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CARBOTHERMAL PRODUCTION OF MAGNESIUM: CSIRO'S MAGSONIC™ PROCESS

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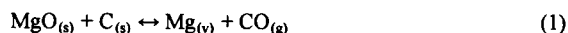
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Abstract

Carbothermal production has been recognized as conceptually the simplest and cleanest route to magnesium metal, but has suffered from technical challenges of development and scale-up. Work by CSIRO has now successfully demonstrated the technology using supersonic quenching of magnesium vapor (the MagSonic™ Process). Key barriers to process development have been overcome: the experimental program has achieved sustained operation, no nozzle blockage, minimal reversion, and safe handling of pyrophoric powders. The laboratory equipment has been operated at industrially relevant magnesium vapor concentrations (>25% Mg) for multiple runs with no blockage. Novel computational fluid dynamics (CFD) modeling of the shock quenching and metal vapor condensation has informed nozzle design and is supported by experimental data. Reversion below 10% has been demonstrated, and magnesium successfully purified (>99.9%) from the collected powder. Safe operating procedures have been developed and demonstrated, minimizing the risk of powder explosion. The MagSonic™ Process is now ready to progress to significantly larger scale and continuous operation.

Introduction

Magnesium is the lightest of the structural metals and is useful for a wide range of industrial applications [1]. The production of magnesium via carbothermal reduction is not a new concept; indeed, a process using this chemistry was patented as far back as 1932 [2]. The basic chemistry depends on the use of carbon as the reductant to produce magnesium and carbon monoxide from magnesia and carbon:



The well-known primary issue with the carbothermal process is reversion – the reaction above proceeds in the reverse direction very easily; this can be minimized by cooling the gaseous reaction products very rapidly. The largest industrial-scale operation of carbothermal technology was at Permanente, CA [3, 4]. Cooling of the gases was achieved either by heat transfer with surfaces [3] or shock-chilling by dilution with, for example, natural gas [4], nitrogen [5], molten magnesium chloride [6], or even molten magnesium itself [7]. Other versions of the chemistry focused on removing magnesium from the vapor phase by reaction in a solution [8, 9].

The idea of supersonic quenching is also not new. The reaction products (gases) are accelerated to several times the speed of sound (typically $Ma \approx 4-5$), achieving very rapid gas cooling. Useful reviews of the literature have been presented by the present authors [9-11]. Previous attempts appear to have failed primarily because of blockage of the supersonic Laval nozzle [12] under sustained operation. This paper describes one form of the

technology, called MagSonic™, developed by CSIRO (Commonwealth Scientific and Industrial Research Organisation) in Australia.

Technology Description

Feed Preparation

Magnesite may be commercially mined at relatively high purity and calcined to produce magnesia (MgO) suitable for reaction. Options exist for additional purification of the magnesite or magnesia, which depend on purity and morphology requirements and may include acid leaching, flotation, and other processing. The MagSonic™ process has demonstrated itself remarkably robust, processing magnesia that has been only calcined (not purposely purified). The behavior of impurities in the carbothermal reduction process has been addressed previously [13], reporting that essentially all the impurity species are reduced before the carbothermal magnesium reaction begins. The species may be detected in the cyclone (used to separate the magnesium powder from the gas) by Laser-Induced Breakdown Spectroscopy (LIBS).

Feed preparation is completed by briquetting calcined magnesia with a carbon source. For much of the experimental program, powdered graphite has been used ($d_{50} \approx 12 \mu\text{m}$, >99.5% C, Merck Pty Ltd, Kilsyth, VIC 3137, Australia). Although briquetting graphite without a binder is difficult, briquettes of the size and shape suitable for piloting have been produced without a binder (Figure 1), and have been tested in the laboratory rig.



Figure 1: Magnesite-carbon briquette

Reaction

The reaction proceeds quickly above 1700 °C, and there is evidence of some reduction/vaporization as low as 1250 °C [13]. In experimental work to date, heating has been achieved by the use of an induction furnace (up to 50 kW), with sustained reaction at temperatures typically around 1800–1900 °C [14]. The reaction kinetics have been described by the present authors [14, 15], including achievement of sustained (60+ minutes) operation and confirmation of kinetic modeling for pilot plant and full-scale design.

Supersonic Quenching

The aerodynamics of supersonic Laval nozzle operation are well known, but the present operation presents a number of novel aspects. These include high temperatures, metal vapor condensation and solidification, and relevant boundary layer interactions. CSIRO has developed a number of novel computational fluid dynamics (CFD) tools that have been implemented and validated, providing significant information for scale-up and further development.

The effect of metal vapor condensation may be illustrated by Figure 2. Condensation adds significant heat to the stream, affecting temperature distributions, expansion shocks, and other aspects of the flow. Early CFD work identifying the condensation effect shown in Figure 2 was reported in [9] with further publication on these topics pending.

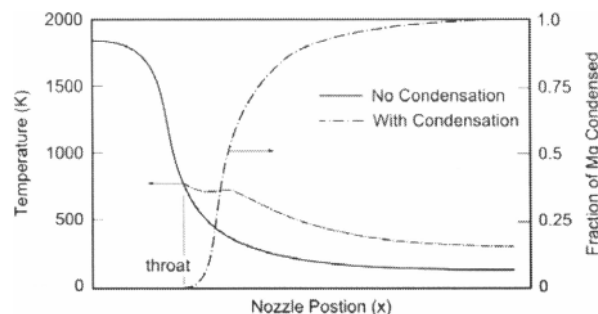


Figure 2: Schematic (illustrative) temperature profile in nozzle calculated with and without metal vapor condensation

Condensation / Solidification

The effect of supersonic expansion, combined with some heat transfer with the walls of the chamber, result in a stream temperature around 200 – 300 °C. The peak rate of cooling during the process is around 10^6 K.s^{-1} . Following rapid cooling, the magnesium completely solidifies, and the reversion reaction is prevented.

Separation

Separation may be achieved by a number of methods, the simplest of which is a cyclone. While some reduced efficiency at moderate temperatures may be experienced [16, 17], separation efficiencies above 90 %, often higher than 95 %, have been consistently achieved. The powder may be conveniently recovered, despite its very low bulk density (typically $< 0.3 \text{ g.ml}^{-1}$), and flows easily.

Gas Handling

Vacuum systems are typically designed to handle one or two of the relevant process conditions – low pressure, high mass flow, high temperature – but rarely all three at once. As such, the vacuum system is a major user of energy, estimated as 0.46 MWh per tonne Mg at full scale [18]. The vacuum system must maintain the absolute pressure downstream of the nozzle below 50 % (but preferably below 10%) of its upstream value to maintain sonic flow. The lower limit of vacuum is determined primarily by the economics of operation; achieving a pressure below 0.5 kPa is likely to be prohibitively expensive, and unnecessary for optimum operation.

Purification

The experimental product powder is rendered safe either by controlled surface oxidation ('passivation') or by covering it with oil to prevent contact with air. The product has been purified from both media, either by direct sublimation from the passivated powder, or firstly by distilling off the oil at 400-500 °C at atmospheric pressure and subsequently distilling the magnesium metal at about 980 °C and 0.8 kPa absolute pressure in a graphite-lined steel retort. The resulting magnesium metal is distilled again and yields metal containing low levels of metallic impurities (200 ppm Al, 90 ppm Ca, 80 ppm Fe, 10 ppm Mn and 60 ppm Si).

Major Technical Challenges

High Temperature Operation and Control

The control of a kinetically-constrained gas-solid endothermic reaction at very high temperatures is non-trivial, though the total system pressure can be relatively easily maintained by the flow rate of an inert cover gas. For maximum efficiency the magnesium concentration in the vapor should be as high as possible, but any higher than a partial pressure of 50 kPa risks over-pressurizing the reactor. The equilibrium partial pressure of 50 kPa is reached at 1764 °C, but the reactor is likely to operate at 1900 – 2000 °C.

In terms of process control, reactor temperature and cover gas flow rate are controlled in the laboratory batch system. Continuous operation will likely operate at constant temperature, with the reaction rate controlled by the amount of reacting bed, and to a lesser extent by the inert gas flow rate. The authors have presented data on the modeling of the reaction kinetics [14, 15, 19], which are useful for sizing and control.

Preventing Nozzle Blockage

Blockage of the gas exit/quenching nozzle has been a significant problem for the carbothermal process [12]. Typically, magnesium and/or impurity metals condense on the surface and revert to oxides with high melting points, thereby accreting and blocking the nozzle. The CSIRO research team has overcome these issues and provisionally patented aspects of the method [11]. Despite demonstrated operation without blockage at laboratory scale, safe design includes the possibility of recurrence and must be included in risk assessments.

Pyrophoric Powder and Process Safety

Issues with pyrophoric magnesium powders are well known, and previous industrial operation has resulted in fatalities [20]. Studies have quantified the conditions for spontaneous ignition [21]. National Fire Protection Association standards 69 and 484 [22, 23] are also useful for magnesium powder explosion prevention and process safety. Given that magnesium powder produced by the MagSonic™ process is relatively fine and is certainly spontaneously combustible, and that operation is under vacuum, conventional measures such as deflagration venting, explosion suppression, or dust concentration control are not likely to be practically effective in ensuring safe operation.

Design for scale-up presently focuses on explosion containment, whereby equipment is designed to withstand a magnesium powder explosion without rupturing. Safety methods under development are relatively novel (and are the subject of future publications), but will ensure exceedingly high safety integrity levels are met for practical full-scale operation.

At laboratory scale, residual internally-adhered powder is oil-sprayed for safety. At larger scales, oil spraying is impractical and undesirable. Therefore, the metal powder must be rendered safe from a “dry” state. Options include a) batch passivation by controlled oxidation; b) melting of powder directly, or after briquetting, or by stirring into a liquid pool of magnesium; and c) distillation and condensation. The latter two options lead directly to the purification stage of the process.

Purification

The temperatures required to achieve reaction also means that the other metals in the feed are also reduced and contaminate the product to various extents. The product metal that is collected will require subsequent purification to achieve commercial magnesium metal purity.

Purification of magnesium by distillation is known technology [24, 25], but difficulties with fine powders are also known [3]. At Permanente the fine powder was briquetted with tar prior to vacuum distillation, but it is unlikely that a similar process will be used for MagSonic™ at full scale. The CSIRO team has overcome the difficulty of fine powder purification by dissolution into a molten metal, from which magnesium may be vacuum distilled. The molten metal may be a metal with low vapor pressure (such as Sn, Pb, Cu), or indeed magnesium itself. Because of its lower oxygen content than Permanente’s powder, incorporation into a melt, and subsequent distillation, are easier to achieve. The CSIRO project team has successfully purified the magnesium produced from the MagSonic™ rig and has data to size pilot plant equipment to purify magnesium.

Experimental Progress

Progress in the experimental program has been rapid following the initial stage (proof of concept) from 2004 - 2007. The charts below illustrate experimental progress.

The concentration of magnesium in the nozzle is an important factor for efficient economic operation. Dungan [3] reported that the (subsonic) “Permanente magnesium plant circulates to each reduction unit from a common system approximately 13,000

ft³.min⁻¹ of natural gas containing up to 6 per cent carbon monoxide.” This implies that the magnesium concentration in the quench section was relatively low. For economic operation of the MagSonic™ process, the concentration target has been 25 % Mg in the nozzle. This corresponds to less than 50 % inert gas, though it may also be recycled as in the Permanente plant.

Figure 3 shows that the 25 % target was consistently met towards the end of this experimental program. Not all experiments aimed for very high concentrations, as other goals of the program included kinetics and control operations and the achievement of ‘pseudo-steady-state’ control [15].

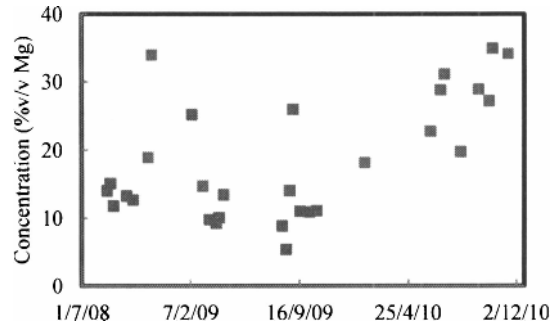


Figure 3: Peak magnesium concentration in nozzle entry gases over main experimental program

The data presented in Figure 3 are higher than reported for similar systems. Odle and McClaine [26] cite experimental work by Mineral Development International (MDI) in Birkerod, Denmark, for which the maximum Mg concentration appears to be around 0.25 %. Hori *et al* [27, 28] worked at reduced reactor pressure, which would also lead to a lower magnesium concentration (per unit volume) than that produced by the MagSonic™ process.

Continuous operation is also imperative. In the laboratory setting the process has been a batch operation, consuming MgO-C pellets. Operation of the reactor, nozzle, vacuum system, and powder recovery process were tested for durations up to around 2.5 hours of operation above 1700 °C (Figure 4). Towards the end of the experimental program, two hours of consistent operation could be reliably achieved, part of which may be considered pseudo-steady-state [15].

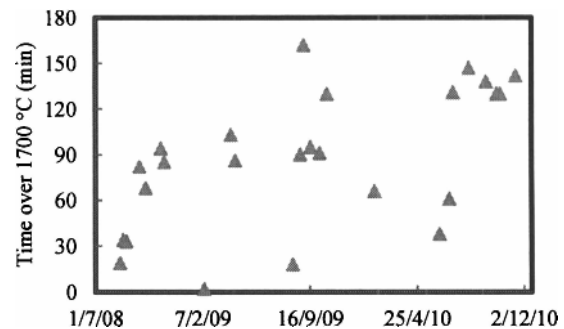


Figure 4: Experiment duration (minutes over 1700 °C) over main experimental program

Finally, another practical measure of continuous operation is the mass of reactants consumed. The laboratory equipment was

upgraded in late 2008 to allow up to 2500 g of reactants to be loaded into the reactor. The charge consumption in each experiment is shown in Figure 5. Some failures are included (from, for example, nozzle blockage or operational issues), but since late 2009 consistently good and reliable experiments have been conducted. A 'routine' mass of 2000 g has been used for many of the latter experiments, all of which have gone to effective completion (>99.9 % MgO reacted).

The focus of each experiment was not necessarily maximum charge consumption. As mentioned above, occasionally the purpose is pseudo-steady-state control, or the investigation of alternative cover gases, or modifications to process conditions (e.g. downstream pressure), or simply collection of a batch of powder.

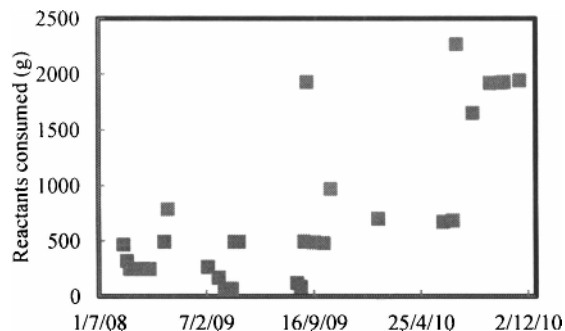


Figure 5: Consumption of reactants in each experiment (g) over main experimental program

The mass of magnesium produced in a batch may be compared with some data available in the literature. Hori *et al* [27, 28] report the consumption of around 1000 g of MgO and carbon, for two experiments listed. Odle and McClaine [26] report that 11 experiments 'processed about 90 to 285 grams of feed'. Engell *et al* [29], whose work may underpin Odle and McClaine's, give examples of consumption of 10-15 g reactants. Larger-scale work was undertaken by Cameron *et al* [30, 31], who reported feeding tens of kg per hour. By contrast, kinetic work by Sano's group [32, 33] operated at the mg scale. Nusseh *et al*'s recent work [34] was also at mg to μ g scale. Donaldson and Cordes [12] did not provide data for magnesium experiments.

Future Development

The development of a novel process for the production of a mass-produced material necessarily involves significant scale-up factors. The MagSonic™ process has proceeded from the gram scale to the kilogram (and from Mg concentrations below one percent to upwards of 25 %), yet significant scale-up factors remain. For example, from Figure 4 and Figure 5 one may deduce a laboratory productivity around 500 g Mg per hour. Full scale may be around 30,000 tonnes Mg per year, which at 80% utilization is around 4.3 tons per hour, or nearly 10,000 times laboratory scale.

The next step in the development of MagSonic™ technology is a pilot plant, for which CSIRO has developed a relatively detailed preliminary design and costing. Such a plant would aim to operate continuously and produce both purified magnesium for

industry evaluation and good data for design and operation control. Sustained continuous operation would also validate the environmental claims of MagSonic™ [18], provide data on process robustness, and lead to further scale up and process development.

Conclusion

CSIRO's MagSonic™ carbothermal magnesium technology has been under development in Australia since mid-2003. Recent advances have demonstrated that sustained operation can be achieved, and the laboratory equipment and experimental program have achieved concentration, reaction time, consumption, recovery, and purification targets. The technology is now ready to progress to the next stage, a continuous Pilot Plant.

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