Final Technical Report

Efficient One-Step Electrolytic Recycling of Low-Grade and Post-Consumer Magnesium Scrap

DOE Award Number DE-EE0003454

Project Period: August 1, 2010 – December 31, 2011

Principal Investigator: Adam C. Powell, IV
(781) 898-3430 apowell@moxst.com

Recipient Organization:
Metal Oxygen Separation Technologies, Inc.
11 Michigan Drive, Natick, MA 01760-1334

Other Project Team Members:

MOxST: Soobhankar Pati, Steve Derezinski, John Strauss
Boston University: Uday Pal, Peter Zink, Xiaofei Guan

Date of Report: July 19, 2012

Acknowledgment:

“This report is based upon work supported by the U. S. Department of Energy under Award No. DE-EE0003454.”

Disclaimer:

Proprietary Data Notice:

This report contains no proprietary data and may be published in full.

Table of Contents

List of Acronyms

BTU: British Thermal Unit(s), ~1055 J
BU: Boston University
CAGR: Compound Annual Growth Rate
CFD: Computational Fluid Dynamics
CO_2e: GHG equivalent CO_2 emissions
ECS: Electrochemical Society
EDS: Energy-dispersive Spectroscopy
EIS: Electrochemical Impedance Spectroscopy
EPA: Environmental Protection Agency
FEA: Finite Element Analysis
GHG: Greenhouse Gas
MMT: Million Metric Tonnes
MOxST: Metal Oxygen Separation Technologies, Inc.
OCV: Open-Circuit Voltage
PDS: Potentiodynamic Scan
PSH: Potentiostatic Hold
PI: Principal Investigator
PSZ: Partially-Stabilized Zirconia
SEM: Scanning Electron Microscope
SOPO: Statement of Project Objectives
TBTU: Trillion British Thermal Units of energy
TMS: The Minerals, Metals and Materials Society
tons/tonnes: English (2000 lb)/metric (1000 kg)
USAMP: U.S. Automotive Materials Partnership
YSZ: Yttria-Stabilized Zirconia

List of Figures

List of Tables

List of Appendices

Executive Summary

Metal Oxygen Separation Technologies, Inc. (abbreviated MOxST, pronounced “most”) and Boston University (BU) have developed a new low-cost process for recycling post-consumer comingled and heavily-oxidized magnesium scrap, and discovered a new chemical mechanism for magnesium separations in the process. The new process, designated MagReGen™, is very effective in laboratory experiments, and on scale-up promises to be the lowest-cost lowest-energy lowest-impact method for separating magnesium metal from aluminum while recovering oxidized magnesium. MagReGen™ **uses as little as one-eighth as much energy as today's methods** for recycling magnesium metal from comingled scrap. As such, this technology could play a vital role in recycling automotive non-ferrous metals, particularly as motor vehicle magnesium/aluminum ratios increase in order to reduce vehicle weight and increase efficiency.

Project Purpose The goal of this project was Concept Definition of the MagReGen™ magnesium recycling process to demonstrate the process and show its commercial potential.

Project Scope This project directly addresses the priorities of the High-Temperature Processing platform of the Energy Intensive Processes R&D portfolio of the DOE Advanced Manufacturing Office. MagReGen™ has strong potential for energy savings, GHG, and other emissions reduction in magnesium recycling. The process would also facilitate increased usage of magnesium in automobiles, leading to additional energy savings and GHG reduction.

MagReGen™ process technical challenges defined the scope of this study's four tasks:

- Estimation of potential energy and emissions benefits of process deployment;
- Laboratory experiments to demonstrate the process and study its chemical mechanisms;
- Mathematical models for understanding experimental results and scale-up design;
- Scale-up studies including preliminary design, cost modeling, and market analysis.

Project Results Project accomplishments include:

- Energy use modeling indicates that MagReGen™ magnesium recycling output per unit of energy is nearly eight times higher than chlorine-based separation, and can potentially **save as much as 340 trillion British Thermal Units (TBTU) of industrial energy per year.** Without the direct carbon usage of competing processes, it can **reduce GHG emissions by as much as 45 million metric tonnes (MMT) CO_2e/year.**
- A successful experimental program **discovered and demonstrated the new chemical separation mechanism** in two separate experiments. Separation of magnesium from aluminum and other metals happens in two stages: magnesium in a scrap metal charge preferentially dissolves into a molten salt, and argon bubbling through the salt accelerates its evaporation. Other metals have lower solubility and/or lower evaporation rate. Experiments demonstrated **close to 100% yield and near-perfect separation.**
- We invented two new (patent pending) electrical measurement methods to estimate the amount of magnesium in the scrap charge and dissolved in the molten salt at any time, these can serve as **inline process control signals and diagnostic tools.**
- Though mathematical modeling was originally geared toward our patent-pending electrorefining mechanism, we also modified the model and **ran simulations of recycling by the new mechanism.** Complete model validation and unknown parameter estimation will require additional experiments, and when complete, the model

will simulate an industrial-scale recycling cell.

- A **3-D design concept** ties together the process features into a highly scalable and flexible recycling system, with a new configuration which could even further reduce the energy required for recycling.
- An industrial survey revealed that despite acute and growing needs, **there is currently no economically viable magnesium-aluminum metal separation technology.**

In addition to the electrorefining patent application, MOxST and BU have filed three provisional patent applications on methods of use and apparatus for using the new separation mechanism and inline diagnostics for magnesium recycling. We presented the above results in a public conference presentation and two posters, all three accompanied by proceedings papers.

Conclusions Based on experimental and modeling results outlined above, growing market demand for magnesium, and the low cost of our technology, MOxST has concluded that **the MagReGen™ process will likely be a profitable method to dramatically reduce the industrial energy for producing magnesium from dross, automotive scrap, and other low-cost scrap sources.** When widely deployed, it could create a market for post-consumer magnesium, including that found comingled with aluminum such as shredded motor vehicle scrap. This would increase magnesium's recycling rate from mid-30% range today to as high as the 70%+ range of steel and aluminum. It will also reduce the cost of magnesium, facilitating growth of its use in motor vehicles and other applications.

In short, the MagReGen™ process could help to usher in a sea-change in automotive materials, away from heavy steel parts and the GHG and other emissions associated with aluminum and steel production, toward cleanly and efficiently-produced light-weight magnesium.

Recommendations Because of the novelty of the new refining mechanism discovered here, this Concept Definition study makes clear the work required for scale-up engineering of the process. Follow-up tasks include the following:

- **Develop anodes,** particularly options for improved resistance to electronic current. Using this process for dross and oxidized magnesium requires anode improvements, particularly because of the intentionally high magnesium metal concentration in the salt.
- **Evaluate reaction mechanisms and kinetics** using designed experiments. At this point, we need to understand the rate-limiting step(s) of this new separation mechanism in order to design a high-throughput recycling cell.
- **Measure model parameters and validate models** using experiments. Models of magnesium mass transfer into flowing molten salt, and then its evaporation into bubbled argon, have many unknown parameters. These include molten salt viscosity and surface tension, magnesium activity and vapor pressure when dissolved in the molten salt, and argon bubble foaming or breaking behavior on the salt surface.
- **Design and demonstrate large-scale equipment.** A high-throughput cell using this novel separation mechanism will require a very new design, and demonstrating the performance of this cell design will be essential to commercialization.

When these tasks are accomplished, it will be possible to build, test and deploy recycling cells at many types of sites, including die-casters, non-ferrous vehicle scrap sorters, and other users and scrap sorters. This on-site testing and long-term demonstration are key commercialization tasks on the way to large-scale deployment of MagReGen™ technology, leading to realization of its energy savings and emissions reduction potential.

1. Introduction

Magnesium is the least dense structural metal at 1.74 g/cm³ *cf.* aluminum at 2.70, and has the highest stiffness-to-weight ratio. For this reason, U.S. auto makers would like to replace 286 kg of steel and aluminum parts per vehicle with 155 kg of new magnesium equivalents by the year 2020,[1] reducing vehicle weight by 131 kg and fuel consumption by 2 gallons/1000 miles, thus reducing light vehicle transportation energy consumption by 732 trillion BTU/year.[2] Two of the main obstacles to achieving this goal are the cost of magnesium metal and poor recyclability of low-grade post-consumer and heavily-oxidized magnesium scrap. This project concerns Concept Definition for a novel process focused on recycling such low-grade magnesium scrap.

Today's motor vehicle recycling industry cannot economically separate aluminum from magnesium, so the mixed Al/Mg scrap stream is sold as a master alloy for aluminum alloys with magnesium. As the auto magnesium alloy content of vehicles increases, Al/Mg scrap will need more dilution and have lower value; its volume will also exceed its demand for this market. When necessary, chlorine bubbling through liquid aluminum with small amounts of magnesium can produce purer aluminum and $MgCl_2$, but the subsequent chloride electrolysis uses 28 kWh/kg making it energy- and cost-prohibitive. This situation will not only keep magnesium cost high, as primary production remains the dominant means of supply, but could also lead to landfilling of considerable amounts of Mg/Al scrap, along with some magnesium chloride.

Today China produces about 80% of the world's magnesium by using ferrosilicon to reduce magnesium oxide, which is an extremely energy- and carbon-intensive process. Because of this high carbon penalty, European auto makers have been reluctant to increase their use of magnesium, as the much higher production process carbon emissions outweigh lower emissions due to light weight over the life of a vehicle.[3] The problem of limited magnesium availability has been particularly acute in Japan, which has limited energy resources to produce the metal, and unfortunate recent history of rare-earth metal dependence on China.[a] Energy-efficient recycling of low-grade magnesium scrap could thus have significant worldwide impact.

For all of these reasons, this project initiated development of the MagReGen™ magnesium recycling process, shown schematically in Figure 1, which can recycle many grades of magnesium scrap in a single step. This process melts post-consumer parts, heavily-oxidized machining chips, die-casting dross, and other low-grade magnesium alloy scrap, together with aluminum. Magnesium and its oxide preferentially dissolve into a molten salt bath. Argon bubbling removes dissolved magnesium metal from the salt as a vapor, and electrolysis between steel cathodes and anodes inside stabilized zirconia tubes separates any MgO "contamination" into magnesium metal vapor at the cathode and an oxygen by-product at the anode. The magnesium vapor travels to the condenser which produces liquid magnesium, and a pump recycles the argon.

This process is not intended for recycling high-quality magnesium scrap, such as prompt or primary industrial scrap *e.g.* die-casting runners. It is more economical to simply remelt such scrap than to use MagReGen™. This process is intended for magnesium co-mingled with other metals and its oxide, such as die-casting dross and post-consumer material.

In another project, MOxST is developing the MagGen™ magnesium primary production system which produces magnesium metal from its oxide. MagGen™ continuously feeds magnesium oxide into a molten salt bath, then reduces it using the same zirconia-encased inert anodes and

---

[a] Based on interviews with Toshihiko Koseki and Yasunari Matsuno in Appendix A on p. 72.

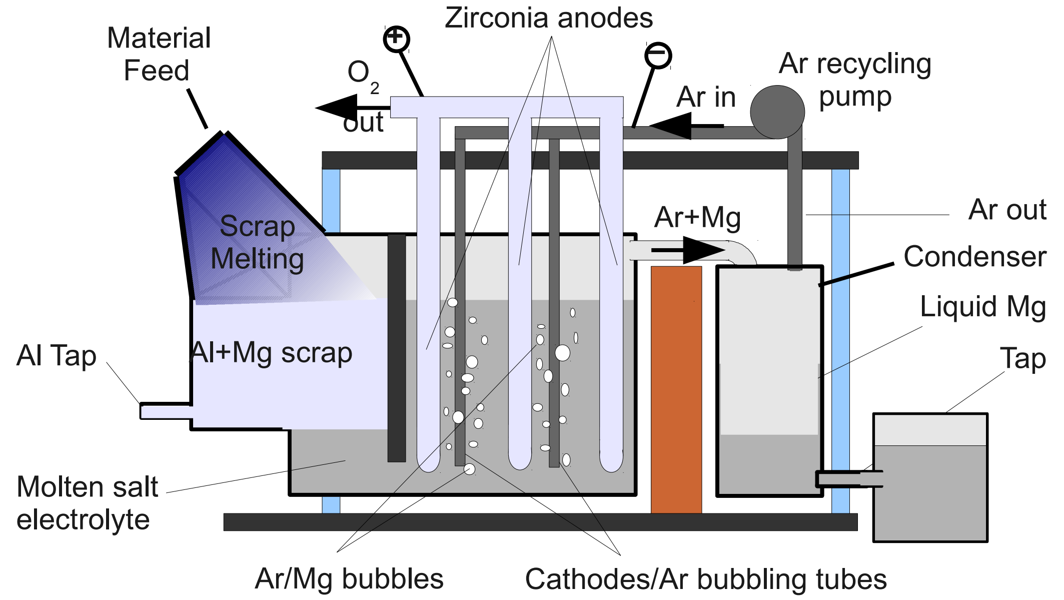


Figure 1: Schematic diagram of the MagReGen™ magnesium recycling process.

steel cathodes as are in MagReGen™. In both cases, the stabilized zirconia solid electrolyte between the salt and anode serves three purposes: it prevents back-reaction between the magnesium and the oxygen by-product; it helps to block electronic current to keep current efficiency high; and it acts as a highly selective filter such that the oxygen by-product is very pure. The production of magnesium vapor leads to inherent purification, as impurities such as iron, silicon and aluminum plate on the cathodes. In MagReGen™, aluminum, zinc, manganese and other metals remain in the scrap charge as a liquid alloy due to their much lower solubility in the salt than that of magnesium. Development of the MagGen™ primary processing and MagReGen™ secondary processing technologies are synergistic, and they can work together in the marketplace to facilitate wider motor vehicle adoption of magnesium.

This report describes the work of this project in several sections. The Background on page 12 describes technological difficulties inherent to magnesium recycling, particularly for automotive scrap. The Results and Discussion on p. 18 describes the project's experimental, modeling, and industrial scale-up design activity with detailed procedures and results. In particular, experiments showed outstanding magnesium-aluminum separation via this new chemical mechanism of molten salt dissolution and argon-assisted distillation, and demonstrated a new method for estimating the magnesium content of the remaining scrap and the molten salt. Technical cost modeling shows that MagReGen™ should be profitable at today's prices.

The Benefits Assessment section describes both the direct impact of the technology and the changing magnesium market on page 40. Our models show that recycling magnesium metal mixed with aluminum will require 3-4 kWh/kg Mg, which is about one eighth of that required for chlorine bubbling and $MgCl_2$ reduction. In total, based on motor vehicle industry plans for increased magnesium use to meet new EPA fuel efficiency targets, **the MagReGen™ and MagGen™ processes can potentially save as much as 340 trillion British Thermal Units (TBTU) of manufacturing energy per year.** MOxST's commercialization plans on page 48 focus around a capital equipment business model.

Finally, conclusions are on page 52, follow-on recommendations are on page 54, and an appendix of notes on interviews with industry leaders begins on page 58.

2. Background

2.1 The Magnesium Recycling Problem

Understanding the magnesium recycling problem begins with the industrial ecosystem, known as material flow. The USGS conducted the most recent magnesium material flow study in the United States in 1998,[4] the result of which is shown in Figure 2. Though somewhat dated, this flow study bears several important lessons still valid today,[5] including:

- The magnesium die-casting dross stream is about 5% of the die casting volume, *i.e.* about 5000 tons/year today and in 1998;
- Another 8,000 tons/year of "Processing losses" is not recovered;
- Of the 108,000 tons of "Old scrap generated", close to 2/3 (68,000 tons/year) is "Unrecovered old scrap" *i.e.* landfilled; recycling this scrap remains economically non-viable today.[5]

The ~37% post-consumer recycling rate for magnesium is much lower than the 60-80% typical for steel and aluminum, and generation of industrial processing waste, including dross, is quite high. This is due to the low recyclability of many grades of magnesium scrap. Figure 3 shows a

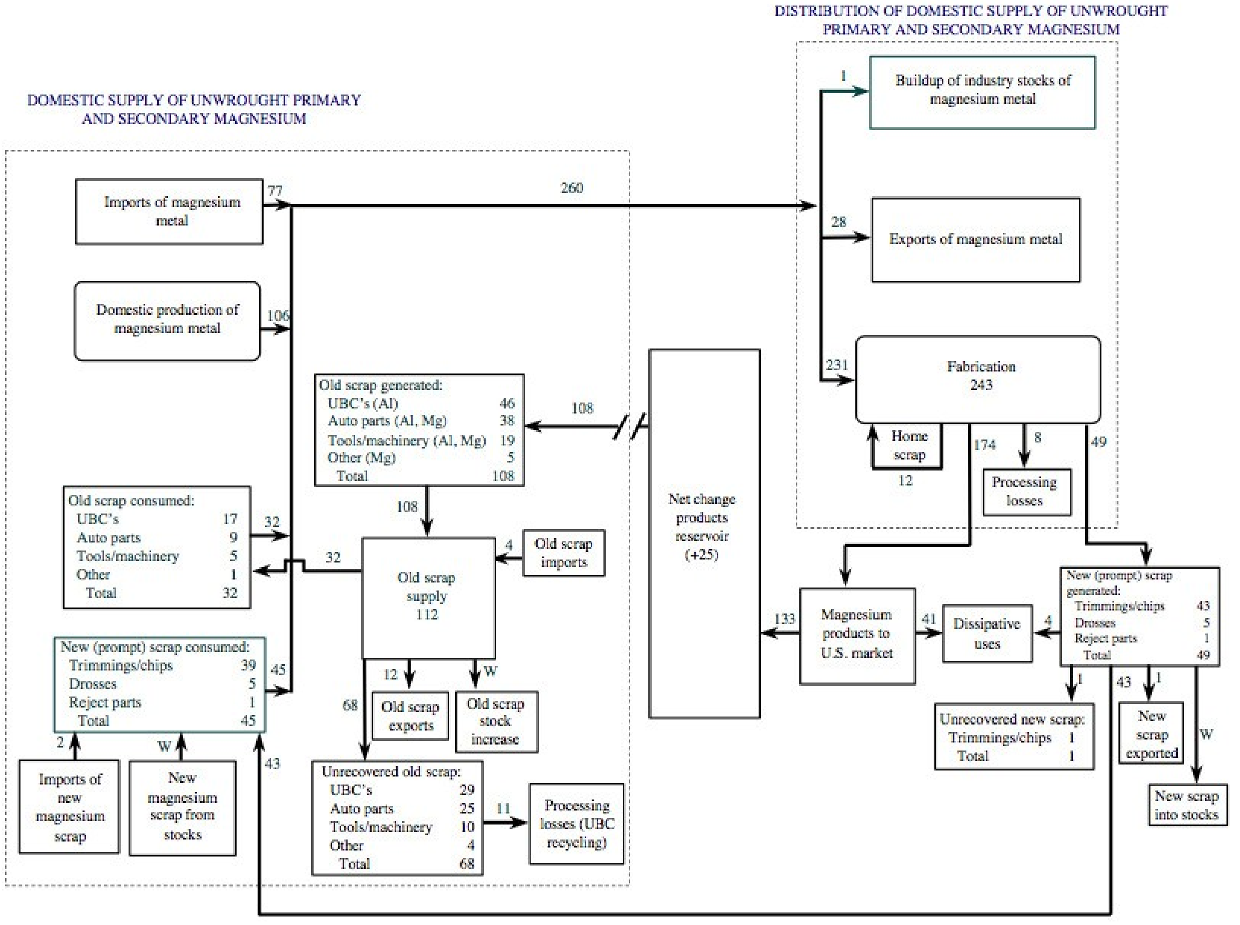
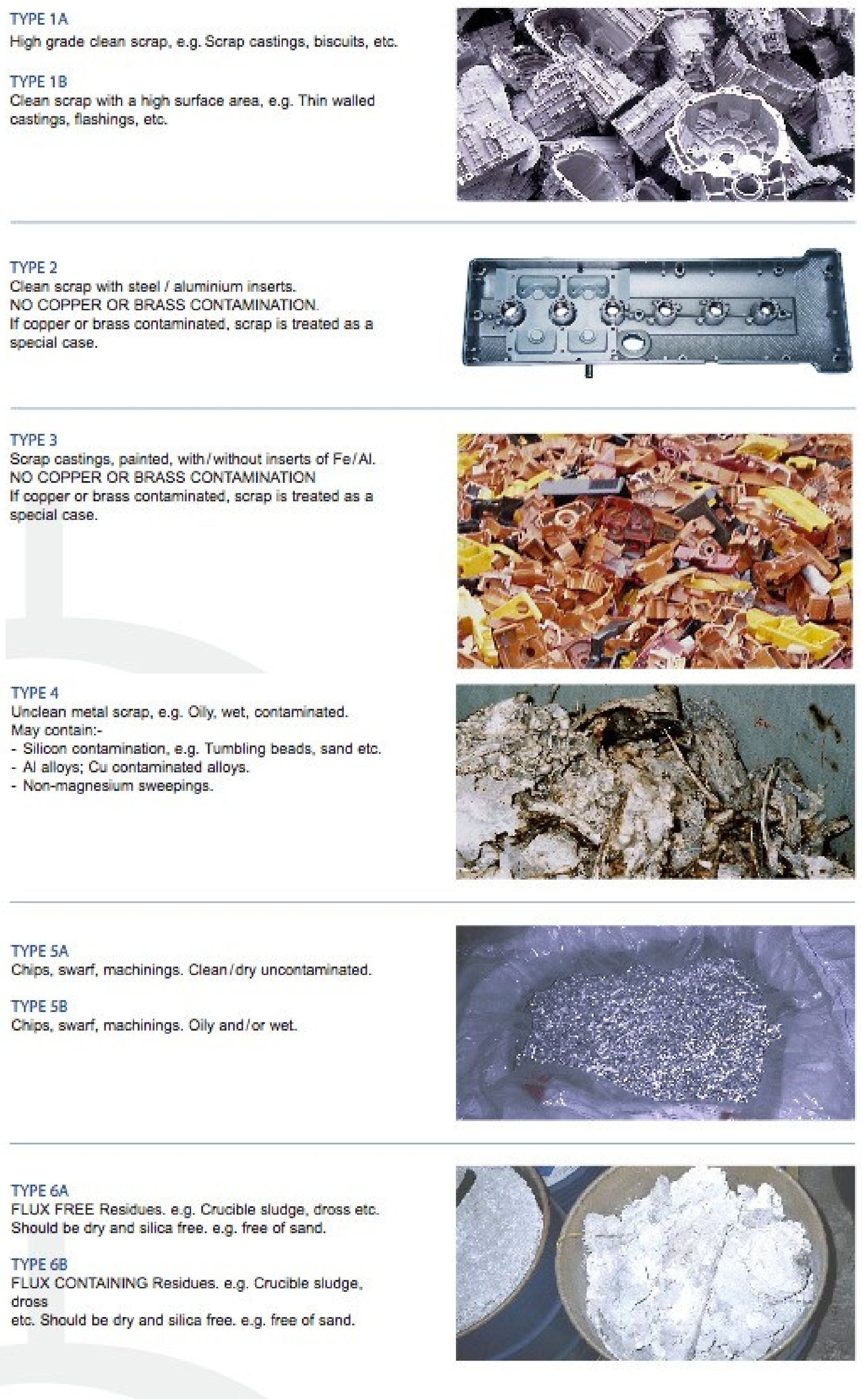


Figure 2: Magnesium recycling flow, 1998, in thousand metric tons contained magnesium.[4]



TYPE 1A
High grade clean scrap, e.g. Scrap castings, biscuits, etc.

TYPE 1B
Clean scrap with a high surface area, e.g. Thin walled castings, flashings, etc.

TYPE 2
Clean scrap with steel / aluminium inserts.
NO COPPER OR BRASS CONTAMINATION.
If copper or brass contaminated, scrap is treated as a special case.

TYPE 3
Scrap castings, painted, with/without inserts of Fe/Al.
NO COPPER OR BRASS CONTAMINATION
If copper or brass contaminated, scrap is treated as a special case.

TYPE 4
Unclean metal scrap, e.g. Oily, wet, contaminated.
May contain:-
- Silicon contamination, e.g. Tumbling beads, sand etc.
- Al alloys; Cu contaminated alloys.
- Non-magnesium sweepings.

TYPE 5A
Chips, swarf, machinings. Clean/dry uncontaminated.

TYPE 5B
Chips, swarf, machinings. Oily and/or wet.

TYPE 6A
FLUX FREE Residues. e.g. Crucible sludge, dross etc.
Should be dry and silica free. e.g. free of sand.

TYPE 6B
FLUX CONTAINING Residues. e.g. Crucible sludge, dross
etc. Should be dry and silica free. e.g. free of sand.

Figure 3: Magnesium scrap types, from USGS.

typical classification of magnesium scrap. Type 1 is nearly as good as new metal, and types 2-3 may require some dilution or paint removal but are generally usable in new products.[b] These types of material command a high price with little to no margin available for recyclers,[c] particularly in the U.S. where the magnesium price is higher than the rest of the world due to import tariffs on Chinese magnesium.[d]

However, most post-consumer “old scrap” material, including automotive scrap, is of type 4. Much of the industrial “new scrap” is of types 5 and 6, and some type 4, all of which are very difficult to recycle. This is because the copper and nickel present in these scrap types are very harmful to magnesium ductility and corrosion resistance, even in very small concentration.

Figure 4 gives a brief outline of automobile scrap recycling. Dismantlers remove parts from automobiles which either have value or diminish the value of the remainder of the vehicle, then flatten the bodies for shipment. Shredders operate large machines which tear apart a vehicle in about thirty seconds into pieces no bigger than about four inches across, then use magnets to separate out ferrous metals and eddy current separation to remove non-ferrous metals. Non-ferrous sorters use proprietary techniques to separate out aluminum and copper and sell into those markets.

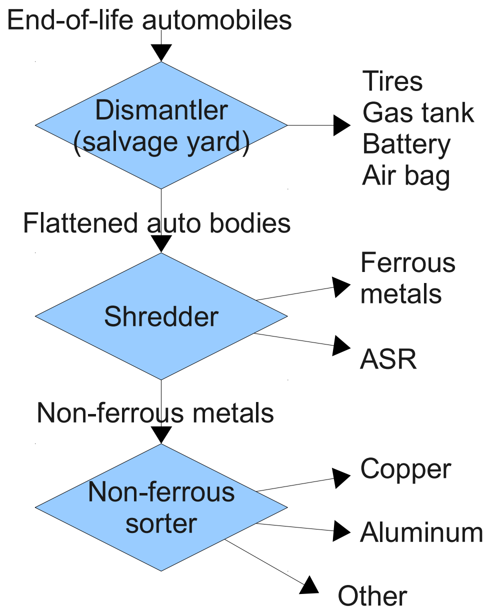


Figure 4: Automobile recycling flow diagram.

Magnesium alloy pieces leave shredders in the non-ferrous metals stream. Non-ferrous sorters in turn include them in the aluminum stream, because of the difficulty in separating aluminum from magnesium.[e] Thus it is mixed with aluminum, and has some copper from aluminum alloys, and imperfect separation leaves small amounts of copper from copper parts, nickel from stainless parts, and even ferrous metals, glass, and polymers. As a minority mixture with

---

[b] See the large die-caster interview on p. 70.

[c] See the MagPro, LLC magnesium recycler interview on p. 64.

[d] For example, the January 31, 2012 *Magnesium Monthly Review* (vol 40 #12) quotes Chinese prices as \$2950-3000/ton i.e. ~\$3.00/kg, and U.S. prices at \$2.00-2.20/lb i.e. \$4.40-4.64/kg, with the difference due to U.S. anti-dumping tariffs.

[e] See the wTe interview on p. 59.

aluminum, this magnesium is therefore not available for re-use in new magnesium alloy parts, its only use is in aluminum alloys containing magnesium.

At present, the relatively small amount of post-consumer magnesium scrap which is of type 4 or 5 goes into aluminum alloys and steel desulfurization, which are not sensitive to quality, but are relatively fixed in size. A significant increase in vehicle magnesium use would quickly overwhelm those markets, and without new industrial capability to separate it from aluminum, could lead to lower post-consumer recycling rates, and considerably more landfilling. New light-weight vehicle designs from the U.S. big three (GM, Ford, Chrysler), Magna, and Volkswagen call for 40-50% by weight magnesium alloys in the unibody frame and exterior panels,[6] and will use even more magnesium than the Magnesium Vision 2020[1] USAMP goals.[f] This could cause severe problems in today's automobile recycling system: added landfill costs for magnesium-containing metal and lower value of contained aluminum could imperil the profitability of many companies in the vehicle recycling chain.

Current Options for Magnesium Recycling

Although the low-value markets mentioned above (aluminum alloys and steel desulfurization) have been able to absorb low-quality post-consumer magnesium, there have been three options for upgrading its value or separating it from aluminum:

1. Hydro Magnesium developed a system for continuous melting magnesium in contact with a molten salt in order to remove oxides from the liquid metal.[7,8] However, this process cannot separate magnesium from other metals.
2. Distillation takes advantage of the high vapor pressure and low boiling point of magnesium relative to aluminum and many other metals. Magnesium's melting point vapor pressure is the highest of all metals, at about 3 torr. However, magnesium-aluminum chemical affinity and formation of surface oxides result in poor separation: one study starting from magnesium alloys such as AZ91, AM60 and AZ31 found it difficult to reduce the magnesium content of the unevaporated Al-Mg residue below about 60%.[9] Also, although zinc has lower melting-point vapor pressure than magnesium, it also has a much lower melting point, and its vapor pressure at the melting point of magnesium is higher, such that distillation leaves zinc in the distillate stream.
3. If there is relatively little magnesium in an Al-Mg scrap stream, as is the case for beverage can stock or today's automobiles, then chlorine bubbling through the liquid metal can remove it by reaction to form $MgCl_2$ with various impurities, leaving purer and higher-value aluminum. However, as the magnesium content of vehicles increases, this will require very large amounts of chlorine, and thus large amounts of energy, as well as large new markets for $MgCl_2$. This method also wastes the energy content of the magnesium metal: reducing $MgCl_2$ back to magnesium would require an additional 28 kWh/kg, and the low purity of the chloride might make even that impractical.

For these reasons, it is impractical to recycle magnesium in automotive scrap, and without new recycling technology, increasing magnesium use in motor vehicles increases the likely fraction of post-consumer vehicle material going into landfills.

---

[f] Magnesium 2020 goals are slightly scaled back from the 173 kg total of non-frame magnesium alloy parts used in various vehicles to date, *e.g.* seat frames, steering wheel, instrument panel beam, transmission case.

2.2 MOxST's Process for Magnesium Recycling

Project Goals

The above needs in the automobile recycling industry, and a technological synergy with our MagGen™ primary processing technology described in the Introduction (p. 10 bottom), motivated MOxST to pursue a new magnesium recycling technology in this project. The original proposal related to a MOxST patent application on using electrorefining to refine magnesium (or other metals), and electrolysis to reduce its oxide present in scrap.[10,11] In electrorefining, one applies a DC potential between a metal mixture as the anode, and a pure target metal as the cathode, separated by a liquid electrolyte. The target metal, here Mg, becomes oxidized to a positive ion in the electrolyte, here a molten salt, while more electronegative metals, here Al, Zn, Mn, Fe, remain behind in the mixed-metal anode. At the cathode, target metal ions (Mg^{2+}) in the electrolyte are reduced to metal, leaving less electronegative ions (Ca^{2+}, Y^{3+}) behind in the salt.

The goals for this Concept Definition project, and its top-level tasks, were as follows:

1. Estimate the cost, energy use, and GHG emissions of using electrorefining to refine magnesium, relative to current practice;
2. Demonstrate efficacy of electrorefining and electrolysis by laboratory-scale experiments;
3. Use experiments to build validated mathematical models of transport phenomena in the process which can estimate its performance at larger scales;
4. Develop large-scale industrial design concepts, and estimate their performance using mathematical modeling.

Electrorefining was assumed to overcome the three problems with distillation: the molten salt would dissolve any oxide which would get in the way of distillation; an anodic potential at the mixed liquid would create a driving force for spontaneous separation down to 1% magnesium using only about 0.25-0.35 V (Figure 9 on page 24 shows that the distillation reaction is not spontaneous below about 60% Mg); and zinc's higher electronegativity would cause it to remain with the aluminum resulting in a higher-purity magnesium product.

Project Team and Relevant Experience

This project built on MOxST's expertise with molten salt electrolysis of metal oxides, including magnesium oxide, which the company is scaling up for industrial use. MOxST won SBIR Phase I and Phase II grants from the National Science Foundation, a research subcontract from Oak Ridge National Laboratories, and a large $6M award from the Department of Energy Vehicle Technologies Program, to fund the many aspects of MagGen™ scale-up R&D. Synergies between MagGen™ and the originally envisioned electrorefining process are as follows:

- General high-temperature molten salt electrochemistry;
- Production of magnesium vapor at a steel cathode from its ions in molten salt solution;
- Argon stirring of a molten salt and dilution of magnesium to prevent its reaction with components of other oxides such as zirconia;
- Electrolysis of magnesium oxide in particular.

MOxST team members on this project are:

- Adam C. Powell, IV Ph.D., Principal Investigator, and CTO and Co-Founder of MOxST. Powell had worked on the MgO reduction process as a consultant to its inventor Uday Pal at Boston University, and had over 10 years of experience beyond his degree in materials process modeling and scale-up engineering. Powell is also the lead author of MOxST's metal electrorefining patent application.

- Uday B. Pal, Ph.D., Co-Principal Investigator, Professor, and Head of the Division of Materials Science and Engineering at Boston University. Pal invented the general electrolysis technology for producing metals from their oxides which the MagGen™ process uses to produce magnesium.[12,13] He is a recognized research leader in solid oxide fuel cells, steelmaking, copper refining, and related technologies. He has authored 81 refereed journal articles and 83 other publications. He is an inventor or co-inventor of 20 issued United States patents.
- Soobhankar Pati, Ph.D., Research Engineer at MOxST. Pati had over five years of experience in Prof. Pal's research laboratory at BU working on metal electrolysis and related technologies, and has led much of the experimental work at MOxST.
- John Strauss, VP of Business Development at MOxST. Strauss had over 20 years of entrepreneurship experience prior to joining MOxST. He started working on this project in October 2011 and performed much of the commercialization study.

New Magnesium Refining Chemistry

This project took an unexpected turn when the first two experiments produced about twenty times more magnesium than the integrated electrorefining current would have predicted. This shifted the project's experimental focus to understanding the phenomena behind this high rate. Experiments demonstrated that this was due to metallic magnesium dissolution in molten salt, followed by argon bubbling-assisted evaporation of that magnesium from the salt. Effectively this new refining chemistry is indirect distillation mediated by the molten salt and argon.

By way of background, magnesium metal is much more soluble in the molten salts used in this study than many other metals such as aluminum, iron, and zinc.[14] This study used MgF_2-CaF_2 eutectic salt because of its excellent compatibility with the yttria-stabilized zirconia (YSZ) inserted to protect the electrolysis anodes and anode product gas (oxygen or CO_2) from the molten salt and magnesium vapor product. Prior work had found that magnesium metal solubility in this salt at process temperatures around 1150-1190° C is approximately 0.1 wt% in equilibrium with vapor at 1 atm, which is much higher than that of many other metals.

This new chemistry mechanism of salt dissolution with argon-assisted evaporation retains the advantages listed above which electrorefining would have had over plain distillation and which motivated this project: the molten salt dissolves oxides which would otherwise block metal reactions; the salt catalyzes magnesium removal from the scrap liquid; and solubility of magnesium in the salt is higher than that of zinc, resulting in high magnesium product purity. But it accelerates the kinetics, and simplifies the process because the new MagReGen™ process does not require a high-current electrode to operate in the liquid scrap metal.

This unexpected turn forced a shift in MOxST thinking on industrial design and modeling approach. It introduced new questions and unknown parameters, such as those which govern kinetics of magnesium transport through the alloy melt, into the salt, and into the argon. The modeling and industrial design sections of the report on pages 32 and 37 describe those aspects of this project work in detail.

Because of the novelty of the new refining chemistry, commercialization will require significant further R&D to bridge the “valley of death” between research and industrial-scale production, as described in the Recommendations section on page 54.

3. Results and Discussion

This section is organized around project tasks as described in the Statement of Project Objectives with two exceptions: Benefits Assessment on p. 39 describes Task 1 Potential Benefits Assessment, and we do not present Task 5 Project Management and Reporting.

3.1 Experimental Study

Boston University performed five experiments at laboratory scale to develop the MagReGen™ magnesium recycling process. The experimental goals were to understand the electrochemical fundamentals of magnesium electrorefining from a magnesium-aluminum alloy, to test the performance of electrolysis of magnesium oxide in a refining cell, to investigate recovery of magnesium from a mixture of magnesium-aluminum alloy and magnesium oxide, and to provide input and validation for scale-up models. This report presents a brief overview of the first three experiments, followed by detailed results of the last two experiments, which were performed to test the hypothesis that refining proceeds by selective dissolution and transport through the molten salt with argon-assisted evaporation, rather than electrorefining and distillation.

Experimental Design and Procedure

Figures 5 and 6 show the designs of the setups for all five experiments in this project. The setup consists of an upper reaction chamber, heated to 1175ºC and a lower condensing chamber with a temperature gradient from 1100 at the top to 200ºC at the bottom. The setup was fabricated using grade 304 stainless steel (SS-304) and heated in an argon atmosphere.

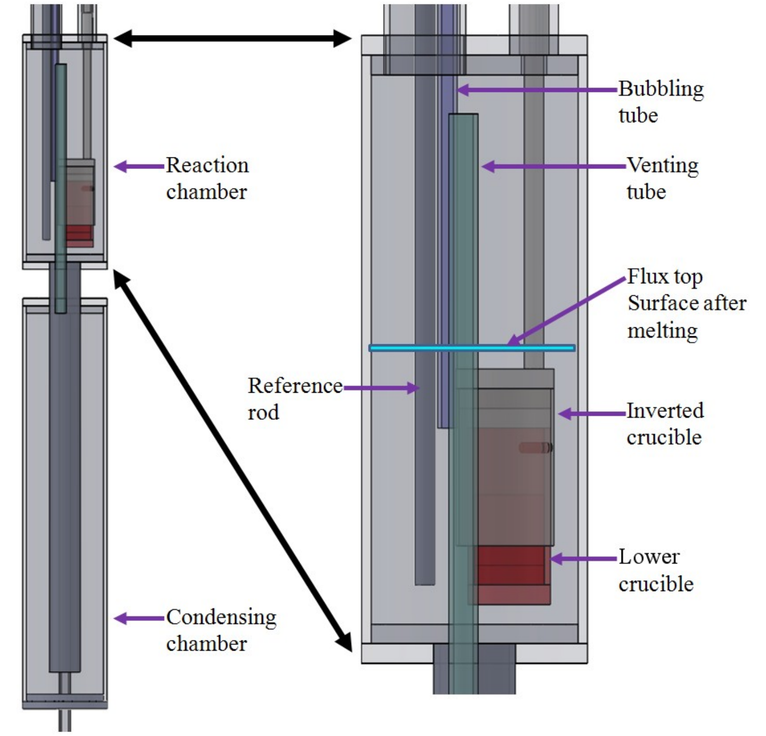


Figure 5: Experimental apparatus for alloy refining experiments.

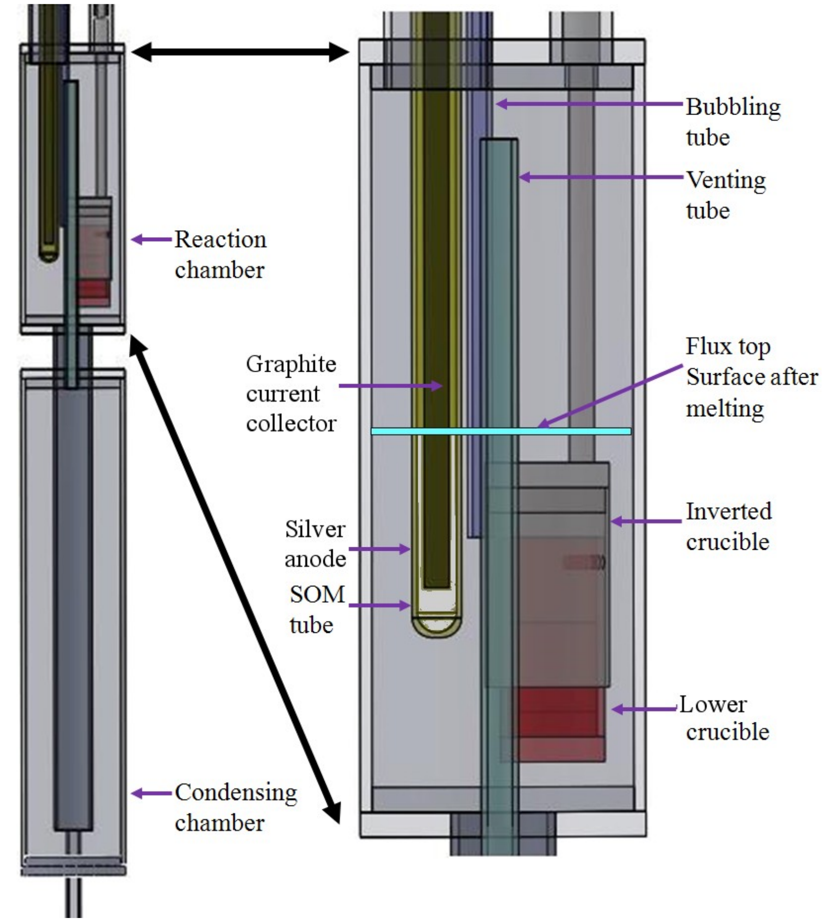


Figure 6: Experimental apparatus for alloy refining and magnesium oxide reduction.

In all experiments, the reaction chamber was continually purged with a forming gas (95%Ar) at 15-20cc/min through the bubbling tube, and at 30-40cc/min through each of the two annuli at the top of the reaction chamber. This was done to lower the partial pressure of magnesium vapor over the flux and to carry the magnesium vapor to the condensing chamber. The inlet of the venting tube was well above the salt surface to prevent any of it from entering the condenser. In the scaled-up process, it will be possible to recycle nearly all of this argon.

All experiments used a powdered flux electrolyte (MgF_2-CaF_2-10wt.%MgO-2wt.%YF_3) containing a eutectic mixture of 45wt.%MgF_2-55wt.%CaF_2 with a melting point of 974ºC.[15] We used a mixture of aluminum and magnesium in the scrap charge in order to reduce the partial pressure of magnesium in the system. The presence of aluminum or other dilutant is a general requirement of the process, though dilutant reuse is possible when recycling magnesium alloys rather than Al-Mg scrap mixtures.

Experiments 1, 2 and 3

The first experiment used the refining apparatus shown in Figure 5. Unfortunately, the forming gas stopped bubbling when the temperature reached 1150°C, before attempting any refining. The problem started when the venting tube clogged due to its small inner diameter (1/8 inch). The forming gas flow rate (400 cc/min) was very high and magnesium vapor which got carried by the forming gas could not all deposit in the stainless steel condenser and instead collected in the venting tube resulting in clogging the tube. This also resulted in an increase in the pressure inside the reaction chamber which pushed the flux back into the bubbling tube and the flux solidified in the colder parts of the bubbling tube. When both the bubbling and venting tubes became clogged the experiment had to end prematurely.

In the second experiment, the venting tube had a larger inner diameter (1/4 inch). Potentiodynamic scans (PDS) were performed and the current-voltage relationships were measured. In each of the current-voltage sweeps, it was observed that the current increased linearly with applied potential, except at two potentials when a jump in the current was observed. The current-voltage curve also shifted in the positive direction over time, indicating that the alloy was being refined. Unfortunately, the inert gas flow rate into the molten salt bath was very high (200 cc/min) which caused it to splash and enter into the venting tube and clog it. The experiment thus ended prematurely.

In the third experiment, the inert gas stirring of the salt was lowered to 50 cc/min and a new design change in the setup for alloy containment was implemented. The alloy was first prepared in a stainless steel crucible with holes in the lower part of its walls, and then the flux was packed on the top of the alloy inside the crucible. A stainless steel endcap was welded on the top of a crucible. The crucible was then inverted and placed inside the reaction chamber. During this experiment, at temperature, the alloy came out of the sealed crucible through both the holes and openings created by crucible dissolution into the alloy, and no refining could be done. The experiment also ended prematurely.

Based on this experiment, it was decided that the alloy should be placed in the bottom crucible inside the inverted crucible, instead of in the upper inverted crucible, and that the alloy should contain 2 g iron in order to saturate it and prevent chemical attack on the crucible. These decisions resulted in two successful experiments.

Experiment 4: Alloy Refining and Magnesium Oxide Reduction

Procedure

This experiment used the setup shown in Figure 6, with a zirconia anode tube, in order to carry out magnesium oxide reduction from the oxide present in the flux, as well as alloy refining.

The Mg-Al alloy was prepared by melting a 9.6 g piece of magnesium (Alfa Aesar, 99.8%) and another 9.4 g piece of aluminum (Alfa Aesar, 97.9%) together inside a small SS-304 crucible. The mixture of magnesium and aluminum was stirred with a SS-304 rod for 15 minutes at 800ºC in an argon atmosphere, then held at the same temperature without stirring for 15 minutes and subsequently quenched. The alloy was homogeneous and the composition was 50.5wt%Mg-Al.

Since there is some solubility of iron in Mg-Al alloy, 2 g of iron powder was added on the top of the Mg-Al alloy to decrease dissolution of iron from the crucible during the experiment. The iron powder addition also increases the density of the alloy (which sinks to the flux bottom in the lower crucible). Flux was packed both inside and outside the inverted crucible shown in Figure 6. The inner diameter of the inverted crucible is slightly bigger than the outside diameter of the lower crucible so there is a gap between the lower crucible and the inverted crucible through which the molten flux can pass through. In order to prevent the distillation of magnesium from the Mg-Al alloy during heating to 974ºC, a layer of flux was melted on the surface of the lower crucible to hermetically seal the opening of the lower crucible before heating. Thus, the alloy was trapped inside the lower crucible, and direct distillation of magnesium was avoided. A result of pre-melting the flux at the top of the lower crucible was that some of magnesium in the alloy became oxidized. This magnesium oxide was later reduced by the electrolysis process.

During the refining process, the lower crucible and inverted crucible served as the anode, and the reaction chamber wall and bubbling tube served as the cathode for the PDS. The zirconia solid electrolyte tube was held above the salt. An alumina spacer was used to insulate the rod connecting the inverted crucible from the reaction chamber. Multiple PDS were performed to determine the electrorefining potential for magnesium as the refining of magnesium proceeded.

During the electrolysis process, the stainless steel wall of the reaction chamber still served as the cathode. Liquid silver anode inside a yttria stabilized zirconia (YSZ) solid electrolyte tube was used as the anode, and a graphite rod immersed in the silver acted as the anodic current collector and reactant with produced oxygen. When the applied electric potential between the cathode and anode exceeds the dissociation potential of magnesium oxide, magnesium vapor is produced at the cathode, and carbon reacts with oxygen to generate carbon monoxide.[16,17] With 680 g of flux, the system started with 68 g of MgO. The overall cell reaction is given as:

$$MgO + C \rightarrow Mg(g) + CO(g) \qquad (1)$$

Magnesium Refining

Once the reaction chamber was at the desired temperature (1175°C), PDS was performed as shown in Figure 7. The initial melted flux is entirely ionic and acts as an electronic insulator between the anode and the cathode. The current increases linearly as the applied potential increases, except at the two current jumps corresponding to magnesium dissolution and magnesium bubble nucleation at the cathode, as can be seen in each scan. The current-voltage curve is shifting in a positive direction over time from PDS1 to PDS5 labeled in Figure 7, which were taken at 4:13, 5:36, 6:28, 7:38 and 8:45 PM respectively. This shift is due to decreasing magnesium concentration in the alloy as explained later. The ohmic resistance of the system was measured to be as low as 0.066 Ω using EIS as shown in Figure 8.

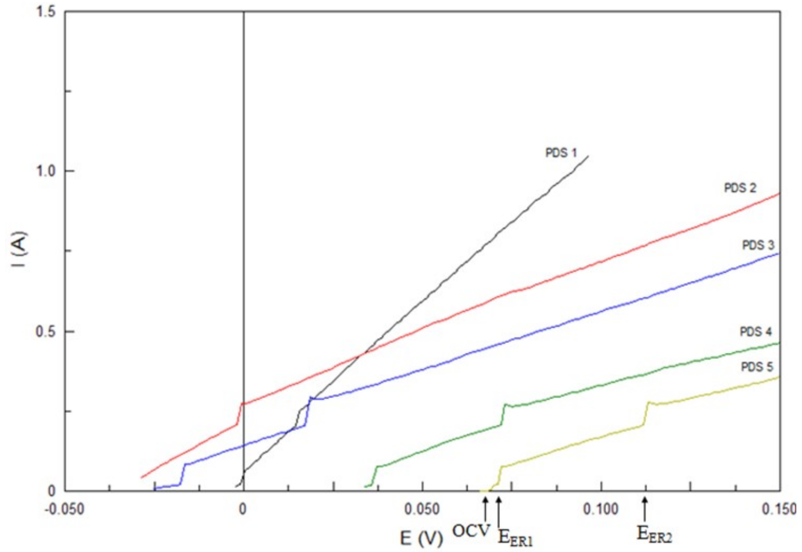


Figure 7: Current-voltage relationships for the refining process at various times. The open circuit voltage and two electrorefining potentials (OCV, E_{ER1}, E_{ER2}) for the last scan are indicated by arrows.

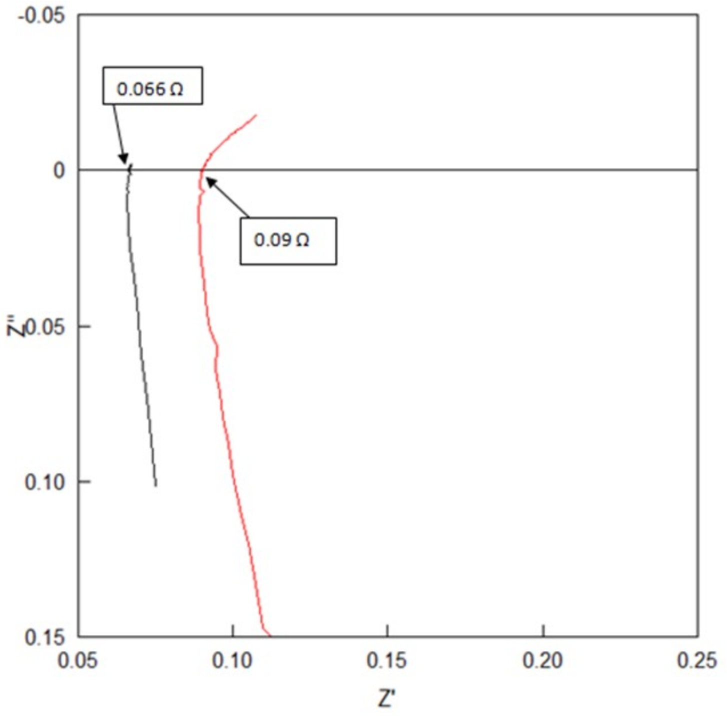


Figure 8: EIS results at two different times during refining.

One potential reason for the low resistance, or high electronic conductivity, is the dissolution of metallic magnesium in the flux. It has been shown that magnesium has a monotectic solubility of 0.3 to 0.6 mol% in MgF_2.[18] The magnesium metal solubility inside the salt after the experiment was found to be 0.03wt% as measured by hydrogen evolution. In that method, dilute acid was added to powdered flux in a closed container and the volume of gas produced, due to hydrogen evolution, was measured. The flux was powdered in an argon-filled glove box to avoid the oxidation of magnesium in the flux. The magnesium solubility inside a flux of similar composition ($50.5\%MgF_2$-$39.5\%CaF_2$-$10\%MgO$) was reported to be 0.02-0.05wt.%.[19] The measured magnesium solubility in the flux after the experiment should be smaller than the magnesium solubility in the molten flux during the experiment, because the dissolved magnesium is continuously carried away by the bubbling gas.

For each PDS, there are two current jumps which correspond to two different electrochemical reactions (Figure 7). The current jump at the first potential, close to the open circuit voltage is due to the following electrochemical reactions:

Anode: $$\mathrm{Mg\ (alloy)} \rightarrow \mathrm{Mg^{2+}} + 2e^- \qquad (2)$$

Cathode: $$\mathrm{Mg^{2+}} + 2e^- \rightarrow \mathrm{Mg\ (flux)} \qquad (3)$$

Overall: $$\mathrm{Mg\ (alloy)} \rightarrow \mathrm{Mg\ (flux)} \qquad (4)$$

This reaction is different from direct dissolution of magnesium from Mg-Al alloy into flux. It is the reduced magnesium at the cathode that dissolves in the flux. The electrorefining potential corresponds to the first current jump is named as the electrorefining potential for dissolution (E_{ER1}). Theoretically, the electrorefining potential for dissolution should be equal to the open circuit voltage, and its expression is given by:

$$E_{ER1} = OCV = E_{anode} - E_{cathode} = \frac{RT}{2F} \ln \frac{a_{Mg(flux)}}{a_{Mg(alloy)}} = \frac{RT}{2F} \ln \frac{P_{Mg(flux)}/P^0_{Mg}}{\gamma X_{Mg(alloy)}}, \tag{5}$$

where γ is the activity coefficient of magnesium in the Mg-Al alloy; $X_{Mg(alloy)}$ is the magnesium mole fraction in the alloy, P_{Mg}^0 = 1.9 atm is the Mg vapor pressure at 1175° C, $P_{Mg(flux)}$ is the partial pressure of Mg vapor in equilibrium with liquid Mg dissolved in flux at the cathode.

According to Equation (5), the electrorefining potential for dissolution and the open circuit voltage depends on the ratio of the activity of magnesium dissolved in the flux and the activity of magnesium in the alloy. There is a minor difference between the open circuit voltage and the electrorefining potential for dissolution in the experimental measurement caused by the fluctuating value of $P_{Mg(flux)}$.

The second current jump at the higher potential is due to the following reaction:

Anode: $Mg\ (alloy) \rightarrow Mg^{2+} + 2e^-$ (6)

Cathode: $Mg^{2+} + 2e^- \rightarrow Mg\ (g)$ (7)

Overall reaction: $Mg\ (alloy) \rightarrow Mg\ (g)$ (8)

In this reaction, reduced magnesium at the cathode accumulates and nucleates into bubbles. The electrorefining corresponding to the second current jump is named as the electrorefining potential for bubble nucleation (E_{ER2}). The theoretical expression of electrorefining potential for bubble nucleation for Reaction (8) is given by Equation (9), and is plotted in Figure 9 when the partial pressure of the magnesium bubble nucleated $P_{Mg(g)}$ is assumed to be 1 atm. The electrorefining potential for bubble nucleation depends on the ratio of the activity of the nucleated magnesium at the cathode and the activity of the magnesium in the alloy.

$$E_{ER2} = E_{anode} - E_{cathode} = \frac{RT}{2F} \ln \frac{a_{Mg(g)}}{a_{Mg(alloy)}} = \frac{RT}{2F} \ln \frac{P_{Mg(g)}/P^0_{Mg}}{\gamma X_{Mg(alloy)}}, \tag{9}$$

where $P_{Mg(g)}$ is the partial pressure of a magnesium bubble nucleated at the cathode.

Figure 9 shows that as the magnesium content in the scrap goes down, the electrorefining potential for bubble nucleation (E_{ER2}) increases. The experimental result of the dependence of the electrorefining potential for bubble nucleation and the open circuit voltage on time is shown in Figure 10. The electrorefining potential for bubble nucleation and open circuit voltage increase with time, which indicates that the magnesium content in the scrap is decreasing as refining proceeds. The magnesium content in the scrap decreases due to the solubility of magnesium in the flux. These values E_{ER1} and E_{ER2} thus give us electrical measurements which correlate with magnesium content of the scrap alloy.

Magnesium dissolution in the flux is followed by vapor phase removal of the dissolved magnesium from the flux. The refining process can be expressed as: Mg (alloy) → Mg (flux) → Mg (g). Overall, pure magnesium is refined from magnesium scrap.

Magnesium Oxide Reduction

Once the electrorefining potential for bubble nucleation reached 0.13 V, the anode was switched from the scrap anode to the liquid silver and carbon rod inside the YSZ tube, which was lowered into the flux, and a new potential was applied. When the potential reaches the magnesium oxide dissociation potential, oxygen ions are pumped out of the flux through the YSZ membrane and are oxidized at the liquid silver anode by the graphite current collector; meanwhile, magnesium ions at the cathode are reduced to magnesium, which is then collected in the condenser.

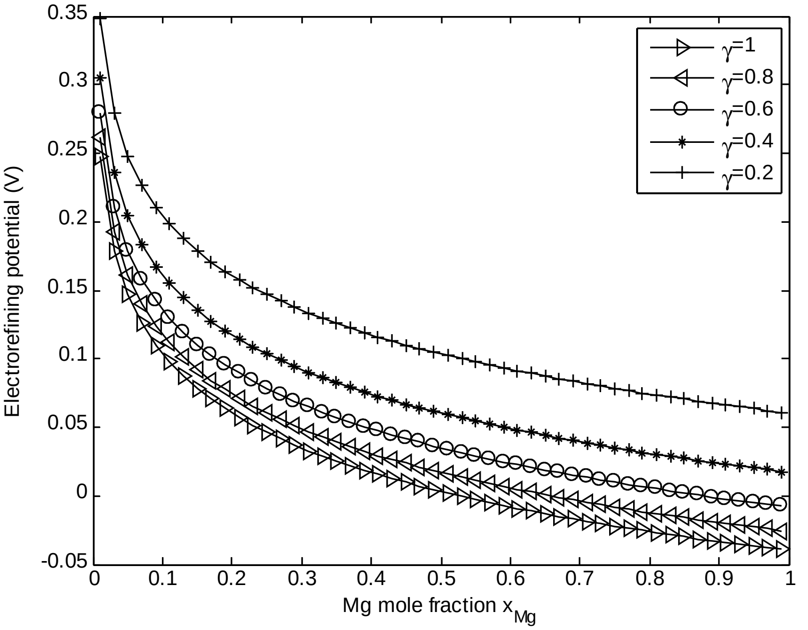


Figure 9: Theoretical electrorefining potential for magnesium bubble nucleation vs. Mg-Al scrap anode composition for several values of γ (from equation 9).

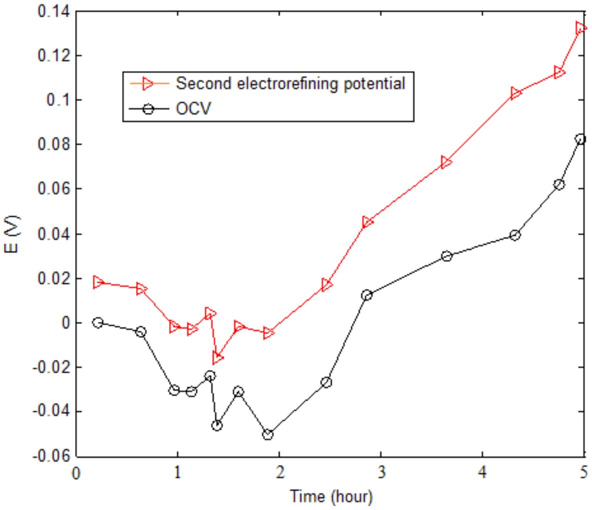


Figure 10: Electrorefining potentials for bubble nucleation (triangles) and OCV (circles) during refining.

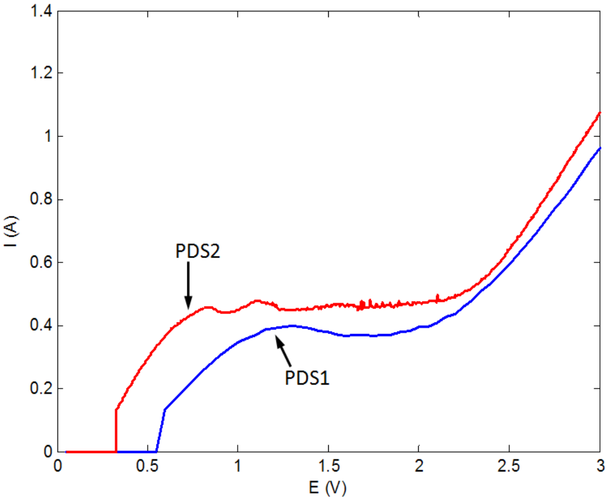


Figure 11: Current-voltage relationships before (PDS1) and after (PDS2) two hours of electrolysis.

Electrolysis was performed for a total of two hours at a potential of 3V. The curve labeled “PDS1” in Figure 11 shows the initial PDS before any electrolysis was performed, and shows an electronic current of 0.35A due to the dissolution of magnesium from the scrap into the flux. The curve labeled “electrolysis 1” in Figure 12 shows the current-time relationship during the first hour of electrolysis. Current efficiency is defined as the ratio of Faradic current to total applied current, and was calculated to be approximately 41% for the first hour of electrolysis. Faradaic current is calculated by measuring the flow rate of carbon monoxide produced from the reaction of the graphite current collector and oxygen on the anode side of the YSZ membrane. Based on the volume of carbon monoxide generated, magnesium reduced at the cathode was calculated to be 0.18g during the first hour of electrolysis.

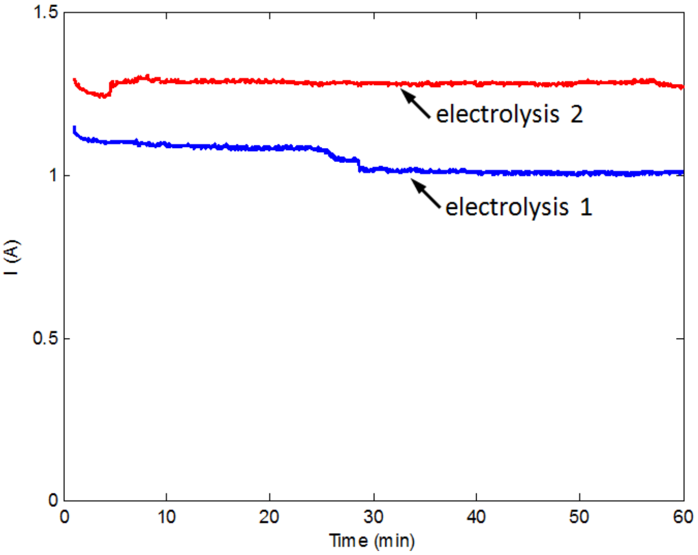


Figure 12: Current-time relationships for the first hour (electrolysis 1) and second hour (electrolysis 2). Both were performed at 3V.

The curve labeled “PDS2” in Figure 11 shows the PDS before the second hour of electrolysis, and shows an increase in leakage current due to a higher concentration of magnesium dissolved in the flux. The curve labeled “electrolysis 2” in Figure 12 shows the current-time relationship during the second hour of electrolysis. For the second hour of electrolysis, the current efficiency was 39%, and the amount of magnesium reduced was 0.22 g, very similar to the first hour. The total amount of magnesium reduced in the entire two hours of electrolysis was 0.40 g. This corresponds to reduction of approximately 1% of the 68 g MgO present in the salt at the start of the experiment. An industrial cell would run at higher potential for much higher current density and use other methods to increase current efficiency.

Overall Production and Composition

The total magnesium collected in the condenser from both the refining and electrolysis processes was weighed and found to be 7.4 g. With 0.4 g coming from oxide electrolysis, the 7.0 g from refining is 73% of the initial 9.6 g Mg in the charge. Energy-dispersive X-ray spectroscopy (EDS) results for the collected magnesium are shown in Figure 13a. From these results, the purity of the collected magnesium was determined to be 99.6wt%.

The scrap residue remained at the bottom of the lower crucible. The iron powder as well as iron and chromium from the SS 304 crucibles alloyed with the scrap, which has a density higher than the flux. EDS was performed on the magnesium residue, and the results are shown in Figure 13b. Only trace magnesium remained in the alloy, thus approximately 100% of the magnesium was removed from the alloy. It is likely that the Mg which didn't reach the condenser condensed in other parts of the apparatus, *e.g.* in and above the crucible. Future experiments may replace stainless steel with other metals to minimize dissolution of certain elements (Cr, Ni).

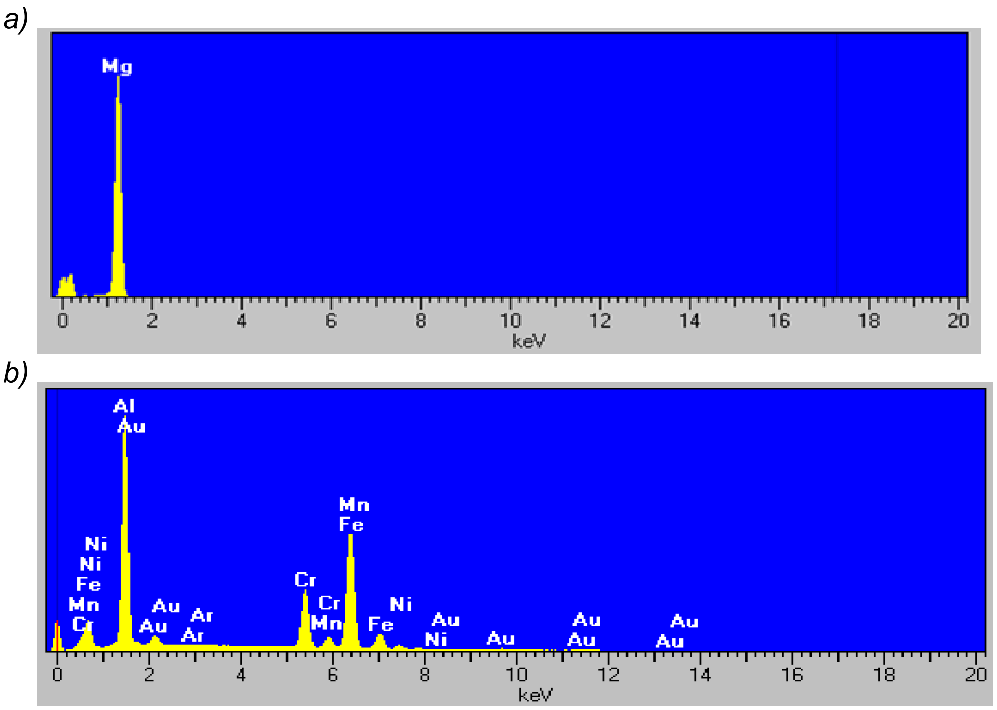


Figure 13: Energy-dispersive spectra (EDS) for (a) collected magnesium and (b) scrap residue remaining in the lower crucible.

Experiment 5: AZ91D magnesium alloy refining

Experimental Procedure

Figure 5 shows the design of the setup used in the Experiment 5. The setup was the same as the one used in Experiment 4 except that the YSZ tube and silver electrolysis anode was replaced by a stainless steel reference electrode. The reference electrode was insulated from the reaction chamber by an alumina spacer. The setup was also heated in an argon (Ar) atmosphere, and the upper reaction chamber was heated to 1150ºC.

Aluminum	8.3-9.7 wt%
Zinc	0.35-1.0%
Manganese	0.15%
Si	0.10% max
Cu	0.030% max
Fe	0.005% max
Ni	0.002% max
Other (each)	0.02% max
Magnesium	balance

Table 1: Composition limits of AZ91D magnesium alloy

The composition specification for AZ91D is shown in Table 1. 10.7 g of AZ91D magnesium alloy was first melted in the lower crucible. Then, a 9.2 g piece of aluminum (Al>97.9%) was melted together with the AZ91D to form 48.4wt.%Mg-Al-Zn alloy, in order to decrease the magnesium and zinc partial pressure in the alloy. In addition, 2.5 g of iron powder was added on the top of the Mg-Al-Zn alloy. A powdered flux (MgF_2-CaF_2-9wt.%MgO-1.8wt.%YF_3) containing a eutectic mixture of 45wt.%MgF_2-55wt.%CaF_2 with a melting point of 974°C was used as the electrolyte and was packed both inside and outside the inverted crucible shown in Figure 5. In order to prevent the distillation of magnesium and zinc from the alloy during heating to 974°C, a layer of flux is melted on the surface of the crucible to hermetically seal the opening of the lower crucible before heating. Thus, the alloy is trapped inside the lower crucible, and the direct distillation of magnesium and zinc are avoided.

During the refining process, PDS was performed between the lower crucible together with the inverted crucible as the anode and the reaction chamber wall as the cathode to determine the electrorefining potential for magnesium. The potentiostatic holds (PSH) and Electrochemical Impedance Spectroscopy (EIS) scans were performed between the reference rod as the anode and the reaction chamber wall as the cathode to measure the electronic and ionic resistances of the molten salt.

Experimental Results

Once the reaction chamber reached the desired temperature (1150°C), PDS was performed as shown in Figure 14. Like the previous experiment, in each PDS, the current increased roughly linearly with the applied potential, except at the two current jumps. As explained earlier, the first current jump corresponds to the magnesium dissolution at the scrap electrode; and the second current jump corresponds to the magnesium bubble nucleation at the cathode. The current-voltage curve shifted in a positive direction over time. Figure 15 shows electrorefining potential for bubble nucleation as a function of time.

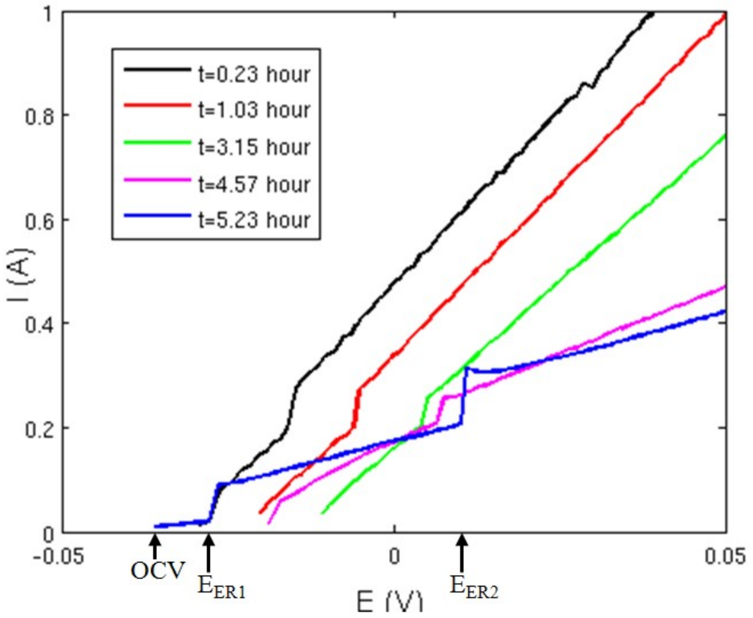


Figure 14: Current-voltage relationships from the refining experiment at different times. The OCV, E_{ER1} and E_{ER2} potentials for the last scan are indicated by arrows.

During the experiment, the PSHs were performed between the reference rod as the anode and the chamber wall as the cathode. It should be noted that the anode was switched from the lower crucible to the reference rod, labeled in Figure 5, for the PSH. Figure 16 shows a PSH at t=2.6 hours, where the applied voltage is 0.105 V and the total current on average is 0.26 A.

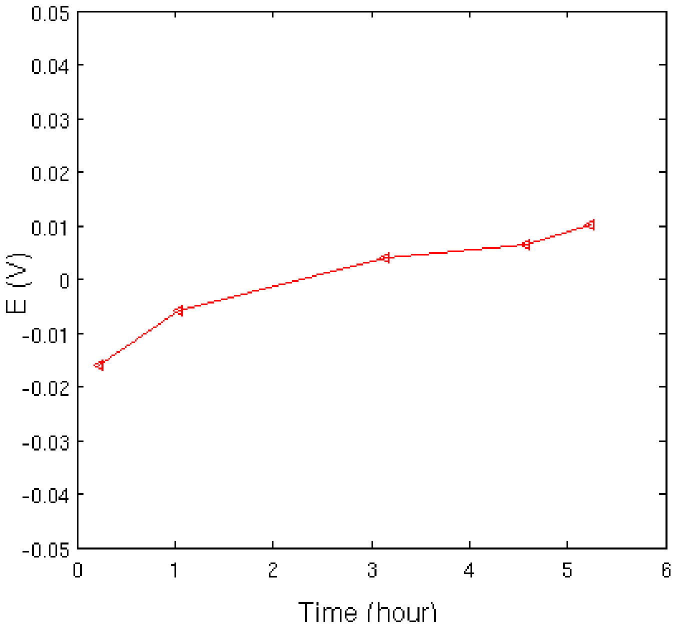


Figure 15: Electrorefining potential for bubble nucleation vs. time.

The electronic resistance (R_e) can be calculated by dividing the applied voltage by the non-Faradaic current. The non-Faradaic current equals the total current minus the Faradaic current. The Faradaic current is calculated from the current-voltage curves obtained by PDS between the reference rod and the chamber wall shown in Figure 18. Each current jump corresponds to a Faradaic current. The Faradaic currents for the two current jumps in each PDS shown in Figure 18 are estimated to be 0.032 A and 0.038 A, respectively. Figure 17 shows the dependence of this calculated flux electronic resistance on time.

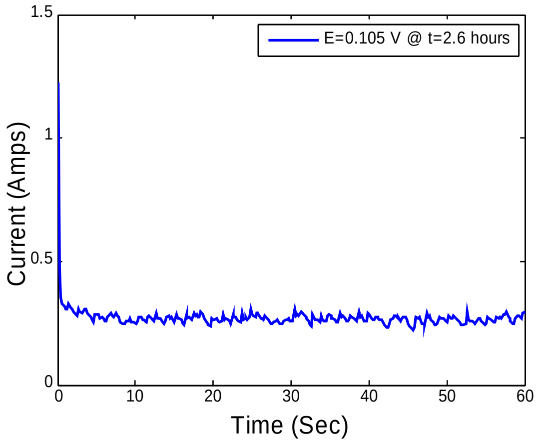


Figure 16: Current-time relationship from the PSH between the reference rod and chamber wall at t=2.6 hours.

The flux electronic resistance is related to the amount of the dissolved magnesium in the flux,

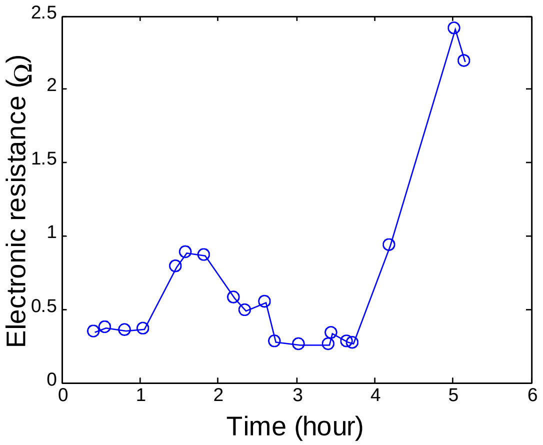


Figure 17: Dependence of electronic resistance on time.

which is determined by the dissolution rate of magnesium from the magnesium alloy into the flux and the evaporation rate of the dissolved magnesium from the flux into the gas phase. From t=0.4 hour to t=3.7 hours, the electronic resistance is approximately 0.5 Ω as shown in Figure 17, indicating constant concentration and a balance between dissolution and evaporation. From t=3.7 hours to t=5.2 hours, the electronic resistance increases, because the dissolution of magnesium from the alloy slows down as the magnesium content decreases in the alloy.

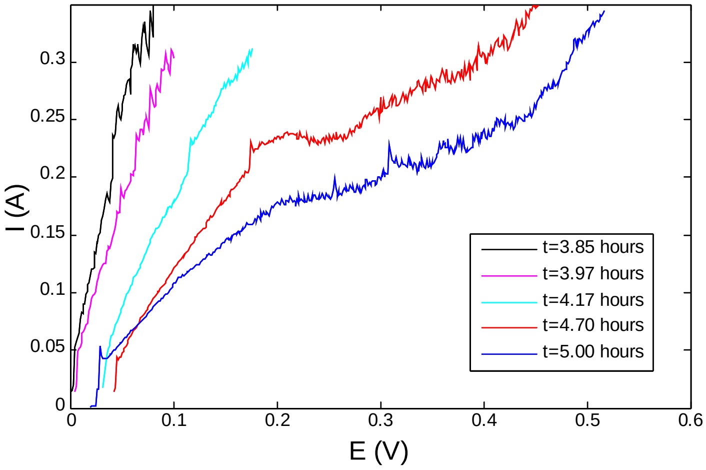


Figure 18: Current-voltage relationships during PDS between the reference rod and chamber wall from t=3.85 to 5.00 hours.

The slope of the each PDS curve is decreasing from t=3.85 hours to t=5 hours as shown in Figure 18, that is, the electronic resistance is increasing, consistent with the result in Figure 17. It should be noted that there are also two current jumps in each PDS as shown in Figure 14. The first current jump corresponds to the electrochemical reactions:

Anode: $$\text{Mg (flux, anode)} \rightarrow Mg^{2+} + 2e^- \quad (10)$$

Cathode: $$Mg^{2+} + 2e^- \rightarrow \text{Mg (flux, cathode)} \quad (11)$$

Overall reaction: $\mathrm{Mg\ (flux,\ anode)} \rightarrow \mathrm{Mg\ (flux,\ cathode)}$ (12)

In the above equations, Mg(flux, a) is the magnesium dissolved in the flux at the anode, and Mg(flux, c) is the magnesium dissolved in the flux at the cathode. The second current jump corresponds to the electrochemical reactions:

Anode: $\mathrm{Mg\ (flux,\ anode)} \rightarrow \mathrm{Mg}^{2+} + 2e^{-}$ (13)

Cathode: $\mathrm{Mg}^{2+} + 2e^{-} \rightarrow \mathrm{Mg\ (g)}$ (14)

Overall reaction: $\mathrm{Mg\ (flux,\ anode)} \rightarrow \mathrm{Mg\ (g)}$ (15)

EIS scans between the reference rod and chamber wall measured the total ohmic resistance of the flux. Figure 19 shows that total resistance of the flux vs. time. The electronic and ionic resistances of the flux can be considered two resistors in parallel, and the relationship between the total ohmic resistance (R_T), and its electronic and ionic components can be expressed by:

$$\frac{1}{R_T} = \frac{1}{R_e} + \frac{1}{R_{i.}} \tag{16}$$

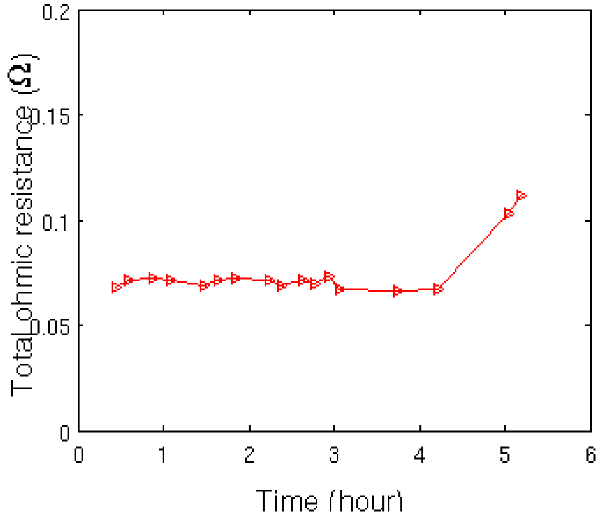


Figure 19: Total ohmic resistance of the flux measured by EIS.

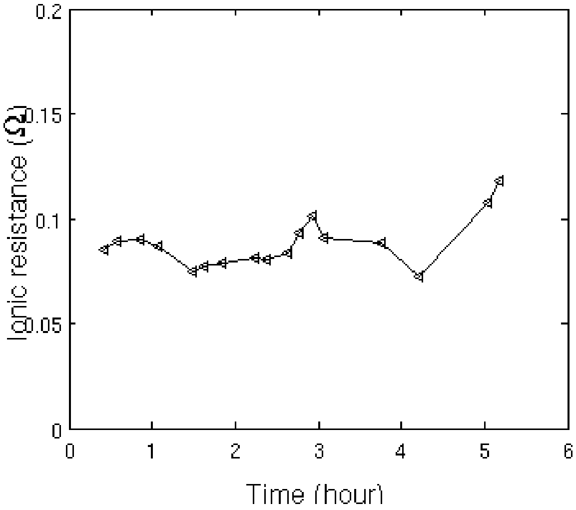


Figure 20: Calculated flux ionic resistance.

From Equation (16), the flux ionic resistance (R_i), as shown in Figure 20, can be calculated based on the measured values of the flux electronic resistance and the flux total resistance. The ionic transference number,[20] shown in Figure 21, can be calculated using the expression:

$$t_i = \frac{R_e}{R_e + R_i}. \tag{17}$$

The ionic transference number is close to 1; that is, flux conductivity is dominated by ions.

Overall Production and Composition

The total magnesium collected in the condenser from refining was weighed and found to be 6 g, i.e. 62% of the magnesium in the charge. EDS results for the collected magnesium are shown in Figure 22a. From these results, the purity of the collected magnesium was determined to be 99.35wt% (metal basis).The content of Zn is 0.46wt.% (metal basis), approximately half of that in the starting AZ91D magnesium alloy.

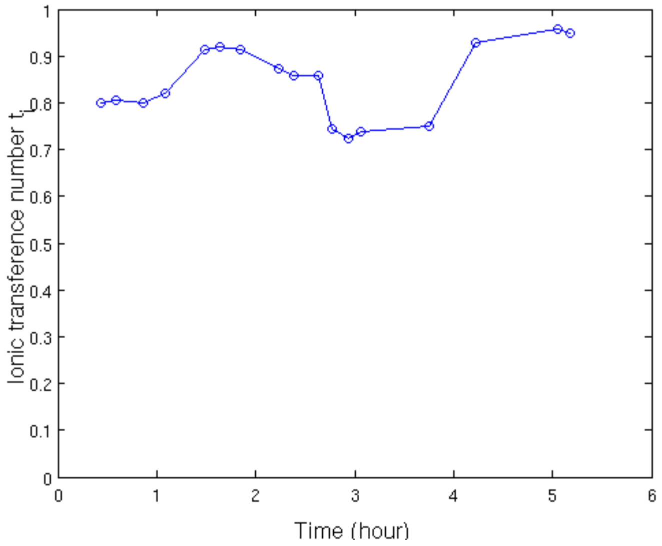


Figure 21: Ionic transference number of the flux.

The alloy residue remained at the bottom of the lower crucible. The iron powder as well as iron and chromium from the SS 304 crucibles alloyed with the scrap, which has a density higher than the flux. EDS was performed on the alloy residue, and the results are shown in Figure 22b. No measurable magnesium remained in the alloy, thus approximately 100% of the magnesium was removed from the scrap. The portion which did not reach the condenser either dissolved in the molten salt or collected elsewhere in the apparatus. An industrial cell would recover the magnesium in the salt by reusing that salt, and model-based industrial feed and condenser designs should be able to prevent magnesium losses to other parts of the apparatus, such that industrial yield should be very close to 100%.

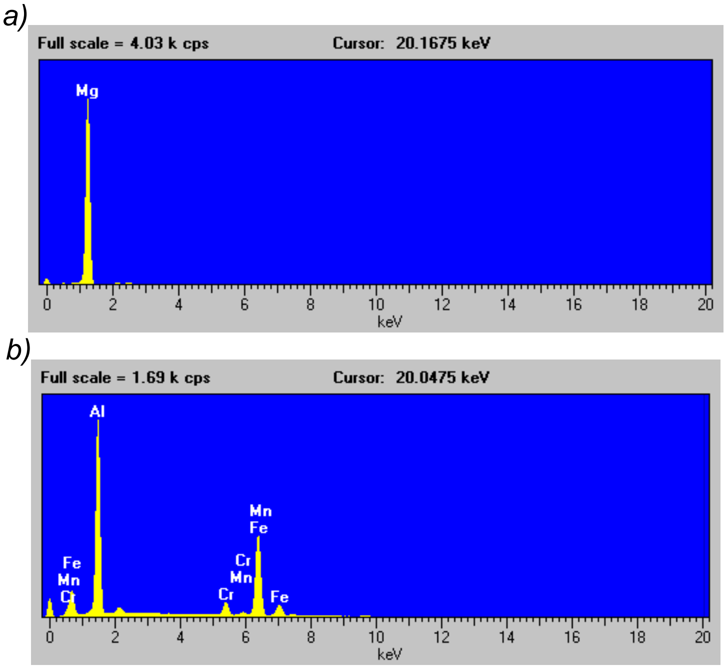


Figure 22: EDS results for (a) collected magnesium and (b) lower crucible scrap residue.

3.2 Mathematical Model

Mathematical modeling is an essential tool for any scale-up engineering effort, as changing the size of a process can result in qualitative changes to its behavior which can enhance or impede its operation in an industrial context. This is particularly true when experiments are very difficult or expensive at large scale, as is the case for this high-temperature process in a controlled atmosphere. For this reason, MOxST proposed modeling as a high-level task for this project.

This modeling task proceeded in three parts. First, MOxST developed the modeling formulation for understanding transport phenomena in combined electrorefining and electrolysis, and performed a general 2-D simulation of the process components. Next the BU group used COMSOL in 2-D and 3-D models of the new refining mechanism in the experimental apparatus. Finally, MOxST brought the lessons learned in both of these studies together to simulate transport in a 3-D geometry representing a full-scale MagReGen™ magnesium recycling cell.

Model Formulation

The main transport phenomena model for this project simulates magnesium transport from the scrap charge to the argon bubbling tubes through the molten salt whose flow is driven by argon bubbles and thermal buoyancy. The model combines the Navier-Stokes equations for fluid flow, Fourier's equation for heat transfer, electrostatics, and species transport. Assumptions are as follows:

- Uniform properties (viscosity, thermal conductivity, heat capacity, diffusivity, electrical conductivity);
- Incompressible fluid flow, so velocity has zero divergence;
- Boussinesq thermal buoyancy assumptions *i.e.* uniform density with a pressure term to provide the buoyancy driving force;
- Negligible solutal buoyancy effects;
- Negligible electrostatic force or magnetohydrodynamics effects;
- Negligible local accumulation of charge, so current density has zero divergence;

The resulting equation set is as follows:

$$\nabla\cdot\vec{v}=0 \tag{18}$$

$$\rho\left(\frac{\partial\vec{v}}{\partial t}+\vec{v}\cdot\nabla\vec{v}\right)=-\nabla P+\mu\nabla^2\vec{v}+\rho_0(1-\beta)(T-T_0)\vec{g} \tag{19}$$

$$\rho c_p\left(\frac{\partial T}{\partial t}+\vec{v}\cdot\nabla T\right)=k\nabla^2 T+\sigma\nabla V\cdot\nabla V \tag{20}$$

$$\nabla\cdot(\sigma\nabla V)=0 \tag{21}$$

$$\left(\frac{\partial C_i}{\partial t}+\vec{v}_i\cdot\nabla C_i\right)=\rho\nabla\cdot(D_i\nabla C_i)+S_i+\nabla\cdot(\rho D_{i,T}\nabla T)+\nabla\cdot(C_i nFD_i\nabla V), \tag{22}$$

where: v is the velocity vector, ρ is fluid density, T is temperature, ρ_0 is reference density at reference temperature T_0, t is time, P is pressure, μ is fluid viscosity, β is volumetric thermal expansion coefficient (three times the linear thermal expansion coefficient), g is gravitational acceleration, c_p is constant-pressure heat capacity, k is thermal conductivity, σ is total electrical conductivity (ionic and electronic), *V* is electrical potential, C_i is the mass concentration for species *i*, v_i is the convection velocity for species *i* (different for argon bubbles *vs.* other species), D_i is species *i* diffusivity, and S_i is a source term for chemical generation of species *i*. The last term is the electromigration term of the Nernst-Planck equation describing ionic flux in response to an electric field (potential gradient), with Nernst-Einstein mobility $nF\,D_i$ where *n* is the ion charge and *F* is Faraday's constant (charge per mole of electrons).

MOxST extended the Elmer open source Finite Element Analysis (FEA) suite[21] to add a Nernst-Planck electromigration term to its Advection-Diffusion module for ionic species transport, contributed this extension to the Elmer authors along with a case study.[22] Implementing electromigration in Elmer involved adaptation of its Soret thermal diffusion code, which is the second-last term in equation 22. Elmer authors reviewed all MOxST patches and merged them into the main Elmer source code tree.

General 2-D Electrorefining and Electrolysis Simulation

Figure 23 shows the FEA mesh and calculated electrical potential, temperature, and molten salt flow velocity in a 2-D model of the process. In this simulation, reference temperature and outer boundary temperature are set to 1150° C, the electrorefining scrap anode is at 0.25 V, and the oxygen-generating anode is at 3.5V, both relative to the cathode.

Most of the calculated temperature variation is due to Joule heating in the zirconia tube. This has been MOxST's experience also for magnesium electrolysis, and the resulting thermal stress can lead to tube failure. As a practical matter, at a current density of 1 A/cm² or lower, this does not pose a problem.

The similar current densities to the left and right of the cathode, indicated by similar proximity of the electrical iso-potential curves, show that it is possible to balance the currents in the refining and deoxidation circuits despite very different applied voltages. This is for two reasons: much of the voltage drop occurs in the zirconia tube, and current through the zirconia is proportional to oxygen concentration (not shown) such that if there is low oxygen in the molten salt adjacent to the tube, that circuit will pass very little current and use very little power.

This simple model runs well on a modern computer, such as a 2.2 GHz Intel Core Duo laptop.

Model of New Refining Mechanism in Laboratory Geometry

Model Description

This work differs from the general model and industrial cell model in that it uses the COMSOL finite element analysis package with its multiphase flow model to simulate argon bubbling. The model geometry shown in Figure 24 consists of one domain with an inlet for the forming gas (the bottom of the bubbling tube) and another inlet of magnesium (the gap between the inverted crucible and the lower crucible). The molten flux has a diameter of 2.64 inches and a height of 3.5 inches. The model uses a predefined mesh of normal element size.

Boundary Conditions

The following boundary conditions are adopted in the simulation. For the laminar bubbly flow mode, (1) the bubbling tube bottom is the inlet of the forming gas at the flow rate of 20cc/min, and there is no liquid slip; (2) the top surface of the molten flux is the outlet of the forming gas, and there is liquid slip; (3) at the remaining walls, there are neither gas flux nor liquid slip; (4) for the transport of diluted species, the gap between the inverted crucible and the lower crucible is the inlet of the magnesium with an inward flux of 0.1 mol/(m^2s); (5) at the top surface of the molten flux, the magnesium concentration is set to be zero; (6) at the remaining walls, there is no magnesium flux.

Initial Conditions

The following initial conditions are adopted in the simulation. For the laminar bubbly flow mode, the initial molten flux velocity field is zero. For the transport of diluted species, the initial magnesium concentration throughout the flux is zero.

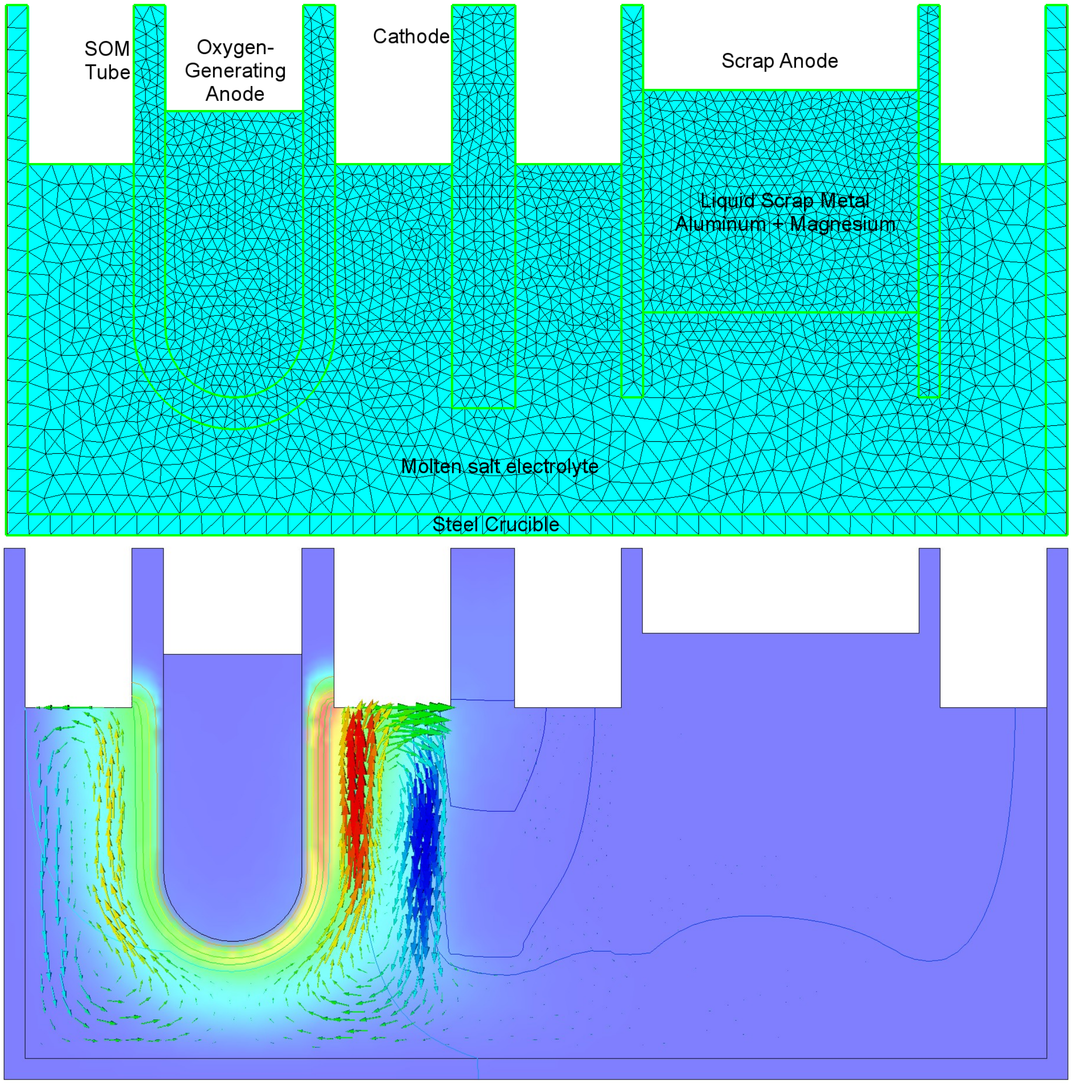
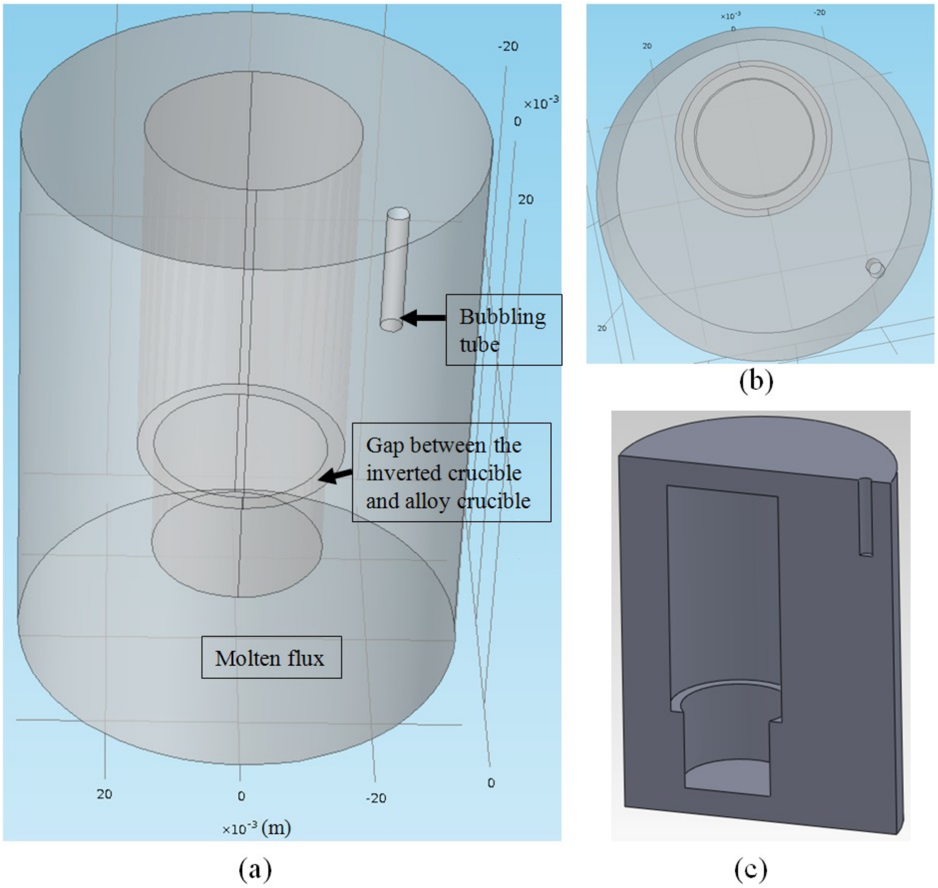


Figure 23: 2-D mathematical model mesh and output showing electrical potential (contours), temperature (background color), and molten salt flow velocity (arrows) with arrow color indicating the vertical component of velocity (red=up, blue=down). Note that several domain boundaries are not shown by the post-processor in the model output.

Results and Discussion

Figure 25 shows the flow profile of the molten flux with the forming gas flow rate of 20cc/min. The left side shows the flow profile of the molten flux on the surface where the maximum velocity magnitude of the molten flux is 2.56 cm/s. The right side shows the molten flux flow profile of the molten flow on the vertical slices where the maximum velocity magnitude of the molten flux is 3.03 cm/s. The forming gas bubbling induces a circulating motion of the flux on the upper part shown in the right of Figure 25. There is a dead zone at the bottom part of the molten flux, which means the velocity magnitude is almost zero and the flux is stagnant.

Figure 26 shows the forming gas volume fraction in the vertical slices. The maximum gas volume fraction at the front slice is 4.52%. Figure 27 shows the magnesium concentration distribution in the flux on the middle vertical slice at t=600 s. The magnesium diffuses out of the gap between the inverted crucible and the lower crucible, and transports through the flux due to the diffusion and convection. As shown in Figure 27, the magnesium at the side close to the bubbling tube rises up, and the magnesium at the other side away from the bubbling tube goes downward. The magnesium transport mainly follows the circulation motion of the molten flux.



(a) (b) (c)

Figure 24: (a) Geometry of the molten salt system. The cylindrical hole on the top surface represents the bubbling tube; the hollow space inside the flux represents the inverted crucible and the lower crucible, between which there is a gap as labeled in the figure. (b) A top view of the geometry of the molten flux system. (c) A full section view of the molten flux system.

The modeling simulates and predicts the flow behavior of the molten flux and also the magnesium transport during the refining process. However, the simulation of the magnesium

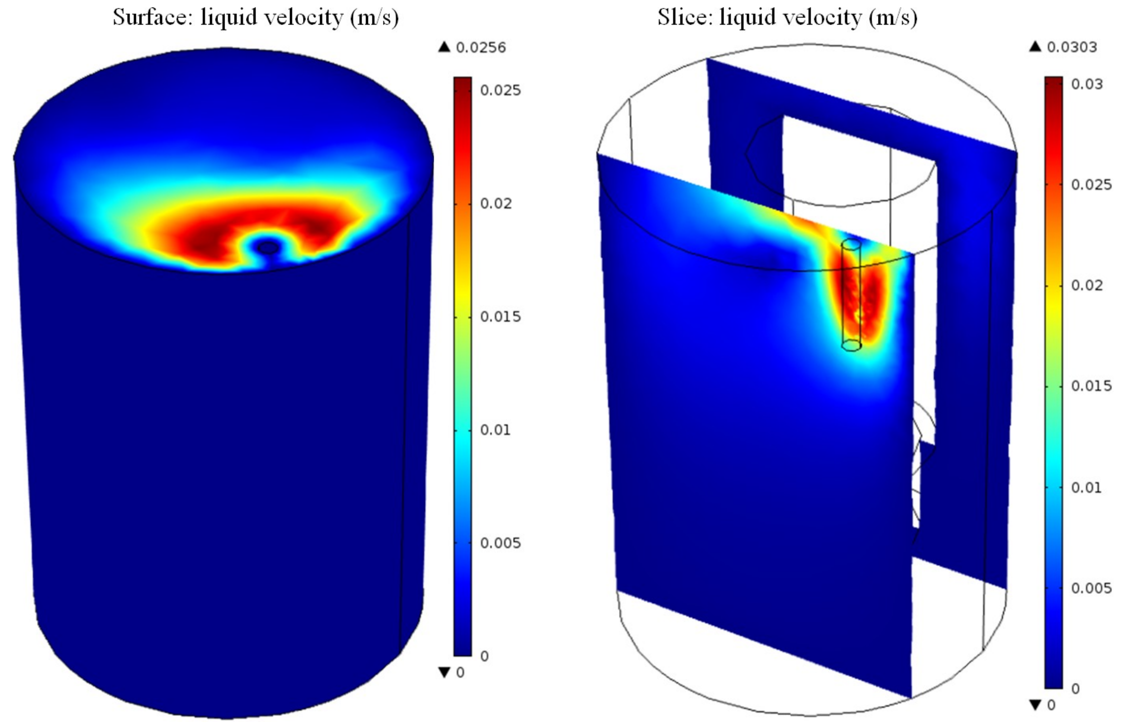


Figure 25: Molten salt velocity profile on the surface (left) and vertical slices (right).

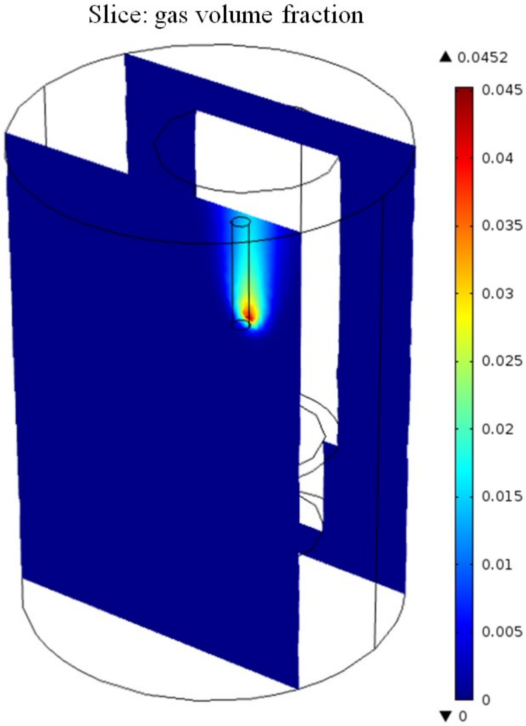


Figure 26: Gas volume fraction of forming gas in the mixture of molten salt and forming gas.

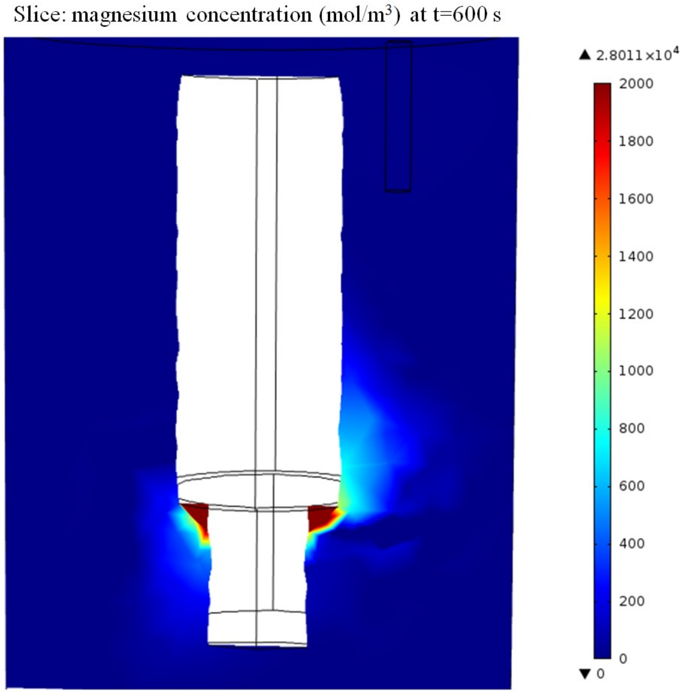


Figure 27: Magnesium distribution on the middle vertical slice at t=600 s.

transport could be improved. For example, instead of setting the rate of magnesium generation R_{Mg} to be zero, R_{Mg} could be expressed by:

$$R_{Mg} = -k\, C_{Mg}\, \Phi_g \tag{26}$$

where k is a positive coefficient describing kinetics of magnesium evaporation into gas bubbles, C_{Mg} is the magnesium concentration, and Φ_g is the volume fraction of forming gas. A future experimental and modeling effort will try to estimate the kinetic constant k.

Industrial MagReGen™ Cell Model

The industrial recycling cell model is based on the MOxST MagReGen™ scale-up design concept. The open source CAx (CAD/CAM/CAE) suite FreeCAD[23] specifies the model geometry within a Python script to ensure that the design and model geometries are always consistent. The model geometry makes use of a repeat unit within that scale-up design geometry for high resolution without excessive computational cost. MOxST generates the FEA mesh using the open source high-quality meshing software NETGEN[24], this mesh has 70,000 nodes and 354,000 elements, and simulations requires a small cluster of computers to solve the system of equations on this mesh.

The advantage of using Elmer or other parallel open source software for this model is that it runs well on a cluster without requiring any license management, such that MOxST can turn on a set of compute nodes at a remote cloud computing service and deploy and run the model quickly and easily.

Because of the proprietary nature of the design geometry, this report does not include the model mesh or results.

3.3 Scale-Up Engineering

This task as specified in the Statement of Project Objectives began with industrial interviews for market research, then used the data from those interviews to inform market strategy and industrial recycling cell design. The cost modeling work is presented on page 38.

Market Research and Process Specifications

SUMMARY RESULTS: Process specifications determined by industrial interviews in Appendix A on page 58 are as follows:

- Safety is *extremely* important, several companies have had very dangerous magnesium fires. Recyclers prefer not to handle magnesium powders for this reason.
- Due to longer time-in-service for vehicles “13 years”, Mg is a very small part of current auto recycling operations.
- There is little Mg in auto body scrap, and it is an annoyance, because there is no good method for separating it from aluminum at this time.
- Sophisticated sorting methods currently in use such as X-Ray Fluorescence (XRF) do a poor job of differentiating between aluminum and magnesium.
- It is possible to recycle 30-40% of the magnesium from dross using retort furnaces (MagPro) or mechanical methods (MagReTech), but much of it is currently landfilled.
- At time of survey, the U.S. market appears to support pricing at <$1.80/lb.
- The market for alloys is much larger than for pure metals.
- Japanese auto producers avoid magnesium use because of supply stability concerns

and inability to separate magnesium from aluminum in post-consumer recycling streams.

Based on these considerations, the industrial MagReGen™ magnesium recycling system must satisfy the following design criteria:

- Safety: design must be extremely sensitive to fire hazards to minimize the probability of fires, and facilitate extinguishing them.
- Scale: a relatively small number of machines should be able to treat all of the dross at a die-caster, amounting to 5% of their volume, so 50-500 tonnes/year capacity is a useful target size.
- Ruggedness: die-casting plants will dump material in using something like a front-loader, so the machine must be able to withstand collisions and shock.
- Flexibility: the machine must be able to deal with a wide variety of scrap types, from vehicle shreds to machining chips to large dross plates.

Industrial Scale Design Concept

MOxST has synthesized the above design goals and criteria into a design concept which incorporates scrap melting, magnesium dissolution in the molten salt, argon bubble-driven distillation, electrolysis cathodes and anodes, magnesium condensation, and argon recycling. The design is compact and highly productive, with a large area for rapid magnesium transport from the liquid metal scrap to the argon bubblers. Because of the proprietary nature of the design geometry, this report does not include any further detail.

The recycling system is expected to operate as a semi-batch process as follows:

1. Heat the system to at least 1000° C to melt the salt.
2. Fill the scrap melting region with magnesium-containing metal, dross, etc. and melt the scrap charge.
3. Dissolve and distill out all of the magnesium metal from the charge, while dissolving all magnesium oxide from the scrap into the molten salt, measuring the remaining magnesium quantity by the electrical signals mentioned in Task 2 above.
4. Tap out the remaining magnesium-depleted metal in the scrap melting region.
5. Operate the electrolysis cell to reduce magnesium oxide in the molten salt.
6. Repeat from Step 2.
7. Cool down, then very slowly introduce air into the system in order to avoid rapid oxidation of any fine magnesium dust present.

MOxST is also evaluating design concepts featuring internal heat transfer between the condenser and molten salt for very high energy efficiency.

Cost Model

MOxST has conducted a detailed cost modeling study of this process. Although details and model results are proprietary, results showed that cost of magnesium metal recycled by the MagReGen™ process are not only much lower than current U.S. prices, but are also well below current magnesium prices F.O.B. China (see footnote d on p. 14).

4. Benefits Assessment

The MOxST MagReGen™ magnesium recycling system goes hand-in-hand with the MOxST MagGen™ primary production system, so estimating their impact requires considering them together. This is because creating a large magnesium scrap stream for MagReGen™ will require increasing the supply of metal into the industrial ecosystem. And because of severe emissions, energy use, and other problems with existing magnesium technology, MagGen™ will be important to meeting the rapidly-growing magnesium needs of the motor vehicle industry.

The U.S. magnesium die casting market is growing very rapidly in the short term,[25] as shown in Figure 28, and if more stringent fuel emissions standards cause the automotive industry to follow the recommendations in the report *Magnesium Vision 2020,*[1] then magnesium adoption may increase from 5 kg/vehicle when the report was written in 2005 to as much as 160 kg/vehicle in 2020, a compound annual growth rate (CAGR) of 26% per year.

Magnesium's natural abundance can easily support this growth: it is the third most abundant structural metal in the earth's crust, the U.S. produces about ½ million tonnes of magnesium oxide annually, and inflation-adjusted oxide prices have been stable since the late 1940s.[26] World resources are estimated at 12 billion tonnes, and the oceans are 0.13% magnesium by weight,[27] or 1.8×10^{15} tonnes, and sea water extraction of MgO is commercially viable.

Since the release of *Magnesium Vision 2020,* although the price of magnesium has nearly doubled in the U.S., several automakers have committed to extensive magnesium use. Magna (Vehma) is building a 50% magnesium alloy small vehicle body and frame,[28] and Ford is pursuing a magnesium alloy frame for its F-series pickups[29] which are the best-selling vehicles in North America. That said, technical, economic, regulatory, and other political factors will affect the growth rate of die-cast magnesium, so estimating MOxST technology impact requires evaluation of several scenarios of magnesium market growth and recycling fraction.

Note that by providing a market for automotive magnesium scrap and lowering the cost of

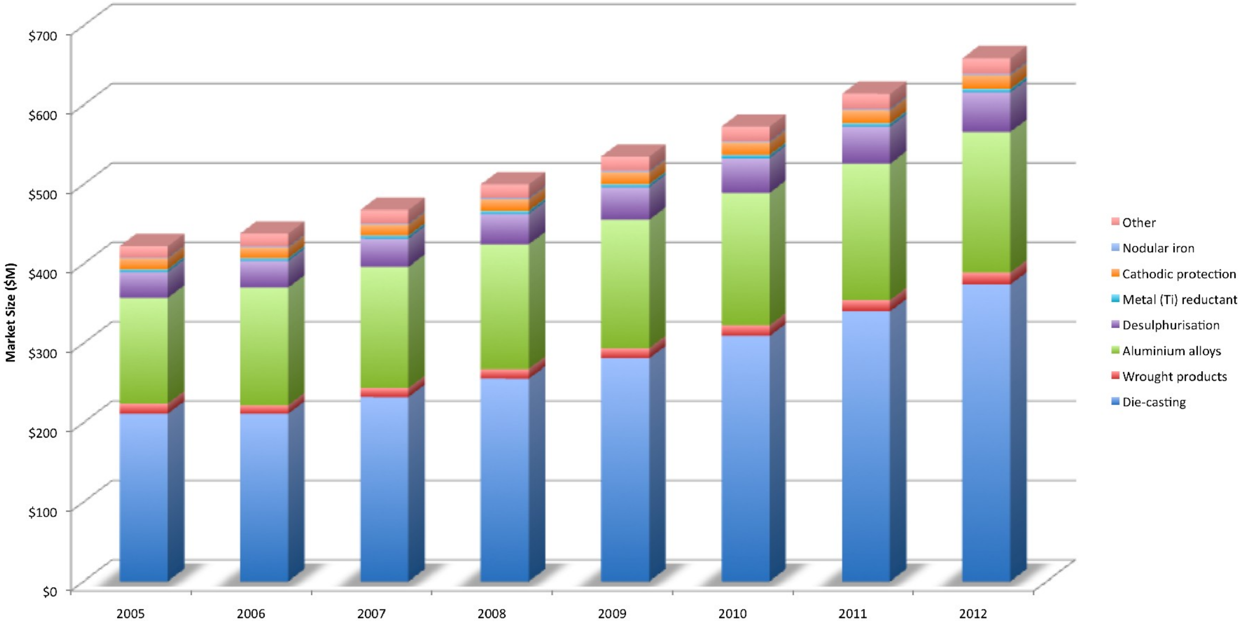


Figure 28: U.S. magnesium market by end-use segment, 2005-2012.[25]

producing automotive magnesium, the MOxST processes could play a major role in the growth of the magnesium market. In order to compare magnesium market scenarios, we will estimate long-term demand elasticity, and then compare fast-growth and slow-growth scenarios based on the MOxST cost advantage.

This Benefits Assessment will consists of three parts: (1) economic, energy, greenhouse gas (GHG) and other environmental modeling; (2) market scenarios and the effect of the MOxST processes on the market, (3) resulting economic, energy and GHG impact of MOxST process deployment across the economy based on those scenarios.

4.1 Energy, GHG Emissions, Economics and Other Wastes

MgO Electrolysis for Primary Production and Oxidized Scrap Recycling

Energy Use

For a self-heated electrolysis cell, energy modeling begins with two energy balances: one for free energy, the other for heat. The Nernst equation: $\Delta G = -nFV$ indicates that voltage and free energy are equivalent but use different units: free energy is the energy per mole of reaction extent, and voltage is the energy per coulomb of charge passed. For recycling of oxidized magnesium, the reaction is: $MgO \rightarrow Mg + \frac{1}{2}O_2$ with two moles of electrons per mole of reaction extent. At the process temperature of 1150° C, its enthalpy and free energy are 735 kJ/mol (8.41 kWh/kg) and 439 kJ/mol (5.02 kWh/kg) respectively,[30] corresponding to 3.81 V and 2.27 V respectively.

The reaction proceeds and current flows if applied voltage is above the 2.27 V dissociation potential, corresponding to reaction free energy. This and other overpotentials in the cell sum to the total voltage, as shown on the left side of Figure 29. The free energy budget consists of the following components:

- Cathode and anode resistances are minimum possible energy losses through the leads.[g]
- 1.5 V for the zirconia tube is based on 1 A/cm^2 current density through a 3 mm thick YSZ tube with conductivity 0.2 S/cm.
- The molten salt has 20 times the conductivity of YSZ, but the anode-cathode distance is roughly 20 times the zirconia thickness (6 cm), and effective area is roughly twice that of the YSZ, making for half the resistance and voltage drop.
- The oxygen ion mass transfer number is based on its concentration (roughly 1/10 of the anions) and boundary layer thickness (roughly 1/12 of the anode-cathode distance), making it about 70-80% of the molten salt resistance.
- MgO dissociation $V = \Delta G/nF$ (see above).

The thermal energy budget on the right side of Figure 29 sums thermal energy use of the cell. The enthalpy ΔH of MgO dissociation to Mg vapor and oxygen consumes most of the heat. If one supplies sufficient free energy but not sufficient enthalpy, then the reaction proceeds but cools the cell and shuts it down. Resistance in the cell or an external heater provides this heat, and excess heat beyond the enthalpy leaves the cell through the cell leads and vessel walls.

---

[g] The Wiedmann-Franz law indicates that good electrical conductors are good thermal conductors, so low-resistance leads lose a lot of heat and vice versa. There is thus an unavoidable minimum energy loss due to leads. At the process temperature, this minimum is ~0.21 V (0.46 kWh/kg) I-R drop in each lead lost to the environment as heat, plus an additional 0.46 kWh/kg heat conducted from the crucible through each lead to the environment.

The thermal energy budget consists of the following:

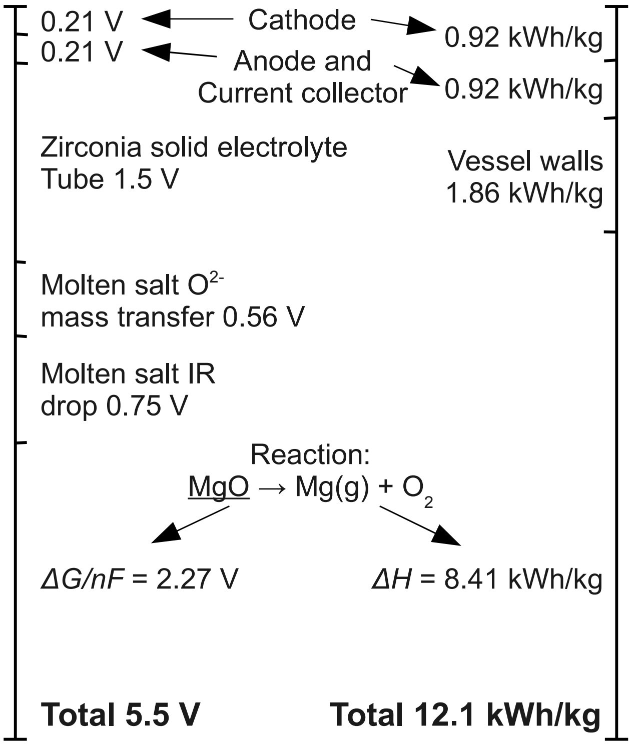


Figure 29: Free energy and thermal energy budgets for magnesium oxide electrolysis.

- Losses through cell leads mentioned above.
- Furnace vessel walls and gas flows, which we estimate will lose about as much heat as the total through electrical leads. With good insulation and heat exchangers, this could be as low as half of this value (0.8 kWh/kg), or various contingencies could increase it up to 3.8 kWh/kg.
- Enthalpy of magnesium oxide dissociation ΔH as mentioned above.

Based on these energy balances and the range of heat loss values, MOxST believes that operating at a cell potential of 5-6.5 V, corresponding to 11-14 kWh/kg, will achieve self-heating and 1 A/cm² zirconia tube current density. Overall energy efficiency of Mg vapor generation (ΔH/input energy for the reaction in Figure 29) is then between 63% and 76%. Because the enthalpy of dissociation to liquid magnesium is lower, with no condenser heat recovery, liquid Mg energy efficiency is between 52% and 63%.

Greenhouse Gas Emissions

There are no direct greenhouse gas emissions for MgO electrolysis, so Table 2 uses the U.S. average 0.688 kg CO_2e/kWh.

Economic Benefits

Economic benefits begin with energy savings above. This process is similar to the Hall-Héroult cell in its low labor utilization and modular cell deployment for flexible capital cost. With these advantages, Sujit Das of Oak Ridge National Laboratories estimated total costs for this process well below those of alternatives.[31] The Pidgeon silicothermic reduction process used in China, and development-stage carbothermic reduction process, both use much more energy than MagReGen™ and MagGen™, but burn coal with lower unit energy cost.

In terms of automotive materials changes, this will substitute higher-priced magnesium for lower-priced aluminum and steel. Manufacturing benefits of magnesium, such as lower part count due to easier die casting, will offset some of this cost, e.g. Field *et al.* showed that a magnesium automotive instrument panel beam die-cast in one piece can be less expensive than the equivalent steel part made from 27 stampings welded together.[32] But much more than this, the biggest economic impact will be approximately 732 trillion BTUs of gasoline energy saved in the transportation sector and greenhouse emissions by 51.6 MMT CO_2e/year.[h]

Solid and Liquid Waste

For this process there is minimal solid or liquid waste. For each 1000 kg of magnesium production from refractory-grade MgO, the MagGen™ process makes:

- ~10 kg of mixed iron, aluminum, silicon and other more electronegative oxide impurities, which the steel industry can potentially use to reduce porosity of ingot castings;
- ~5 kg of $MgCl_2$ in the condenser, which separates from the product by flotation;
- ~50 kg process salt with slightly elevated levels of chlorides and less electronegative impurities e.g. KF, BaF_2. MOxST is investigating recycling this stream as a task in our Vehicle Technologies Program contract, Award DE-EE-0005547. If this salt recycling process uses any water, that will constitute the only liquid waste of this system.

Magnesium Metal Recycling

Energy Use

The magnesium refining process requires much less energy than the electrolysis circuit. Its reaction is Mg (liquid in solution) → Mg (vapor), for which the enthalpy of vaporization ΔH_v at the 1090° C boiling point is 128 kJ/mol (1.46 kWh/kg), and the free energy of demixing to 1% Mg solution in Al is 48 kJ/mol (0.55 kWh/kg). Then again, advanced designs can recover most of the vaporization enthalpy, so the lower bound of this process energy use is as low as 48 kJ/mol (0.55 kWh/kg). To be conservative, MOxST estimates the process energy use at 10% above twice the vaporization enthalpy or 3.3 kWh/kg, (12.1MJ/kg), also corresponding to the demixing free energy plus 2.8 kWh/kg heat losses.

The only Mg-Al separation technology in use today bubbles chlorine through a liquid metal mixture, producing Al but very impure $MgCl_2$. Full reduction to magnesium metal then requires a further 28 kWh/kg (100 MJ/kg). As the Mg:Al ratio in motor vehicles increases from 1:20 to above 1:1, as expected per *Magnesium Vision 2020*,[1] this scales to 16 GJ/vehicle, or 192 PJ/year (181 TBTU/year). In contrast, the MagReGen™ process would use under 2 MJ/vehicle, or 24 PJ/year (22 TBTU/year).

Greenhouse Gas Emissions

As with MagGen™ MgO reduction, Table 2 uses GHG emissions of 0.688 kg CO_2e/kWh.

Economic Benefits

Process cost is expected to be very low, as it recycles its argon, uses very little energy, and has the same low labor cost and capital deployment flexibility of the primary production process.

---

[h] Source: http://www.epa.gov/greenpower/pubs/calcmeth.htm#gasoline – see also endnote 2.

Solid and Liquid Waste

MOxST expects that MagReGen™ recycling will net less solid and liquid waste emissions because it will reduce landfilling of magnesium dross and the magnesium component of automotive recycling. That said, the chemical composition of the waste streams may lead to higher solid waste production than the figures given above for primary production from refractory-grade MgO.

Summary

MOxST estimates the energy use of magnesium refining at 3.3 kWh/kg, and MgO electrolysis energy consumption for primary magnesium production at about 13 kWh/kg as calculated above. These assume zero energy recovery in the magnesium condenser, which could yield up to 1.5 kWh/kg for raw material treatment and other uses. Energy use and GHG emissions estimates are presented as Table 2.

The above summarizes the calculations for energy use by the MagGen™ primary production and MagReGen™ oxide/metal recycling processes. Today most of the world's magnesium comes from the Pidgeon silicothermic process in China or magnesium chloride electrolysis in the US and Israel, the numbers in Table 2 reflect the mean of those two as presented by Sujit Das.[33] Aluminum and steel data are from the literature as indicated by table foot/endnotes.

Per kg metal	Mg today	MagGen™	MagReGen™	Primary Al	Scrap Al	Primary steel
Energy use, kWh	64[33]	13-14[i]	3.3-3.4[i]	24[34]	11[j]	9.5[35]
GHG, kg CO_2	32[k]	8.9[l]-9.4[i]	2.3[l]-2.35[i]	16.5[l]	7.6[l]	2.1[35]

Table 2: Energy use and GHG emissions per kilogram of metal production.

4.2 Market Scenarios and Effect of MOxST Processes on the Magnesium Market

Changes in energy use and GHG emissions due to MagGen™ and MagReGen™ adoption depend strongly on the growth of demand for magnesium and the change in magnesium production technology penetration. The demand component of the market balance assumes that the automotive industry is the main driver of growth, and the question is to what extent they will realize growth from 5 kg/vehicle in 2005 to the 160 kg/vehicle projected for 2020. Starting with that projection, one can envision three magnesium demand growth scenarios:

1. Low magnesium growth: with new fuel economy standards, the automotive industry is likely to increase magnesium use by at least 7% CAGR, which would result in use of

---

[i] The high number reflects energy use and GHG emissions for MOxST processes with fueled anodes.

[j] J.A. Pomykala *et al.*, “Automotive Recycling in the United States: Energy Conservation and Environmental Benefits,” *JOM* 59(11):41-45 (November, 2007), p. 44: recycling saves 13 kWh/kg aluminum.

[k] Based on 50% U.S. Magnesium chloride electrolysis at 21 kg CO_2e/kg Mg (source: www.epa.gov), 50% Chinese Pidgeon process at 42 kg CO_2e/kg Mg (source: Gao Feng, *Trans. Nonferrous Met. Soc. China* 18:749, 2008).

[l] Using the 0.688 kg CO_2e/kWh from http://www.epa.gov/greenpower/pubs/calcmeth.htm#kilowatt ; this overestimates direct emissions because primary metal production plants tend to locate near hydroelectric power sources, though primary metal energy consumption makes that low-GHG power unavailable to the rest of the grid.

about 14 kg/vehicle in 2020.

2. Moderate magnesium growth: improved economics and stringent fuel economy requirements lead to changes in vehicle platforms amounting to 14% CAGR, and 36 kg/vehicle in 2020.
3. High magnesium growth: dramatically increased demand for light-weight materials in internal combustion engine as well as plug-in hybrid electric vehicles (PHEV) and/or battery electric vehicles (BEV) lead to magnesium growth at 26% CAGR to average 160 kg as projected in *Magnesium Vision 2020*.[5]

These consumption changes, particularly in scenario 3, could lead to enormous increases in industrial energy use if today's processes continue to dominate production. But if MOxST is successful, our extraction or recycling process, or both, could meet this entire demand by 2020 using much less energy.

Although MagReGen™ can recycle die casting dross or post-consumer scrap, process growth is somewhat constrained by the availability of post-consumer scrap. Again, this is not meant to replace remelting of prompt or primary scrap generated at the production facility, the die-caster, or the automobile assembly plant. Market penetration therefore will be defined in terms of the fraction of parts *shipped in automobiles several years earlier.* For example, if the 2014 model year includes 23 kg/vehicle of magnesium, with 12 million vehicle sales in North America, then at end-of-life approximately 276 million kg, or 276,000 tonnes, of new post-consumer scrap will enter the market, of which the MagReGen™ process will claim and recycle some fraction.

We can therefore posit the following supply technology scenarios for the magnesium market:

1. <u>No technology change</u>: continue to produce magnesium using 50% chloride electrolysis and 50% Chinese Pidgeon process, and no new recycling, including no post-consumer recycling – only remelting of prompt and primary scrap as happens today.
2. <u>MOxST extraction</u>: technology change for automotive parts from current methods to MOxST electrolysis for primary production, but also with no new recycling.
3. <u>MOxST extraction with moderate recycling</u>: use MagReGen™ recycling to produce 40% of the motor vehicle magnesium in 2015 vehicle production, and MagGen™ for the rest.
4. <u>MOxST extraction with high recycling</u>: use MagReGen™ recycling to produce 70% of the motor vehicle magnesium in 2015 vehicle production, and MagGen™ for the rest.

The impact of process deployment thus depends on where in the above scenarios actual consumption and technology penetration will fall. That said, the above scenarios imply that supply technology and consumption are independent. But the present technology mix is not economical, nor acceptable from a GHG standpoint, for production at the highest consumption level described above. And the penetration of MOxST technologies could significantly improve the magnesium price, to the point where it moves markets from one consumption scenario to another.

Demand for magnesium is a strongly nonlinear function of its price: a price below the density-adjusted price of aluminum enables widespread substitution. With aluminum at $2.20/kg, and an Al:Mg density ratio of 1.55:1, *and the prospect of a steady supply of magnesium at that price,* large markets switch from Al to Mg at a price below $3.10/kg in a matter of just a few years.[m] (Current US Mg price is $5.00/kg.)

---

[m] Source: interviews with Mag-Tec Casting on p. 69 and a large midwest die-caster also on p. 70.

Based on this, lower prices due to MOxST extraction and recycling could change consumption patterns from scenario 1 to 2 or 3 over time. Indeed, successful scale-up of these processes and concrete plans to build capacity could cause vehicle makers to commit to very significant growth within as little as 5 years. Furthermore, automakers are reluctant to make a large materials change if it will jeopardize the recycling industry by increasing landfill costs, and the MagReGen™ process provides a profitable private sector path to very high recycling rates.

4.3 Overall MOxST MagGen™ and MagReGen™ Process Deployment Impact

The framework above allows us to estimate the impact of MOxST magnesium extraction and recycling process adoption on industrial energy use and GHG emissions according to a matrix of demand and supply technology scenarios. This analysis assumes a steady 12 million vehicles/year, and a 2005 baseline of 5 kg magnesium per vehicle. This matrix is given in Table 3 below, with energy savings summarized in Figure 30.

		2020 magnesium consumption scenario		
		Low	Medium	High
Magnesium use, kg/vehicle		14	36	160
Aluminum use change, kg/vehicle[n]		-3.4	-11.8	-59
Steel use change, kg/vehicle[n]		-13.2	-45.4	-227
1. No technology change	Δ Energy, TBTU/yr	15.6	53.9	269
	Δ GHG, MMT/yr	2.56	8.80	44.0
2. MOxST extraction	Δ Energy, TBTU/yr	-3.16	-10.9	-54.4
	Δ GHG, MMT/yr	-0.07	-0.22	-1.12
3. MOxST extraction, moderate recycling	Δ Energy, TBTU/yr	-4.72	-13.8	-62.3
	Δ GHG, MMT/yr	-0.25	-0.37	-0.49
4. MOxST extraction, high recycling	Δ Energy, TBTU/yr	-5.89	-16.0	-68.4
	Δ GHG, MMT/yr	-0.49	-0.81	-1.70

Table 3: Changes in industrial energy use (TBTU/year) and GHG emissions (MMT CO_2e/year) vs. today for magnesium consumption and supply technology scenario combinations.

As Table 3 indicates, the first technical scenario of no technology change leads to an increase in industrial energy use and GHG emissions across the board. For this reason, Europe has curtailed its long-term plans for large-scale motor vehicle adoption of magnesium.[3]

MOxST extraction by itself leads to a dramatic reduction in industrial energy use and GHG emissions, which one can readily see by comparing technology scenarios 1 and 2. Recycling further increases the energy and GHG savings, but not by extraordinary amounts. This is because of the constraint on recycling mentioned above: in 2020, post-consumer scrap will be generated from earlier primary production, so only 40% (supply scenario 3) or 70% (scenario 4) of the much-lower production year will be available for recycling. The benefits become much

---

[n] Assumes each 155 kg of magnesium replaces 59 kg of aluminum and 227 kg of steel, per *Magnesium Vision 2020,*[5] and that 30% of automotive aluminum and no steel comes from post-consumer scrap.

greater in subsequent years as the increasing magnesium usage in 2020 vehicles progresses through consumer use and into the recycling stream.

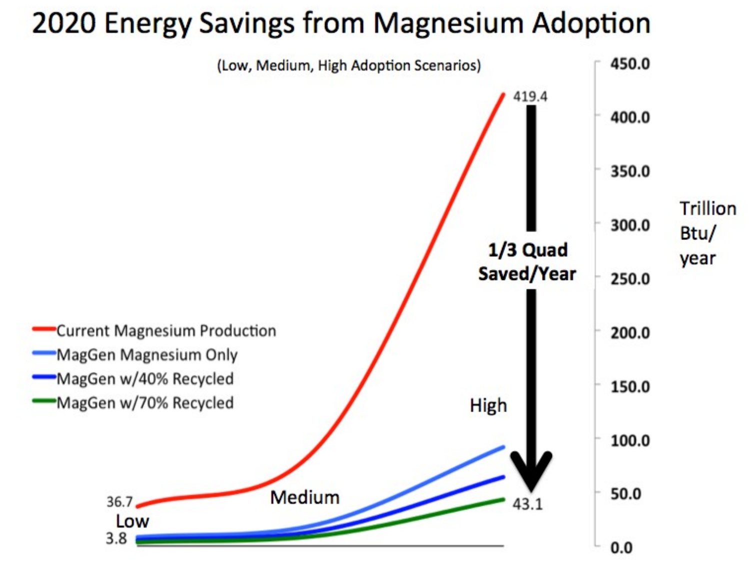


Figure 30: Energy savings from MOxST process adoption in 2020.

Based on the above presentation, one can envision the following three primary scenarios in 2020, shown in light gray cell backgrounds in Table 3 above:

1. No technology change and low magnesium growth: U.S. auto industry magnesium use grows at 7% CAGR to 14 kg/vehicle (30 lbs), contributing minimally to meeting fuel economy standards. Industrial energy use increases by 15.6 TBTU/year and GHG emissions by 2.56 MMT CO_2e/year vs. today.
2. MagGen™ extraction, no magnesium recycling, and medium magnesium growth: With a new domestic source of low-cost magnesium, the industry expands magnesium use at 14% CAGR to 36 kg (~80 lbs), but no more than this out of concern for the recycling ecosystem. Industrial energy use falls by 10.9 TBTU/year, and GHG emissions by 0.22 MMT CO_2e/year, but substantial quantities of post-shredder magnesium is landfilled as Al-Mg scrap and/or $MgCl_2$.
3. MagGen™ extraction, high MagReGen™ recycling, and high magnesium growth: Abundant domestic supply and a path to 100% magnesium recycling convince industry to build some 50% magnesium vehicle body-in-white (frame and body panels) platforms and follow Magnesium Vision 2020 to 160 kg/vehicle *average* magnesium intensity. Industrial energy use falls by 68.4 TBTU/year, and GHG emissions by 1.70 MMT CO_2e/year.

If these three scenarios hold, then the MOxST extraction and recycling processes move the industry from scenario 1 to scenario 3, and this project's impact is **industrial energy savings of 84 TBTU/year and GHG emissions reduction of 4.3 MMT CO_2e/year.** If fuel economy regulations or fuel prices force the auto industry into consumption scenario 3 with inelastic demand, **industrial energy savings due to MOxST technologies will approach 340 TBTU/year and GHG emissions reductions will exceed 45 MMT CO_2e/year.** And this is well before these magnesium-intensive vehicles enter the recycling stream, which will further increase the industrial energy and GHG savings.

Indeed, assuming the “High” consumption scenario represents a long-term steady-state, the moderate and high recycling supply scenarios save 79.8 and 98.9 TBTU/year *vs.* today (*cf.* 62.3 and 68.4 TBTU/year in Table 3), and reduce GHG emissions by 4.00 and 7.84 MMT/year *vs.* today (*cf.* 0.49 and 1.70 MMT/year in Table 3).

This also does not include the **approximately 732 trillion BTUs of gasoline energy saved and greenhouse emissions reductions of 51.6 MMT CO_2e/year in the transportation sector** (see footnote h on page 42). This technology is a potential energy and environmental game-changer in both the industrial and transportation sectors.

5. Commercialization

MOxST plans to follow a basic business model of building and supplying capital equipment for recycling magnesium using the MagReGen™ system. This allows us to use the equipment sale price to capture some of the difference between pricing interesting to die casters at $1.60-1.80/lb ($3.50-3.95/kg) and the cost model estimate of $2.38/kg given on page 38, while creating on-site recycling capability for die-casters and non-ferrous metal sorters.

The long term Commercialization Plan laid out here is intended to achieve the goals described in the Magnesium 2020 report. Through the interviews conducted and with the design and development work currently underway, we will deploy closely related, yet slightly different embodiments of the technologies:

1. **MagReGen™ in die-casting operations for economical dross (type 6) and chip (type 5) recycling:** This will recover nearly 5% of primary alloy value by converting these low/no value waste streams into usable alloy. To minimize costs and energy use, these MagReGen™ systems will be co-located at die-casting facilities, potentially allowing recovered Mg to flow directly back into production, skipping a solidification and remelt cycle as well as transportation cost and overhead.
2. **MagReGen™ in vehicle recycling operations:** MagReGen™ systems also effectively separate mixed Aluminum and Magnesium directly back into metals and alloys of the quality and cost required to return these resources to “as new” alloy specifications. Our interviews indicated that “Mg is a headache when recovering Al scrap. The Mg is hard to get out.”[o] This new technology addresses this critical recyclability “need” for post-consumer mixed aluminum/magnesium waste streams.
3. **MagGen™ Primary Magnesium Technology:** This process reduces magnesium oxide at very low cost, and will likely create a reliable US-based cost-competitive supply of magnesium metal.

As noted in our interviews of industry, there will be a significant lag time between the ramp up of primary Mg use in new vehicles and the time when the materials will be available for post consumer recycling.

5.1 Critical Early Customers

MOxST's die casting partners in our Vehicle Technologies Program magnesium project plan to begin testing MagGen™ primary magnesium production equipment for use “in house” as soon as late 2013. With sufficient development resources, MOxST will also provide MagReGen magnesium recycling test equipment to those same partners. MOxST continues to refine and improve cost data and is working closely with these pioneering customers to develop designs. The economics of current production provide pull for the MagReGen™ prototypes into the market first, supported by recovering the 3.5 to 5%+ of the materials currently lost to Dross and chips during current production operations.

Tim Skszek, Technical Specialist at Cosma International and a leader of Magna's magnesium-intensive vehicle program, wrote:

> There are several technical challenges, critical to the commercial use of magnesium

---

[o] Interview with wTe on p. 59.

> for automotive applications. **The MOxST proposal addresses [the first] 4 of the 7 critical issues which must be overcome to enable commercialization.** 1. Primary material supply stability; 2. Primary material cost stability; 3. Primary reduction environmental load (CO_2 footprint); 4. Recycling and secondary scrap recovery; [5. large castings, 6. corrosion, and 7. joining].[36]

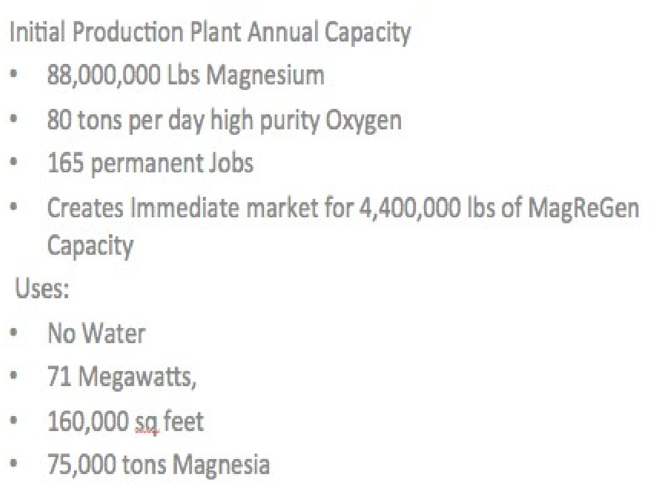
Tier-1 suppliers and automakers, such as Cosma, Ford and GM, have achieved or are near solutions to the remaining challenges 5-7 mentioned above and are ready to scale up magnesium use if the metal is available. MOxST is working closely with Cosma, Ford, GM and Chrysler and their suppliers to ensure a smooth transition to the market. Michael Dierks, Vice President for Lean Manufacturing Systems at Spartan Light Metals, also wrote:

> We are very interested in cutting edge technology, such as MOxST's electrolysis, for metals production... **We see the only real option to competing in a global market to produce magnesium alloy from a cost competitive process such as this...** This process offers this opportunity using an existing stable raw material source with numerous domestic producers.[37]

To reduce risk and accelerate US market adoption, strong interest is also expected and partners and customers are being pursued in the international markets (Initially Japan, Europe and Canada) including those that have curtailed their magnesium use from China due to the high GHG impact of production there. These Impacts are mitigated by MagReGen™ and MagGen™.

Time on Machines

US Die Casing industry partners play a second key role in the commercialization process. Their immediate need for even limited primary magnesium production provides for MagGen™ scale up "right sizing" and risk reduction while the first Primary Production plant is planned, permitted, and constructed as described in Table 4. The pilot systems will be logging important time in commercial production generally required before larger amounts of financing are committed. In 2014, with machines in commercial operations for periods approaching 18 months or more, the primary Magnesium facilities may be able to attract investment from the commercial project finance sector. Funding may be available earlier in partnership with the right strategic partners (discussions underway) as different parts of the industry have different risk/benefit profiles.



Initial Production Plant Annual Capacity

- 88,000,000 Lbs Magnesium
- 80 tons per day high purity Oxygen
- 165 permanent Jobs
- Creates Immediate market for 4,400,000 lbs of MagReGen Capacity

Uses:

- No Water
- 71 Megawatts,
- 160,000 sq feet
- 75,000 tons Magnesia

Table 4: MagGen scale-up characteristics.

Recycling vs. Primary Production Location

Even with the advancements in energy required per unit of material produced, low cost power remains a key driver in locating the new MagGen™ Primary Magnesium Plants. Careful attention is also to be paid to the total carbon footprint that results. As noted earlier in this report, in markets where there is direct (financial) linkage between the carbon footprint and the alloys produced, low cost zero carbon power is key. MOxST has begun early siting investigation and is developing partnerships toward this end.

That said, there is a significant cost advantage to locating recycling capacity close to the die-casters due to metal remelting energy savings, which is in the range 1-10 kWh/kg.[38] The lower energy usage of recycling equipment than primary production makes its siting more flexible.

Commercialization Team

In late 2011, the MOxST team expanded to include experienced engineering and operations leadership as well as experienced project commercialization leadership.

5.2 Sales Projections

In the low, medium and high market scenarios described on page 43, MOxST estimates die-casters will produce roughly 6,000, 11,000 and 30,000 tonnes/year of dross in 2015. This will provide a market big enough to sell 25 to 125 240-tonne/year capacity recycling furnaces. By 2020, these grow to 8,400, 21,000 and 96,000 tonnes/year of dross, resulting in 35-400 cumulative furnace sales.

When 2020 vehicles reach end-of-life in the 2030 timeframe, there will be roughly 170,000-2,000,000 tonnes per year of automotive magnesium scrap, requiring much larger recycling volumes. At such scales, MOxST will probably revisit our machine design decisions and produce and sell recycling furnaces with considerably higher capacity, resulting in lower per-kilogram costs, particularly for labor and capital.

6. Accomplishments

MOxST and BU have met or exceeded nearly all of the goals of this Concept Definition study. More specifically, the Statement of Project Objectives (SOPO) indicated that, "The primary objective of this project is to demonstrate the technical feasibility of a new patent-pending innovative process … for recycling the lowest grades of mixed-magnesium alloys and heavily-oxidized magnesium scrap to produce magnesium metal at low cost," and we have met that objective. The one subtask not yet completed is 3.2 Finite element model validation, because after discovery of the new refining mechanism, we were not able to perform sufficient experiments for a full parameter estimation and validation of model assumptions.

The most significant accomplishment was the discovery of the new refining mechanism, and its confirmation in two separate experiments. In addition to the original electrorefining and electrolysis patent application filed before the project,[10] MOxST and BU have filed three provisional patent applications on the technology:

- The BU-MOxST team co-authored U.S. Provisional Patent Application 61/544,879 in October 2011 describing use of the new refining mechanism for magnesium recycling and related physics to enhance primary production.[39]
- The same team co-authored U.S. Provisional Patent Application 61/609,309 in March 2012 describing new discoveries on the same topic.[40]
- MOxST submitted U.S. Provisional Patent Application 61/609,366 in March 2012 with industrial recycling cell concepts which optimize new refining mechanism performance.[41]

We plan to follow with additional patent filings in order to build a profitable business using this technology and achieve its potential for energy savings and GHG emissions reduction.

MOxST and BU made three conference presentations with proceedings based on this project:

- Xiaofei Guan at BU presented a poster on this project entitled "Magnesium Recycling of Partially Oxidized, Mixed Magnesium-Aluminum Scrap Through Combined Refining and Solid Oxide Membrane Electrolysis Processes" at the Electrochemical Society meeting in Boston in September 2011, and the accompanying paper[42] has been accepted for publication in *ECS Transactions* in 2012.
- Xiaofei Guan at BU presented a poster on this project entitled "Magnesium Recycling of Partially Oxidized, Mixed Magnesium-Aluminum Scrap Through Combined Refining and Solid Oxide Membrane (SOM) Electrolysis Processes" at the TMS 2012 Annual Meeting symposium Magnesium Technology 2012 on March 12, 2012, and the accompanying paper[43] was published in the symposium proceedings with the same title.
- MOxST P.I. Adam Powell presented a keynote lecture entitled "Multi-Physics Modeling of Molten Salt Transport in Solid Oxide Membrane (SOM) Electrolysis and Recycling of Magnesium" at the TMS 2012 Annual Meeting symposium CFD Modeling and Simulation in Materials Processing on March 12, 2012, and the accompanying paper[44] was published in the symposium proceedings with the same title.

Finally, MOxST's modifications to the Elmer open source FEA suite,[21] such as Nernst-Planck electromigration and bubble-driven flow modeling, are already included in that product, and a case study using electromigration is on the Elmer Wiki.[22] Experimental work on this project will comprise much of the Ph.D. thesis of Xiaofei Guan at BU.

7. Conclusions

Based on the project results, MOxST has concluded that due to growing market demand for magnesium and the low cost of our technology, **the MagReGen™ process will likely be a profitable method to dramatically reduce the industrial energy for producing magnesium from dross, automotive scrap, and other low-cost scrap sources.** That said, because of the novelty of the new refining mechanism discovered here, this Concept Definition study leaves much work to do in scale-up engineering of the process, motivating a follow-on project as described in the Recommendations below.

Project conclusions include:

- Energy use modeling indicates that MagReGen™ magnesium recycling output per unit of energy is nearly eight times higher than chlorine-based separation, and can potentially save as much as 340 trillion British Thermal Units (TBTU) of energy per year. Without the direct carbon usage of competing processes, it can reduce GHG emissions by as much as 45 million metric tonnes (MMT) CO_2e/year. Details are in Section 4 starting on page 39.
- In terms of economic impact, automotive material costs will increase *vs.* steel and aluminum, but these will be partially offset by the ease of die-casting for reduced part count, making vehicles only slightly more expensive than they are now. The big economic life cycle cost reduction will come from the likely 732 trillion BTU/year of gasoline energy reduction in the transportation sector (footnote h on page 42).
- A successful experimental program described in Section 3.1 on page 18 discovered and demonstrated a new chemical separation mechanism in two separate experiments. Separation of magnesium from aluminum and other metals happens in two stages: magnesium in a scrap metal charge preferentially dissolves into a molten salt, and argon bubbling through the salt accelerates its evaporation. Other metals have lower solubility and/or lower evaporation rate. Experiments demonstrated near-perfect separation, with details on pages 20 and 26.
- We invented two new (patent pending) electrical measurement methods to estimate the amount of magnesium in the scrap charge and dissolved in the molten salt at any time, these can serve as inline process control signals and diagnostic tools.
- Though mathematical modeling was originally geared toward our patent-pending electrorefining mechanism, we also modified the model and ran simulations of recycling by the new mechanism, as described in Section 3.2 on page 32. Complete model validation and unknown parameter estimation will require additional experiments, and when complete, the model will simulate an industrial-scale recycling cell.
- A new proprietary 3-D design concept ties together the process features into a highly scalable and flexible recycling system, with a new configuration which could even further reduce the energy required for recycling.
- An industrial survey in the Appendix on page 58 revealed that despite acute and growing needs, there is currently no economically viable magnesium-aluminum metal separation technology.

More broadly, MOxST has learned a great deal about the fundamentals of magnesium-molten salt interactions, and how they could be leveraged in new and very beneficial ways. This is having an impact on our MagGen™ magnesium primary production technology, as well as related methods for producing other reactive metals.

In terms of commercialization, despite the long slow ramp-up ahead for automotive magnesium, the current market for recycling technology is much stronger than we had thought. Japan and Europe are particularly promising markets. In Japan, the very high costs of energy, and eagerness to avoid raw material dependence on China, make that country's auto industry very eager for a new magnesium recycling process – particularly one which can separate it from aluminum without losing the very high stored energy in magnesium metal. And Europe's sensitivity to greenhouse gas emissions is steering vehicle producers there toward low- or zero-carbon technologies such as MagGen™ and MagReGen™.

Nearly all vehicle weight reduction strategies require higher cost, energy use, and GHG emissions in production, in order to reduce cost, energy use and GHG emissions during vehicle use. The MagReGen™ magnesium recycling system, and its companion MagGen™ magnesium primary production system, together break that trade-off by creating savings in industrial energy for vehicle production, while saving weight and reducing transportation energy consumption. At the same time, it can boost magnesium's recycling rate from mid-30% range to the 70%+ range seen in steel and aluminum, eliminating most of the solid waste disposal that would otherwise result from greatly increased automotive magnesium.

Industrial technology changes in the 1970s implemented in the 1980s brought us soaring rates of auto body recycling with the automobile shredder, and a sea change from cast iron to aluminum engine blocks and other light-weight components, boosting efficiency tremendously. Today, the breakthrough MOxST magnesium technologies can once again tilt the scales of industrial economics toward the same kind of sea change in automotive materials, ushering in a new generation of cleaner more efficient vehicles made by cleaner processes, and with a viable path to maintaining universal private-sector recycling through this transition.

MOxST is grateful to the Department of Energy for the opportunity to play a pivotal role in this automotive material revolution, and we hope to move forward soon with scale-up R&D to realize the full potential of this technology.

8. Recommendations

The next steps will be to move toward scale-up engineering, prototype equipment construction, and technology demonstrations. Follow-up R&D tasks for this scale-up program are as follows.

Design and build shallow recycling system

Design overall system architecture and components. Purchase and/or fabricate components such as the furnace enclosure, heating element(s), power supplies, electrical connections etc., and complete assembly.

Validate performance

Characterize performance of the initial system. Each experiment will include characterization using open circuit voltage measurement and potentiodynamic scans (PDS) to estimate relationship between electrorefining potential and scrap anode composition, electrochemical impedance spectroscopy (EIS) to determine equivalent circuit component characteristics, and chronoamperometry to measure the molten salt electronic and ionic conductivities independently. They will also characterize process component temperatures and pressures, argon flow rates, etc. to provide maximum possible information for mathematical models of the process. And they will test magnesium separation from other elements e.g. Cu, Fe, Y in WE alloys, Ca in AE44, etc., and from non-metallic scrap contaminants such as CaO and NaCl.

Use designed experiments to evaluate reaction mechanisms and kinetics

Use process models, including Finite Element Analysis (FEA) with fluid dynamics, to design experiments which most efficiently test hypotheses about reaction mechanisms and measure kinetic parameters. These parameters include magnesium mass transfer coefficient through liquid Al-Mg mixture, the magnesium dissolution reaction in molten salt, magnesium diffusivity and evaporation, including effects of argon bubbling flow rate and bubble size.

Anode development, particularly options for improved resistance to electronic current

Dissolved metallic magnesium in the molten salt creates electronic conductivity several times higher than the ionic conductivity. Electronic current reduces the zirconia, reducing anode lifetime. Options for mitigating this could include oxidizing metallic magnesium in the salt before operating the reduction circuit (oxidizing agents could include iron oxide or other oxides), coating the anodes, or other options.

Larger-scale process demonstrations

MOxST anticipates that all process features can be demonstrated at a recycling cell scale of 100-200 tonnes/year. The design, construction, and testing of equipment on this scale and over long time periods will complete the pre-commercial demonstration of this process.

Summary

When the R&D program is complete, the system will be ready for on-site installation and testing at pilot customer facilities, followed by large-scale deployment across die-casters, recyclers, and international markets.

9. References

---

1 U.S. Automotive Materials Partnership, *Magnesium Vision 2020*, Technical Report, USCAR, Nov. 2006.

2 Using 0.35 liters gasoline saved per (100 km driven×100 kg weight reduction) from Christoph Koffler and Klaus Rohde-Brandenburger, "On the calculation of fuel savings through lightweight design in automotive life cycle assessments," *Int. J Life Cycle Assess.* 15:128-135, 2010; muliplied by 2.96×10^{12} miles/year driven by U.S. vehicles from US DOT BTS http://www.bts.gov/publications/national_transportation_statistics/html/table_04_09.html . "Pump-to-wheels" only, does not include reductions in "well-to-pump" oil drilling and refining energy and GHG emissions.

3 Karl Kainer (Head of the Magnesium Innovation Center MagIC at the Institute of Materials Research, Helmholtz-Zentrum, Geesthacht, Germany) , "Global Magnesium Research: State-of-the-Art and What's Next?" Presentation at the TMS Annual Meeting, February 28, 2011, and extended abstract in Wim Sillekens, ed., *Magnesium Technology 2011* TMS, Warrendale, Pennsylvania, 2011, p. 5.

4 Deborah A. Kramer, *Magnesium Recycling in the United States in 1998*, U.S. Geological Survey Open-File Report 01-166, 2001.

5 Based on a conversation with Deborah Kramer at USGS February 7, 2011.

6 See for example the European Super Light Car project and Carol Schutte's presentation at the US Department of Energy Vehicle Technologies Program 2011 Annual Merit Review.

7 Oddmund Wallevik and Jan B. Ronhaug, "Method and apparatus for remelting and refining of magnesium and magnesium alloys," US Patent 5,167,700, December 1, 1992.

8 H. E. Friedrich, B. L. Mordike, Magnesium Technology: metallurgy, design data, applications (Springer, 2006), 638.

9 T. Zhu et al., "Innovative vacuum distillation for magnesium recycling", *Magnesium Technology 2001* (TMS, Warrandale, PA), 2001, pp. 55-60.

10 Adam Powell and Steve Derezinski, "Method and Apparatus for Recycling Magnesium and Other High-Vapor Pressure Low-Electronegativity Metals," U.S. Provisional Patent Application 61/248,036, filed October 2, 2009.

11 Adam Powell and Steve Derezinski, "Method and Apparatus for Recycling High-Vapor Pressure Low-Electronegativity Metals," U.S. Patent Application 2010/0276297 filed October 1, 2010 (provisional filed October, 2009).

12 Uday Pal and Stephen Britten, *Method and Apparatus for Metal Extraction,* U.S. Patent 5,976,354 Nov. 2, 1999.

13 Uday Pal and Stephen Britten, *Apparatus for Metal Extraction,* U.S. Patent 6,299,742 October 9, 2001.

14 Mg salt solubility references from Xiaofei's paper.*

15 P. Chartrand and A.D. Pelton, *Metallurgical and Materials Transactions A*, 32(6), 2001.

16 A. Krishnan, U. B. Pal and X. G. Lu, *Metallurgical and Materials Transaction B*, 36(4), 2005.

17 U.B. Pal, A.C. Powell, *Journal of the Minerals, Metals and Materials Society*, 59(5), 2007.

18 A.S. Dworkin and M.A. Bredig, *The Journal of Physical Chemistry,* 75:15, 1971.

19 E. Gratz, S. Pati, J. Milshtein, A. Powell and U. Pal, *Magnesium Technology 2011*, p. 39-42, Wiley-TMS, 2011.

20 A.V. Virkar, *Journal of Power Sources*, 147:1-2, 2005.

21 CSC – IT Center for Science Ltd., Elmer Open Source Finite Element Software for Multiphysical Problems, http://www.csc.fi/english/pages/elmer, Version 6.1, Debian package versions 6.1.0.svn.5272.dfsg-1 through 6.1.0.svn.5396.dfsg-5.

---

22 See http://www.elmerfem.org/wiki/index.php/Electrochemistry written by P.I. Adam Powell.

23 Juergen Riegel, Werner Mayer and Yorik van Havre, FreeCAD Open Source 3D CAD/MCAD/CAx/CAE/PLM modeler, http://sourceforge.net/apps/mediawiki/free-cad/, Version 0.11.3729.

24 Joachim Schöberl, NETGEN Tetrahedral Mesh Generator, http://www.hpfem.jku.at/netgen/, Version 4.9.13.

25 Roskill, *The Economics of Magnesium Metal,* October, 2008.

26 U.S. Geological Survey, *Magnesium Compounds Statistics,* last modification August 11, 2011, http://minerals.usgs.gov/ds/2005/140/ds140-mgcom.pdf .

27 A. Dickson & C. Goyet eds., *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2,* ORNL-CDIAC-74 Chapter 5 table 6.2.

28 Department of Energy Advanced Vehicle R&D Award Announcement and List of Projects, August 10, 2011.

29 "Ford Could Use Magnesium for Truck Frame," *Magnesium Monthly Review* 39(10) Nov. 30 2010 p. 2.

30 Source: http://webbook.nist.gov/chemistry/ → Formulas "MgO" "Mg" (condensed and gas) and "O_2".

31 Sujit Das, "Primary Magnesium Production Costs for Automotive Applications," *JOM* 60(11):63-69 (November 2008).

32 Frank Field, Randolph Kirchain and Richard Roth, "Process Cost Modeling: Strategic Engineering and Economic Evaluation of Materials Technologies," *JOM* 59(10):21-32, 2007.

33 Based on 50% U.S. Magnesium chloride electrolysis at 43.6 kWh/kg, 50% Chinese Pidgeon process at 102 kWh/kg (source: Sujit Das, DOE Lightweight Materials Annual Merit Review Presentation 2011).

34 William Choate and John Green, "U.S. Energy Requirements for Aluminum Production: Historical Perspective, Theoretical Limits and New Opportunities," U.S. Department of Energy, February 2003, p. 24.

35 John Stumbles, "Energy Use in the U.S. Steel Industry: An Historical Perspective and Future Opportunities," U.S. Department of Energy, September 2000, Tables 2, 5, 17.

36 Timothy W. Skszek, Letter of support for MOxST ITP Grand Challenge proposal leading to this award , July 10, 2009, available upon request. Emphasis added.

37 Michael W. Dierks, Letter of support for MOxST Vehicle Technologies proposal leading to Award DE- EE-0005547, February 2011, available upon request. Emphasis added.

38 Values in four different publications range from 0.83 to 12 kWh/kg for magnesium melting in die casting operations. Jerald Brevick, Clark Mount-Campbell and Carol Mobley, "Final Report on Energy Consumption of Die Casting Operations," U.S. Department of Energy Contract DE-FC07-00ID13843, March 15, 2004, p. 11: 1500 BTU/lb → 0.97 kWh/lb. Also Stephanie Dalquist and Timothy Gutowski, "Life Cycle Analysis of Conventional Manufacturing Techniques: Die Casting," MIT report December 12, 2004, p. 6 Table 3: 3.0 MJ/kg = 0.83 kWh/kg. On the other hand, Robert Eppich, "Energy Use in Metalcasting Facilities – 2003," U.S. Department of Energy Industrial Technologies Program Metal Casting Industry of the Future, May 28, 2004 p. 55: 31,086 BTU/lb × 33.13% = 6.6 kWh/kg. J.F. Schifo and J.T. Radia, "Theoretical/Best Practice Energy Use In Metalcasting Operations," DOE Industrial Technologies Program Metal Casting Industry of the Future, May 2004, pp. 35, 40: 67.8 MBTU/ton × 55% = 12.0 kWh/kg.

39 Uday B. Pal, Eric Gratz, Xiaofei Guan, Peter A. Zink, Soobhankar Pati and Adam C. Powell, *Metals Production Efficiency Improvement in SOM Electrolysis and Refining,* U.S. Provisional Patent Application 61/544,879, October 2011. DOE IP Case No. S-130,251.

40 Uday B. Pal, Eric Gratz, Xiaofei Guan, Peter A. Zink, Soobhankar Pati, Adam C. Powell and

---

John Strauss, *Method and Apparatus for Efficient Metals Production, Separation and Recycling by Salt- and Argon-Mediated Distillation with Oxide Electrolysis, and Sensor Device Related Thereto,* U.S. Provisional Patent Application 61/609,309, March 2012. DOE IP Case No. S-130,646.

[41] Adam C. Powell and John Strauss, *High-Throughput High-Efficiency Primary Production and Molten Salt-Assisted Recycling of Metals,* U.S. Provisional Patent Application 61/609,366, March 2012. DOE IP Case No. S-130,645.

[42] Xiaofei Guan, Peter Zink, Uday Pal and Adam Powell, "Magnesium Recycling of Partially Oxidized, Mixed Magnesium-Aluminum Scrap Through Combined Refining and Solid Oxide Membrane Electrolysis Processes," approved January 24, 2012 for publication in *Electrochemical Society Transactions* February, 2012.

[43] Xiaofei Guan, Peter Zink, Uday Pal, "Magnesium Recycling of Partially Oxidized, Mixed Magnesium-Aluminum Scrap Through Combined Refining and Solid Oxide Membrane (SOM) Electrolysis Processes," in Suveen Mathaudhu, Wim Sillekens, Norbert Hort, Neale Neelameggham, eds., *Magnesium Technology 2012* (TMS, Warrendale, PA), 2012, pp. 531-536.

[44] Adam Powell and Soobhankar Pati, "Multi-Physics Modeling of Molten Salt Transport in Solid Oxide Membrane (SOM) Electrolysis and Recycling of Magnesium," in Laurentiu Nastac, Lifeng Zhang, Brian Thomas, Adran Sabau, Nagy El-Kaddah, Adam Powell, Hervé Combeau, eds., *CFD Modeling and Simulation in Materials Processing* (TMS, Warrendale, PA), 2012, pp. 57-64.

Appendix A: Magnesium Recycling Market Research Interviews

In order to gain a better understanding of the marketplace and market makers involved in magnesium recycling in the U. S. and abroad, telephone and e-mail "interviews" were conducted of 13 firms and experts involved the magnesium supply chain in December 2010 to February 2011. The participants provided input on their current practices and issues and concerns around both current and future magnesium recycling efforts.

- Market size: 5 kT/yr dross, 70-110 kT/yr post-consumer magnesium.
- Current recycling activity status: High recycling rate for high-quality scrap such as die-casting runners and gates, chips, etc.; scant post-consumer, some dross recycling.

Highlights

- Safety is *extremely* important, several companies have had very dangerous magnesium fires. Recyclers prefer not to handle magnesium powders for this reason.
- Due to longer time-in-service for vehicles "13 years", Mg is a very small part of current auto recycling operations.
- There is little Mg in auto body scrap, and it is an annoyance, because there is no good method for separating it from aluminum at this time.
- Sophisticated sorting methods currently in use such as X-Ray Fluorescence (XRF) do a poor job of differentiating between aluminum and magnesium.
- It is possible to recycle 30-40% of the magnesium from dross using retort furnaces (MagPro) or mechanical methods (MagReTech), but much of it is currently landfilled.
- At time of survey, the U.S. market appears to support pricing at <$1.80/lb.
- The market for alloys is much larger than for pure metals.
- Japanese auto producers avoid magnesium use because of supply stability concerns and inability to separate magnesium from aluminum in post-consumer recycling streams.

Interview Sources

1. Michael Freedman, Joseph Freedman Company
2. David Spencer, Founder & CTO, wTe
3. Steve Solomon, Solomon Metals, Inc
4. Rob McInerney, Sales, BuhlerPrince, Inc.
5. Al Boulet, President, MetaMag
6. John Haack, President, MagPro, LLC
7. Dave Wanless, Managing Director, MagReTech
8. Richard Fine, former President, Alabama Cathodic Metals, Inc.
9. Terry Hoarth, Head Buyer, Meridian Magnesium
10. President, Michigan Die-Casting Company
11. Manufacturing Vice President, Large Midwestern Die-Casting Company
12. Alex Monroe, Project Engineer, North American Die Casters Association
13. Toshihiko Koseki, Professor, University of Tokyo
14. Yasunari Matsuno, Professor, University of Tokyo

Interview Questions

- What is the current status of Magnesium recycling as opined by industry players?
- How much Mg do you see?
- Is it a significant part of your operations?
- What would need to change for you to increase your Mg recycling operations?

Metal Sorters

Joseph Freedman Company

Michael Freedman
Springfield, MA
Specializing in aluminum, copper, nickel alloys and aircraft scrap

- Already deals with pure magnesium, so does not have an issue sorting Mg from other metals
- Picks-up CNC machine Mg turnings, sells these to scrap processors
- Equipment to separate metals already exists
- Does not see a need for a new tool/methods to facilitate sorting for Mg from other metals

wTe

David B. Spencer, Founder, wTe – metal recycling facility - ferrous and non-ferrous
Recent NSF Phase II award

- Mg-based alloys are a very small percentage by weight (1-2%) of automotive scrap, so the available quantity is small
- There is not a lot of oxidized Mg in automotive scrap Mg
- Maybe opportunity in processing slags from Al recovery – Al slags contain MgO
- Mg is difficult to identify using Dave's Spectramet technology
    - "If there is a magic bullet to identify Mg & get it out of the metal scrap, this would be interesting to me"
- wTe is sorting metals from automobile scrap and waste-to-energy scrap
- wTe is focused today primarily on aerospace materials – high value materials
- People do recover the Mg from scrap, but using different processes
    - Qty of Mg is not great
    - Getting it out is difficult

Spectramet / wTe sorting technology

- Use high-speed optoelectronics - X-rays, x-ray fluorescence
- Can identify different metals and alloys and sort at high speed

Mg + automotive scrap

- Not a lot of Mg in cars recycled today
    - 1-2% scrap car weight from cars 13 years ago is Mg alloy
    - Most of Mg content in the car is as alloying agent to Al
- Av car life is 13 years for scrapped cars
- Won't see more Mg for 13-15 years more if we increase content starting today – long

lead-time to see increase in scrap

- Most Mg in scrap is as alloying element – part of Al alloy - Up to 6% Mg in Al alloy
- “Mg is a headache when recovering Al scrap. The Mg is hard to get out.”
- Maybe MOxST process can be used to handle Al slags
- A lot of Mg comes out in dross as MgO
- “We struggle with identifying and sorting Mg in scrap metal waste streams today:
    - Mg is a low-Z element, so X-ray not effective at identifying Mg
    - Mg does not create a strong enough signal in the electromagnetic spectrum
    - It is complex to get the Mg out of the waste stream
    - “If there is a magic bullet to identify Mg & get it out, this would be interesting to me”

Solomon Metals

Lynn MA, http://www.solomonmetal.com/
Steve Solomon, President & Owner
Scott Tauben, Vice President Aluminum Division

Mg scrap business

- “We deal in small quantities of magnesium scrap occasionally.”
- “We have no challenges sorting this metal.”
- “I’m not aware of any place where large quantities of magnesium scrap are generated or sorted.”

Fire hazard & Mg turnings

- Most metal sorters won’t accept magnesium turnings due to their fire hazard
- We take solid form magnesium scrap only

Sources of Mg scrap

- Printing plates
- Ladders
- Dock boards
- Used to get old VW parts

Metal Capital Equipment Providers

BuhlerPrince, Inc.

Rob McInerney – New System Sales
Die Casting machine maker
670 Windcrest Drive , Holland, MI 49423

Summary

- Automotive end market may demand Mg spec that precludes simply throwing Mg scrap back into a remelt furnace at the die-casters – material may need to be more cleanly reprocessed
- It would be advantageous to have process to handle Mg chips, not just bigger pieces of scrap – more difficult to handle using traditional methods of recycling
- There is interest in a cost-effective process for recycling Mg

- Unsure what percentage net of Mg is lost – for Al, it is about 10% due to flue evaporation – but this is not an issue for Mg
- Mg die casters are dying or have died over the past two years due to the tariffs

How are Buhler customers recycling Mg?

- Recycling process for Mg depends on the end user
- It is possible to recycle Mg - A lot of smelters do this themselves
- Not all Mg die casters can simply throw scrap back into a remelt furnace
  - Main reason – a lot of the people consuming Mg are automotive
  - Automotive companies want virgin material
  - Recycled material could violate material spec
- Automotive suppliers may be relaxing standards somewhat

Technical challenges with recycling Mg

- Problem with Mg – can't just dump it back into the furnace like you can with Al or Zn
- Either hot chamber or cold chamber machine - furnace always under a cover gas
- Difficult to have an open-furnace to just dump material back in
- Machining of Mg creates Mg chips
- Chips are a fire hazard
  - Need to have systems in place to prevent fires
  - Can't throw "wet" (machining fluid) Mg chips – directly back into furnace
- Chips are different – quantity is lower than large pieces – not as much to send back
  - But they still go back, still have value

Potential customer interest in recycling technologies

- More cost effectively recycle magnesium – there is interest here
- Some Mg die casters working on internally recycling Mg

Economics of Mg recycling

- Device – screw & runner or piston runner
- Lost material
  - Depending on casting – 10-15% of the total cast weight up to 40-50% of cast weight is lost due to scrap
- However, a lot of this material is reclaimed through recycling
  - Supplier of Mg to die caster typically has an agreement to take scrap back
  - Scrap can also be used directly as an alloying element
- What percentage overall is lost, including material recycled?
  - Not sure what the number is for Mg
  - Al – about 10% range lost
    - A lot of this due to melt loss- going up the flue
  - Mg – can't have a flue, so won't have flue loss

Mg industry in US

- Not a lot of Mg suppliers left in US
- Not a lot of demand for Mg die-casting systems today
- Until something happens to level the playing field Mg will be a challenging industry in the

US
  - e.g., CAFÉ standards
  - Mg must become a larger part of automotive industry than it is today
  - Over the long term, Mg should be a better industry in the US

MetaMag

770 Wright St., Strathroy, ON N7G 4K5 , Canada
Capital equipment provider
Mg die-casting systems and recycling cells
Al Boulet, President & Founder

- Most large Mg die-casters recycle their own scrap
- Limited qty of scrap available from smaller die casters
- Retort furnace processes such as those used by MagPro LLC (John Haack) are crude but fairly effective at extracting Mg from the dirtier forms of scrap
  - Al claims Mg is fairly easily extracted from sludge and dross using a retort furnace
- Believes all growth for Mg die-casting will be driven by the automotive industry

MetaMag background

- http://metamag.com/products/recycle/
- “Metamag In-Cell Recycling System includes a two furnace in-cell remelting, pumping systems, furnaces, ingot preheaters, melt protection systems and safety equipment.”
- 32nd year in business for Al Boulet
  - Custom-supplying equipment
  - Need to have a good product
  - “Every cell we make is customized”
  - “Fundamentals are the same, but every customer’s needs are unique”

Opportunity for recycling Mg from die-cast operations

- Trend has been for big die casters to recycle in-house -- a lot of them do this
  - Meridian (Mg die-caster) is the biggest Mg user in the world – they have 3 recycling cells
- Small companies that can’t afford to recycle Mg in-house send their scrap away
  - Only a small qty availability due to size of smaller die-casters

Opportunity for reclaiming Mg from dirtier scrap

- John Haack (MagPro LLC) – starting a Mg recycling system that is going to use retort furnaces
- Meridian – produce quite a bit of sludge and dross from Mg operation
  - “Mg is very easily reclaimed from the sludge and dross”
  - Can put it into retort furnace
- What percentage of Mg can MagPro recover?
  - Bin of sludge or dross – he will recover 85% of Mg out of it
  - “John’s retort furnace system is crude, but it works”
  - Can wind-up burning the Mg if not careful
- John Haack has all his production sold out – he is at capacity

  - Only makes enough Mg to supply a few huge Al producers in the US
  - Using Mg as alloying agent in Al alloy
  - This is all recycled from sludge and chips – mixed with Al – does not have to be of same quality as Mg for die-casting
  - John's material is close to AZ91 type of alloy
- MagPro's process
  - Experimenting with 4-5 different kinds of retort furnaces
  - John Haack talking about building 500 systems
  - Can produce about 300-400 lbs/day per retort

<u>Economics of Mg production</u>

- Noranda started Mg plant in Quebec, when price of Mg fell to 80 cents/lb, they closed down because price too low to make money
  - Price now at $1.50/lb
  - Shut down by bad weather – too expensive to start-up the electrolytic cells
- Today, there is an overstock of Mg in China
- Problem is the tariff – because of US Mag
  - This is hurting the industry
- MetaMag does work for GM, Ford
  - Mg is no longer the material of choice due to availability
- Can get around Mg tariffs by importing Mg scrap
  - Can also import anodes
  - If you brought 25 containers of cheapest anodes from China
  - Re-melt, clean, alloy, sell back as new - "would make a fortune"
- If there are reliable sources of Mg besides US Mag, could sell the product
  - Mg use will increase
- Northwest Alloys closed down because they were in Portland
  - Costs were too high
  - Making alloy to sell to Al industry
- Meridian Global uses 60,000-70,000MT Mg/yr
  - There is not one single producer that makes this much per year
  - Why don't they start their own Mg production facility? Unclear
  - Owned by GE Capital
  - Bought-out from EU consortium that bought them previously, went broke
  - Starting to be profitable again – installing more machines
  - Believes, will sell company off in blocks – plant-by-plant – so GE can get its money out
- 2009-2010 MetaMag had six customers that went broke – all American companies, plus one Canadian company
  - Supply issue is the problem – Mg supply is too expensive
- GM buys Mg and sells back to their die-casters
  - Signed a deal 2 years ago with US Mag 20,000-30,000 MT /yr
  - Enough Mg for GM's production
  - Sell Mg back to Meridian
  - That is how GM manages the supply of Mg and controls price

  - US Mag capacity 50,000 MT/yr
    - Profit margin for US Mag selling to GM is lower due to guarantee of supply from GM

What will drive growth of Mg die-casting?

- Die casters all going to China
  - Black and Decker making parts in China - die casting in China, used to be in US
- Automotive will drive all the growth

Supply of raw materials for producing Mg

- Timmins – way up north in Canada
  - They have a gold mine, nickel mine
  - Found a huge pocket of magnesite and talc from which they can extract Mg
  - Some interest in starting a Mg operation
  - If could get an efficient Pidgeon system – cheapest
  - Electrolytic – too expensive
- Noranda – Asbestos, Quebec
  - Recycling asbestos tailings – rich in magnesite
  - “Would probably give this stuff away”

Magnesium Recyclers

MagPro, LLC

Camden, TN
Mg Recycler with Primary Production
John Haack, President

Summary

- MagPro and recycling of Mg:
  - MagPro recycles all forms of Mg scrap, except type I and powders and have been doing so for decades
    - Can recover 30-40% by weight of low-quality Mg scrap
    - Not much low-grade Mg scrap available in US
- MagPro and primary production of Mg:
  - MagPro is interested in expanding into primary Mg production
  - They do not use Pidgeon process today; use processes involving MgCl, CaCl
  - Would be interested in potential ideas for thermal reduction - thermal reduction has been John’s area of expertise for past 25 years

MagPro background

- Manta.com listing estimates MagPro annual revenues at $3.5M
- Est 29 employees
- “Recycling metal is our business”
- We extract metal in more or less pure form
- Class of scrap they address

  - Class 1 – “there is no margin in this metal”
  - “We don’t do Mg powder”
  - “We can handle any other form of Mg scrap – dirtiest material, oily, etc”

Difficulties in America with the Mg industry

- John / MagPro has been in the Mg recycling business since the 1950’s
- Not much low-grade Mg scrap available
- Environmental challenges with processing scrap are less of a burden in China - burning-up metal, air pollution controls
  - Although this is starting to change in China
  - Recent crack-down / tightening of regulations in China

MagPro expansion plans

- Long-term objectives to not get away from lower quality scrap processing but to expand into production of primary Mg
- Expanding into primary Mg production using distillation processes

Challenges with Mg recycling

- Metal turnings – would be interesting to extract magnesium from turnings
- Lower grades – unusual process required
- Don’t need to use reduction process – physical washing, decontamination required
- This is a hazardous process
  - Requires inert atmosphere
  - Burning problem – challenging / dangerous
  - Every operation that has tried this – had fires / too dangerous
- Equipment and economics are also challenging
  - Low energy required for processing scrap, but challenging equipment
  - Equipment must handle oils, using solvents

Economics of low-grade Mg scrap recycling

- Not that much scrap to go around
  - Does not want competition
  - Limited availability of scrap from the market
- Pay 1 cent – 5 cents per lb max for scrap
- Processing low-grade scrap – e.g., greasy flashings
  - “The freight kills you”
  - Only 30-40% recovery of pure metal from scrap
  - Cost of disposal of remaining material
  - Time & maintenance costs
- Contamination in scrap
  - Rags, gloves, pallets, garbage included in turnings
  - Drill bits – particularly challenging
- John believes that the US duties will come off Mg, and prices will fall to $1.60/lb

Mg recycling companies have struggled with safety

- Who has been in recycling, and what has happened to them?

- Significant psychological & physical barrier to entry
- Problems – fires, cost
  - Garfield, fire in 2001
  - AMACO, fire in 2003
  - MagPro, fire in 2007
  - Spectrolite – fire a few months ago
  - Alabama Cathodic Metals – fire
  - IMCO – had a fire before being bought by Aleris

MagPro Primary production of Mg

- He is not using the Pidgeon process
- Using processes involving MgCl, CaCl
- Thermic process using scrap Al -- mixture of Mg-Al

Value of removal of Cu and Ni contamination from Mg scrap?

- Majority of Mg scrap MagPro goes to Al alloy producers as an alloying agent, so Cu and Ni contamination is not really a problem for him
- Percentage contamination from Cu and Ni so small, not a problem
- Cu and Ni contamination is a problem for automotive use of Mg

Sources of Ni and Cu contamination?

- Ni comes from stainless steels mixed-in with Mg scrap
- Cu comes from Cu inserts in die-cast Mg parts
- Automotive die casters would be interested in a solution to remove Cu and Ni contamination
  - Their spec for Mg alloy is very tight
- Primary Mg alloy producers – would be interested
- Companies selling scrap Mg to automotive suppliers should be interested
- US Mag is selling to automotive
  - Buying and selling scrap

Automotive industry scrap

- Most of scrap in automotive industry is primary scrap and there is not much of it.
- Clean Mg scrap more effective in Al industry.
- Dirtiest scrap too dirty to go to die casters – does not go to Al industry.
  - Dirtiest scrap can be used for other purposes – Al, desulfurization of steel, grinding.

MagReTech

Magnesium Refining Technologies, Inc.
Dave Wanless, Managing Director

Summary

- Dave believes there are no real technical challenges with their business today – feels confident they have solved their major technical obstacles
  - Does not have a problem with Cu and Ni-contamination – solves with blending
- Biggest challenge is the limited demand for Mg alloys – market challenge

- Believes if Mg can be produced for less than overseas producers, then there will be a market for it
- Dave would like to find a way to sell dross / get value from it

Is Ni- and Cu-contaminated scrap a problem?

- “We don’t sit around worrying about how to fight these issues” [with copper and magnesium contamination]
- Fighting element contamination is done using a blending process, which is typical in metal melting industry
    - Essentially diluting the contaminants by blending with alloys that do not have the contaminants
- Bigger challenge for MagReTech is dealing with residues from manufacturing operations (dross)

Is there value to MagReTech in producing high-purity Mg from scrap waste streams?

- Our markets don’t value high-purity Mg
- MagReTech sells alloys instead

Is there value in producing Mg from oxides with a low-cost process?

- “At the point there isn’t enough Mg capacity in industry, we might look at these kinds of technologies.”
- Today, demand for Mg is far below supply
    - Already have plenty of sources for Mg
    - “I’m absolutely sure market utilization is low.”
    - A lot of demand will have to occur to require more Mg production capacity in the world
- The magnesium industry has the potential to help automotive industry – CAFÉ standards are increasing
- If Mg can be produced for less cost than existing processes, then yes, there would be demand for it
- We sell secondary Mg alloys -- not the same pricing dynamics as primary Mg alloy production

MagReTech – sources of Mg scrap & challenges with supply quality?

- Majority of scrap we buy is post-production, not post-consumer
    - We buy scrap types that is on-spec, which facilitates producing secondary Mg alloys that also meet spec
    - Post-production scrap is cleaner and consistently on-spec
- MagReTech also buys post-consumer Mg scrap – but significantly less volume than post-production scrap
    - Post-consumer scrap is a less understood material
    - Still, it typically comes as one of several common alloys
    - Can typically blend post-consumer scrap and still hit spec
- “20% or less of our scrap is sourced from post-consumer Mg materials”
- Key to maintaining quality and hitting spec: sorting the scrap first
    - “Sorting is a core competency of ours.”

  - We also buy scrap from known sources

Waste stream challenges – dross

- Dross – most of what is left after processing Mg alloys are salts
- There may be an opportunity to extract Mg from dross stream
- Today, MagReTech uses a mechanical process to extract “reclaim” – usable Mg metal – from dross
- “A more efficient process for extracting Mg from dross would be of interest to us.”
- Remaining salts from dross are land-filled after reclaim is extracted
  - Not cheap to landfill dross
  - We would like to find a use for these salts – MgO
  - “We are looking to solve this problem, although we’re not necessarily looking to produce high- purity Mg.”

What would make for a compelling solution to the dross problem?

- Would just come down to the math: cost to landfill dross salts versus cost of capital for facility to extract Mg from dross
  - Need to get ROI in 3-5 years versus continuing to landfill salts
  - Customers of this new process would want to see their capital returned in 3-5 years, max

Magnitude of dross recycling opportunity

- There are 3 magnesium recyclers in US (AMACOR, MagReTech, Magnesium Elektron – also MagPro LLC) plus USMag which can also recycle Mg scrap
- Not all recyclers share the same process
- “Dross volumes sourced from all three recyclers probably would not make the model work if multiple-$M investment is required”

What are the problems MagReTech is looking to solve?

- “There are no real technical challenges today” [for MagReTech]
- Dave got involved in company 19 months ago, previously with an Al company
  - Family owner wanted to step away from day-to-day operations
- Dave reshaped the company – technically recycling metal
  - “No one can do a better job than us”
- Former Dow engineer on staff
- Business challenge – reshape business to face current market – different than 10 years ago – i.e., smaller market, less demand for Mg alloys
- Biggest challenge today – “let’s find a home for the dross”

Scrap Metal Brokers

Mag Resources

P.O. Box 2590 , Daphne, AL 36526 http://www.paciron.com/
Richard “Rick” Fine, formerly President and Founder of Alabama Cathodic Metals, 1996-2001
Then President and Founder of Mag Resources, a company developing magnesium plants internationally

Now in the real estate business, but also trying to launch a new magnesium processing facility

Rick's background

- Rick built, owned and operated a magnesium processing facility
- His family has been in the business "for a long time"
- "My technology is cheap, efficient, and works. We proved it after many years of doing it wrong."

Rick's current endeavor in Mg

- Rick is interested in building a new Mg plant
- What would Rick bring to a magnesium facility?
  - Can assure them of scrap supply and sales
  - Rick would supply technology, tolling contracts, sales

Thoughts on opportunity for new technology

- "Cu and Ni fouling is an aggravation, not a holy grail."
- "There is no money thrown away with Mg contaminated from Cu and Ni."
- "I'm intrigued by a technology that can eliminate Cu and Ni fouling, but I've heard this idea before and haven't seen it work at scale."

Magnesium Die Casters

Meridian Magnesium

Terry Hoarth, Head buyer

What do they purchase?

- Meridian does not buy 99.9% Mg – only buys alloys : AZ91D , AM50A , AM60B
- All chemistries found in ASTM B93 '09 spec

Who buys 99.9% Mg?

- Alcoa
- Alcan / RioTinto
- Buy 99.9 Mg as alloying agent to make aluminum

Magnesium alloy suppliers to Meridian

- US Mag makes both 99.9 and alloy
- Majority of Mg made in China
  - Meridian buys primarily from China
  - Since they are Canadian, they aren't subject to the tariff
- They do get some material through US Mag
  - Supplied via purchases from General Motors
  - GM supplies to Meridian
  - Al alloying and Mg die-casting represent 95% of the Mg market

Michigan Die-Casting Company

$20M revenue company, likely early beta field test/customer site.

Markets: medical devices, portable electronics, some automotive.
Met with the company President.

- Magnesium die casting marketplace price sensitivity:
  - If your magnesium is priced at \$1.80/lb, then people will consider it.
  - At \$1.60/lb, they will build parts from it.
  - At \$1.40/lb, you will move markets.

Large Midwestern Die-Casting Company

MOxST CEO Steve Derezinski and VP for Business Development John Strauss traveled to a magnesium and aluminum die-casting company in the midwest, and met with a team including the Engineering Vice-President.

- Discussion focused on commercial deployment of MagGen™ primary magnesium production equipment and continued into new commercial opportunities for magnesium recycling.
- Recycling of dross cuttings and chips was discussed in some detail as they currently are tracking losses of magnesium during die-casting operations to dross, chips and cuttings (the latter from finishing operations) averaging ~5% of their primary metals usage.
- Although they have well developed methods of handling dross now, sale of dross as scrap returns only about 10-15% of the new material cost with no recovery possible of the energy used (~5%) to melt the primary magnesium in the first place.
- Magnesium cuttings and chips produced by their operations present both a challenge and opportunity: they have effectively \$0 value due to handling and storage (fire) concerns and they would be open to recovering/creating revenue from them.
- The company is interested in leading the commercialization by being an early customer, as soon as we can meet their economic requirements.

Chicago White Metal Casting Inc.

Bill Baraglia, Vice President, Manufacturing
649 N. Rt. 83 , Bensenville, IL 60106
Die-caster

North American Die Casters Association

241 Holbrook Drive , Wheeling, Illinois 60090-5809
Mr. Daniel Twarog, President
Interview call conducted with NADCA Project Engineer Alex Monroe

Summary

- Most scrap is either re-melted internally or sold to Al alloy producers
- Dirtiest scrap is still collected and processed by scrap companies
- Only very small qty of Mg scrap available, given declines in Mg consumption
- Due to high pricing of Mg, die-casters invest a lot in minimizing scrap produced
- Biggest opportunity – and significant pain point – is low-cost production of Mg in an environmentally-benign process
- Strong interest in automotive sector in using more Mg – driven by CAFÉ standards
- BAA funding available for enabling expanded use of Mg in automotive sector

Recycling of Mg at die-casters

- Recycling in-house
  - There are a handful of Mg die-casters who take runners and biscuits and throw then back into the furnace
  - They run very low yields on casting, so get a lot of high-quality Mg scrap
- Selling scrap
  - Most die casters don't have capability to re-melt Mg & most don't have large components that need to be re-melted
  - More common practice at Mg die-casters: selling Mg scrap to Al smelters
    - Price premium for Mg today
    - Many Al alloys contain a fair amount of Mg
    - Oxidation on scrap does not affect ability to sell Mg scrap to Al alloy manufacturers
    - No excess oxidation (dross) will remelt and reuse this material
  - Al alloy producers can absorb all the Mg scrap produced these days
- Die casters would prefer to recycle everything in-house

Yield loss in Mg die-casting

- Since Mg is so much more expensive – premium to pay to use Mg – a lot of engineering focused on maximizing die-casting yield
  - As the material gets more expensive, can put more effort into making good castings with high yields, so recycling is not as big of a deal
- Die casters now using more hot chamber die casting
  - Results in much less material consumed in runners and biscuits
- Yield results
  - 90% material in casting for the best – minimize the amount of loss through biscuits and runners
  - Traditionally die casting yield is closer to 50%-70%

How does Mg get contaminated?

- Scrap from die casting is not particularly dirty, surface can be oxidized
- Machining Mg die cast parts in-house generated dirtier scrap

Typical process for dirtier scrap at die-casters

- Die casters send out material from flash and fines from machining
- Trend in industry – casters are moving into machining, too
  - Need to have more value-add than just casting
  - Customers want a finished product from a single source
- Machining – small pieces of Mg, and flash from injection – like machining fines from parting plane are collected
  - Most of this waste collected in a big bin (truck bin) in/next to the die-casting facility
  - Have special procedures for handling fines, small scrap – dangerous form of Mg
- Once bin is full, send out to be recycled
  - "I'm not sure what happens to this material at the recyclers -- recyclers are tight-lipped about what they do."

- Not much difference between Mg recycling versus Al, except handling issues with Mg

Bigger issue than recycle – basic supply of low-cost Mg

- Not troublesome to send out scrap
  - "I've never heard anyone say, 'I don't know how to get rid of my Mg scrap.'"
- Anti-dumping regulations – tariff on Mg - $1/lb more expensive here than anywhere else in the US
  - Because of this, Al is a preferred material
  - Before tariffs – 50/50 Mg/Al – at major die casters
    - Now only 10-15% Mg
  - NADCA has 13 members that cast in Mg – for all of them, Mg is just a portion of what they do
    - They represent 2/3 of the die casting industry
    - Mg scrap is not a big issue due to small volumes
- Low-cost production of environmentally-benign Mg of great interest to Mg die casters – more so than with recycling
  - Believe Mg and Ti are on an inflection point of getting to be cheap enough to be ubiquitous, like Al 60-70 years ago

Japanese Metal Industry Experts

University of Tokyo

Prof. Toshihiko Koseki, Department of Materials Engineering

- Nissan and Toyota are increasing use of magnesium parts to reduce weight
  - They are funding some of Prof. Koseki's work on steel-magnesium joining
  - Likely application will be multi-material bodies
  - Corrosion is an issue in such joints, but auto makers feel coatings are sufficient for corrosion prevention
- Given recent experience with rare earth metals, Japanese auto makers are concerned about buying magnesium from China
  - Prof. Koseki asked about planned capacity expansions in the US
  - I discussed Molycor Gold's plant construction plans which were outlined in Magnesium Monthly Review 8/31/2011
  - I mentioned MOxST's future interest in building a plant if our scale-up R&D goes well
- There is no domestic (Japanese) magnesium industry
  - Industrial energy prices were ¥12/kWh (16¢) before the earthquake, now ¥18/kWh (24¢)!
- In the long term, recycling magnesium is much more attractive to Japan than primary production
  - Energy requirement for recycling is just 10-20% that of extraction
  - However, there is no efficient method for recovering magnesium from mixed Mg-Al scrap in automotive recycling streams
  - Chloridation makes $MgCl_2$ which whose reduction is very energy-intensive
- It will be many years before magnesium in autos will make this an urgent need
- But Japanese auto companies would be more willing to use magnesium if there is a path

to recycling in the long term

- Japanese industry might be interested in participating in an international project on magnesium recycling

Prof. Yasunari Matsuno, Department of Materials Engineering

- Prof. Matsuno's work is in Life Cycle Analysis and Material Flow Analysis (MFA)
  - He has recently published work on MFA for indium and dysprosium
  - His student completed work on MFA for magnesium
- Magnesium MFA highlights:
  - Automotive use of magnesium has been decreasing since ~2005
  - 2005 maximum was around 5 kg/vehicle, today Japanese autos average 1 kg/vehicle
  - Die-casting represents only about 15% of Japanese magnesium use (vs. 35-40% in the US)
  - The largest tonnage of magnesium stocks in Japan is in aluminum alloys in buildings
- Japanese industry has no plans to recycle magnesium from aluminum alloys due to energy requirements with current technology
- There is strong interest in recycling magnesium auto parts in Japan
  - Dismantling is very expensive