARPA-e target	≤\$2.00	≤10	≤27		
RE-12 <sup>™</sup> electrorefining	\$1.6-\$1.7	2	<4	~0	
RE-12 <sup>™</sup> Mg electrore	Units				
Mg product purity	Al		<1	wt%	
	Fe + Si + Mn + Cu + Zn		<0.05	wt%	
Al alloy product purity	Mg		<0.15	wt%	
Electrolytic current efficiency			~96	%	
Electrorefining step			2.5	kWh/kg of Mg	
energy consumption	With 1% Mg electrorefined		~ 0.025	kWh/kg of Al alloy	

Table 1 Cost, energy and emission analyses—current Mg versus RE-12<sup>™</sup> process [13–15]

### Production of AA 6111 Automotive Closure Sheet from New Stamping Plant Scrap

Automotive sheet is currently the fastest growing market for Al alloys. Existing stamping plants tend to have a single scrap chopping and handling line. While the steel scrap is separated magnetically, new Al stamping scrap often is a comingled mixture of 6xxx and 5xxx alloys. Piece-by-piece Al alloy sorting has been considered but not used. The RE-12<sup>TM</sup> process provides an alternative where the high-Mg AA 5754 and lower-Mg AA 6111 mixed new stamping scrap can be melted together and the Mg content of the mix can be electrorefined down to the AA 6111 alloy target concentration.

#### Low Mg-Al Foundry Alloys 356, 380, 319

There are over two million tonnes of secondary foundry alloys produced in the USA. The typical mixed-alloy old scrap mix feeding this market has  $\sim 1.1$  wt % Mg content. The Mg is chlorinated out producing hygroscopic Mg salt contamination of Al dross and leading to the loss of Mg units. The added value of the RE-12<sup>TM</sup> process comes from avoidance of chlorination costs, the value of the recovered Mg product, and reduction of Al losses.

Market sector	Alloys	Expected Al alloy production volume	Magnesium removal potential				
		t/y	Start (wt%)	End (wt%)	Reco Mg	overed (%) t/y	
Automotive-sheet	6111/5754	750,000	2.25	0.75	1.5	11,250	
Automotive-cast	319/356/380	2,000,000	1.1	0.1	1.0	20,000	
Beverage cans	3104/5182	1,500,000	1.5	1.0	0.5	7500	

 Table 2
 Magnesium removal potentials from selected North American market sectors

#### Production of Can Body Sheet from Used Beverage Can (UBC) Scrap

There is over 1.5 million tons of AA3104 alloy can body sheet produced in North America, much of it supplied by UBC and new can sheet production scrap. Can alloys consist of  $\sim 1.1$  wt% Mg AA3104 alloy body and 5.1 wt% Mg AA5184 alloy lid. The Mg concentration is reduced by deliberate preferential Mg oxidation melt, and by dilution with prime Al. Consequently, the RE-12<sup>TM</sup> electrorefiningprocess, which enables batching of the AA3104 alloy can body melt for 100% UBC feed, has the potential for substantial reduction of scrap feed costs, and for allowing melt practices that prevent excessive melt oxidation. These combine for the potential to actually reduce can body alloy production cost, and provide recovered Mg at the same unit price. Some of these numbers are summarized in Table 2.

#### **Results and Conclusions**

Based on extensive experimental and techno-economical modelling using commercially available data, inputs and experience, we have established the technical, economic and environmental viability of this market needed, driven and disruptive RE-12<sup>™</sup> Mg electrorefining process for recovery of Mg from melted Al scrap for recycling.

Three large market segments in Al recycling system were identified as promising areas for profitable implementation of RE-12<sup>TM</sup> process. These total to ~4.25 million annual tons of potential Al alloy feed to the RE-12<sup>TM</sup> process and 45,000 annual tons of potential Mg recovery these three markets alone in North America.

### **Path Forward**

Efforts are underway to scale up the RE-12<sup>TM</sup> process leading to commercialization and broader market adaptations to recover magnesium from aluminum-magnesium-based scrap.

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### References

- S.K. Das, A.J. Gesing, Presentation at energy technologies and carbon dioxide management conference, TMS 2014
- W. Hoopes, Electrolitically refined Al and articles made therefrom. US Patent No. 1,534,315, 1925
- 3. W. Hoopes, Electrolitic refining of Al. US Patent No. 1,534,318, 1925
- 4. K.A. Bowman, Electrolytic process for recovering Li from Al-Li alloy scrap. US Patent No. 4,849,072, 1992
- 5. E.W. Dewing, Refining of Li containing scrap. US Patent No. 4,790,917, 1988S.
- 6. S.K. Das et al., Aluminum purification. US Patent No. 4,115,215, 1978
- E.W. Dewing, A.J. Gesing, Electrolytic refining of molten metal. US Patent No. 4,405,415, 1983
- 8. D.J. Fray et al., Packed bed electrorefining and electrolysis. US Patent No. 4,118,292, 1978
- 9. D.J. Fray et al., Electrode for electrorefining. US Patent No. 4,904,356, 1990
- 10. Sintef, International Aluminium Recycling Workshop, Trondheim 9-11 June 2013
- 11. Advanced Research Project Agency (ARPA-e) of the United States Department of Energy
- 12. FactSage—http://www.crct.polymtl.ca/fact/
- 13. A.J. Gesing, S.K. Das, R.O. Loutfy, JOM 68(2), 585-593 (2016)
- 14. A.J. Gesing, S.K. Das, R.O. Loutfy, REWAS, TMS 2016, pp. 253-254
- 15. A.J. Gesing, S.K. Das, Met. Trans. B (2016)
- A.J. Gesing, S.K. Das, M.A. Gesing, US Patent Application US 2015/0225864 A1, 2015 (Phinix, LLC)
- 17. Phinix, LLC—Trade Mark: RE-12 TM Recycled Magnesium, 2014
- 18. Energy-Funding Opportunity No. DE-FOA- 0000882, 20 Mar 2013
- R.A. Sharma, Fused fluoride electrolytes for MgO electrolysis in the production of Mg metal. US Patent No. 5,427,657, 1995
- P.R. Kruesi, Methods of recovering and purifying secondary Al. US Patent No. 8,002,872, 2011