**Final Report on Refining Technologies
of Magnesium**

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FINAL REPORT ON REFINING TECHNOLOGIES OF MAGNESIUM

by

S. Bell[*], B. Davis[*], A. Javaid[**] and E. Essadiqi[**]

EXECUTIVE SUMMARY

Over the past decade, magnesium recycling has become more important because of its increasing use in the automotive die-casting market. In order for the use of magnesium to continue to grow, all forms of die-cast magnesium scrap need to be recycled – for both economic and environmental reasons. Today, only high-grade magnesium scrap (Class 1) is recycled from die-casting operations using either flux or fluxless refining. This is due to the inability of current refining technologies to adequately clean the variety of scrap produced during the die-casting process. In order for magnesium to remain a competitive automotive material, a better understanding of existing refining techniques needs to be established. The goal of this report is to present current refining technologies used on a commercial, pilot plant, and research scale.

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INTRODUCTION

The amount of magnesium based scrap has grown drastically over the past six years, due to the slow but steady inroads magnesium has made into the automotive industry. Most of the automotive magnesium today is produced by die-casting, and the yield of the die-casting process is estimated to be 50%. The International Magnesium Association (IMA) reported in 1999 that 41% of the magnesium lost in a typical die-casting operation is Type 1 scrap, 5% is dross, 5% is returns and 36% is gates, runners and trim scrap[1]. A description of all the magnesium scrap classes is found in Appendix A.

Natural Resources Canada estimated that, in 2000, 30% of all primary magnesium produced in the world was used in the die-casting industry representing about 110 700 tonnes of magnesium. Based on the IMA numbers, this breaks down to 22 693 tonnes of Class 1 magnesium scrap, 2768 tonnes of magnesium dross, 2768 tonnes of magnesium returns, and 19 926 tonnes of magnesium gates, runners and trim scrap that was produced worldwide in 2000. Most die-casting operations have their own in-house recycling operation because of the high volume and the ease of handling of Class 1 magnesium scrap. However, in-house recycling of scrap classes 2-8 is not considered an economically viable option because of the increased handling and dirtiness of the starting material. These classes require extensive pretreatment, chemical adjustment and refining procedures to convert the magnesium back into a useful product. For a quick description of pretreatment processes required for scrap classes 2-8 refer to Appendix B. The complexity of processes for treating these classes makes methods uneconomical. This ultimately causes the magnesium scrap to be either landfilled on government approved sites, or stockpiled by the manufacturer. Therefore, the increasing use of magnesium and accumulation of scrap is fueling a growing need for more effective magnesium refining systems for the recycling of all scrap types.

REFINING TECHNOLOGIES

Refining technologies can be divided into two categories: flux-based and fluxless.

FLUX REFINING

This particular method of refining magnesium scrap is relatively old but is the most common. It uses two different fluxes to prevent surface oxidation and clean the underlying metal of impurities. A flux used to protect the magnesium surface from oxidizing is referred to as "cover flux". Simple cover fluxes contain a combination of sulfurous compounds and fluoborate salts or boric acid. If the cleanliness of the melt is high (Class 1), then only a small amount of flux is required - typically 1 wt % of the total charge. However, a cover flux will not clean the underlying magnesium, and therefore a secondary flux is required to refine the metal below.

In the refining process, the main purpose of the secondary flux is to agglomerate nonmetallic inclusions present within the original metal and to break apart and pile up oxide particles, films and skins that form during melting. This flux can coat either solid or liquid surfaces as well as selectively wet small magnesium oxide skins, thereby aiding in their removal. Since liquid magnesium has such a low specific gravity, it is more appropriate for the flux to have a higher

density. This causes better mixing with the liquid magnesium and produces a higher refining efficiency. Also, the flux is usually added to the melt surface while the magnesium is slowly stirred with an impeller to ensure maximum contact between the flux and the magnesium metal. Once the desired inclusion composition is reached, the stirring is stopped and the flux is allowed to settle out and collect at the bottom of the crucible as sludge. Sludging (removal of the flux from the bottom of the crucible) is done periodically.

Flux Composition

A typical flux used in magnesium refining is composed of 49 wt % anhydrous magnesium chloride ($MgCl_2$), 27 wt % potassium chloride (KCl), 20 wt % barium chloride ($BaCl_2$) and 4 wt % calcium fluoride (CaF_2)[3]. Each type of salt plays an important role in the magnesium refining process. The combination of magnesium and potassium chlorides provides the low melting eutectic, while the fluoride provides the surface wettability and chemical reactivity with magnesium oxide to cause sufficient removal (dissolution of an oxyfluoride in the flux). The barium compound provides the density requirement for the salt to effectively mix with the magnesium and then settle out at the bottom of the crucible. The $MgCl_2$ minimizes or eliminates surface oxidation by creating a thin-film layer on the metal surface, thus cover fluxes can be avoided if the refining flux contains enough $MgCl_2$. However, the composition of the flux is highly dependent on the type of magnesium alloy being produced. For example, if the magnesium alloy contains rare-earths, the $MgCl_2$ would be replaced by $CaCl_2$. This is because $MgCl_2$ has a tendency to react with rare-earth elements, causing their recovery to be minimal. However, eliminating $MgCl_2$ makes the use of a cover flux essential to avoid surface oxidation.

In order to effectively remove the wetted inclusions, sufficient time must be allowed for settling. The actual settling time depends on certain process variables such as charge size, the cleanliness of the charge, and the quantity of flux added. The temperature of the melt is also a key factor in magnesium refining. It has been found that the best interaction between liquid flux and molten metal is achieved at 705ºC[3]. This is because the surface energy characteristics between the two media at this particular temperature promote good inclusion agglomeration and prevent the formation of finely distributed globules within the melt. However, each type of alloy, and its corresponding flux, has a slightly different critical temperature. The amount of flux required for refining is strongly dependent on the cleanliness of the feed material. For crude magnesium, the flux requirement has been estimated at 7-8% of the weight of the magnesium[4]. As the cleanliness of the magnesium decreases, the amount of flux required increases. This is especially true when melting magnesium scrap that contains a high surface-to-volume ratio, lubrication, and sand from castings. If the magnesium scrap is very dirty, the flux will be melted before the charge is added to coat the surface of the scrap and better agglomerate the impurities.

Additives

If the magnesium metal is contaminated with foreign metallic species, such as iron and silicon, additives are incorporated into the flux to eliminate these impurities. For the additives to be effective refiners, they must form intermetallic compounds with the metallic impurities. The three main factors that determine the likelihood of intermetallic formation are electronegatitivity, ionization potential, and ionic radii. Manganese chloride ($MnCl_2$) and boron (B) have been found to be effective additives for the removal of iron in magnesium[5]. Beryllium, in the form of

a chloride, is also used as an iron refiner in magnesium. The low solubility of beryllium in magnesium makes it a very attractive refiner. However, its high toxicity deters many companies from using it. The resulting intermetallics are then precipitated out of the magnesium and collected as sludge at the bottom of the crucible. Zinc or cobalt chloride is used to remove silicon while titanium and titanium chlorides remove both iron and silicon from the melt. However, some metallic species, such as copper and nickel, cannot be taken out of the magnesium melt by using metallic additives. This is because these species have a strong interaction with the magnesium.

Figure 1 is a representation of a typical flux refining process. Once the magnesium has been refined to specifications, it is transferred to a holding/casting furnace by either pumping or tilt pouring. The molten magnesium within this secondary furnace is protected from oxidation by a cover gas, which can vary in composition. The most common cover gas used is a sulfur hexafluoride gas mixture. The magnesium is then solidified into large ingots.
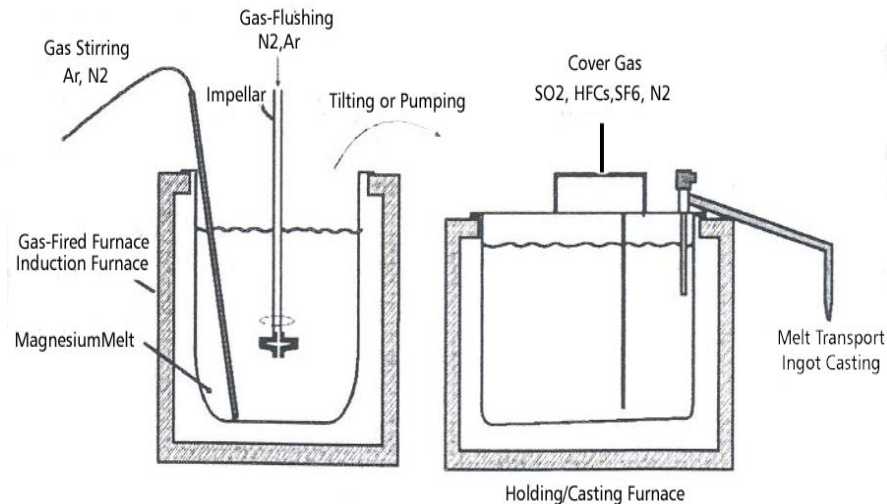

Fig. 1 – Flux refining process[5].

The main advantage of flux refining is its ability to refine dirty magnesium scrap. By adjusting the ratio of flux to the scrap cleanliness, the magnesium can be refined to a purity used for many destructive applications (desulphurization, corrosion protection, etc). Also, the initial capital cost of equipment is low, making the process a fairly economical solution for magnesium refining.

However, the introduction of a flux to the magnesium melt increases the chance of adding additional impurities. Sometimes large flux inclusions get trapped in the magnesium, causing deterioration of certain physical properties. This causes the properties of the magnesium to decline below the chemical and physical standards set for die-casting material. Also, the addition of chlorides to the magnesium melt raises the potential of key alloying elements being tied-up and producing poor alloying-agent recoveries. Moreover, most of the cover fluxes that contain chlorides, including $MgCl_2$, are very hydroscopic. The trapping of water increases the possibility of hydrogen absorption within the magnesium melt and is believed to be the leading

factor in the microporosity and micro shrinkage witnessed in final castings[6]. The dissolved hydrogen can also react with the chloride in the salt to produce hydrochloric vapors, which can rapidly corrode steel equipment surrounding the furnace. To remove the hydrogen or other dissolved gases, inert gas sparging must be utilized. Also, the formation of globules during the wetting and absorption of oxides often traps magnesium inside. This results in high melt losses and requires additional processes to recover the magnesium from the flux. It is also uncertain what the flux disposal procedure is after use, or whether some of it can be recycled back into the process. Clearly, flux-based refining techniques are not the ultimate solution for magnesium refining.

FLUXLESS REFINING

Fluxless refining includes all techniques for magnesium refining that do not include the use of a salt flux. Molten salt can still be employed in some fluxless techniques as a heating medium within the refining furnace. However, the salt has little affect on removing impurities from the magnesium. While there are numerous fluxless techniques, the use of flux for refining is still the predominate method in the industry.

Salt Furnace Technology

This technique, developed by Norsk Hydro, for melting and refining magnesium uses particle sedimentation and adhesion due to convection to clean the magnesium metal. The apparatus consists of a large multi-chamber refining and casting furnace and is illustrated in Fig. 2. Magnesium scrap is first charged into a melting basket, and molten salt is poured over the metal to facilitate melting. Once the charge is molten, it is transported to an alloying furnace to correct the composition of the major alloying elements. This step is critical when magnesium scrap with varying compositions are mixed and melted together, causing disproportionate amounts of
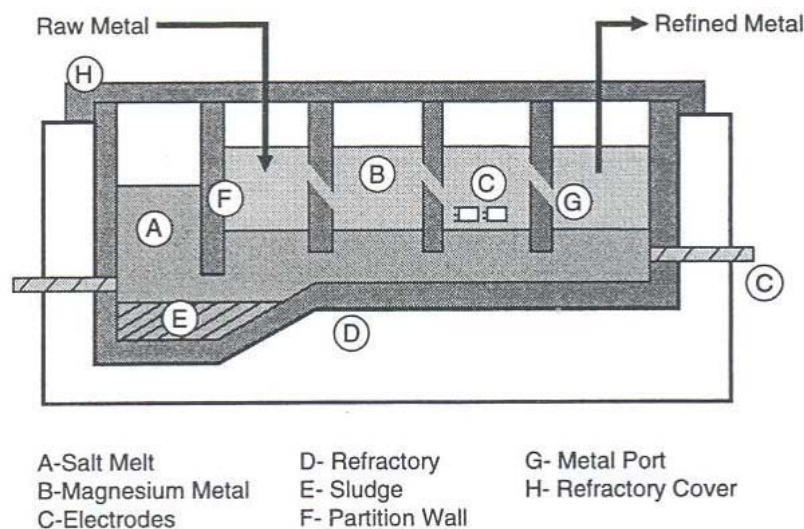

A-Salt Melt   D- Refractory   G- Metal Port
B-Magnesium Metal   E- Sludge   H- Refractory Cover
C-Electrodes   F- Partition Wall

Fig. 2 – Schematic picture of a four-chamber casting refining furnace[7].

certain elements within the melt. Additives are also used to either increase or decrease the concentrations of certain alloying elements.

The mixture of salt and magnesium is pumped into the multi-chamber refining/casting furnace. The refining furnace has a lid with several openings for charging and discharging metal as well as for sludging. A protective gas is fed into the chamber to prevent surface oxidation. Two electrodes regulate the temperature, and the salt enhances heat-transfer kinetics within the chambers. In the furnace, the salt and magnesium first separate by gravity. During this time agglomerated oxides and films, as well as precipitated intermetallic particles, settle out of the magnesium and collect at the bottom of the furnace as sludge. The continuous salt layer at the bottom of the furnace prevents the separated inclusions from reentering the metal. As the clean magnesium metal rises in the chamber, it flows to the next chamber by passing through inlets in the partition walls. The inlets are designed to take the magnesium from the top layer of one chamber to the bottom of the next in a non-turbulent manner. Turbulent flow can sometimes break apart the agglomerated oxide particles and finely distribute the oxide throughout the melt.

This diminishes the likelihood of the oxide settling out by gravity. As the metal moves from chamber to chamber, additional particles are removed by adhering to the sides of the furnace. The furnace's construction is such that sufficient time is allowed in each chamber for effective settling of impurity particles.

The main advantage of this technique is that it can be used to refine all magnesium scrap classes, except used fluxes and sludge, at a fairly high recovery rate[15]. It is also used to condition primary magnesium that has been tapped as a liquid from the electrolysis cells. Process control is vastly improved in this system because the alloying furnace is much larger than the refining furnace resulting in a long holding time before refining. This allows the magnesium to reach thermal equilibrium, which vastly decreases the chance of metastable intermetallics forming in the final cast product. This improved process control allows for the production of high purity magnesium alloys when using Class 1-2 scrap. Moreover, the large capacity difference also allows for an effective switch from a batch (alloying) process to a continuous (refining) process.

The initial cost of equipment is higher for this technique than for flux refining due to the complexity of the furnace. Also, a large quantity of waste products (dross and used salt) is produced. For example, 13 tons of salt is required per ton of magnesium in the furnace and two to three tons of magnesium is melted every hour[15] (~35 tons of salt is used every hour). While the salt can be used to process a significant quantity of magnesium, at some point it must be tapped and new salt added because of impurity build up in the salt. Since $MgCl_2$ is not used to protect the metal, a cover gas must be used. This is problematic given the current switch that is slowly taking place in the magnesium industry from sulphur hexafluoride to other gases.

The casting/refining furnace, shown in Fig. 2, is currently in use by Hydro Magnesium in Norway and Canada and is capable of producing 2-3 tons of refined magnesium per hour[8]. A schematic illustration of Hydro Magnesium's recycling path is shown in Fig. 3.
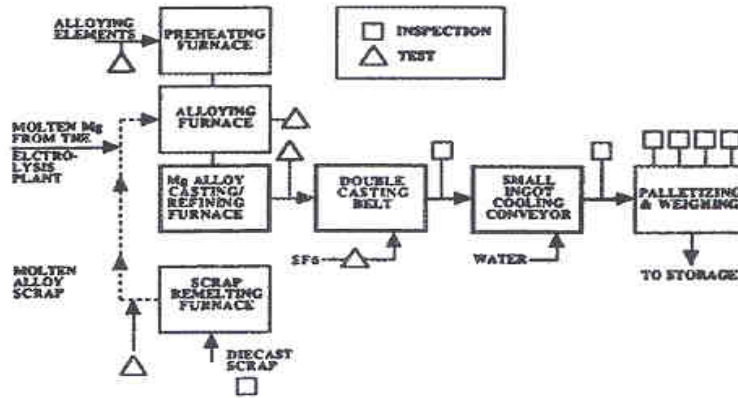
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Fig. 3 – Flowchart for Norsk Hydro Canada Inc.'s magnesium scrap recycling facility[9].

One major drawback of the furnace design is that the sludge has to be removed from each chamber separately. This causes the furnace to be shut down quite frequently. To correct this problem, another furnace has been patented for continuous refining of magnesium. The furnace is cylindrical and is separated by vertical partition walls into a main chamber and peripheral chambers encompassing the main chamber. An illustration of this particular furnace can be seen in Fig. 4. A description of the reference numbers in Fig. 4 can be seen in Appendix C. Openings in the peripheral chambers are used to allow the melt to flow from one chamber to the next, allowing the sludge to drop out slowly in each chamber. The main chamber only receives the salt and no magnesium.

The sloping bottom of the furnace allows most of the sludge from the peripheral chambers to collect in the bottom of the central chamber. This design includes one area for sludge accumulation which can be discharged without interrupting the entire process since the
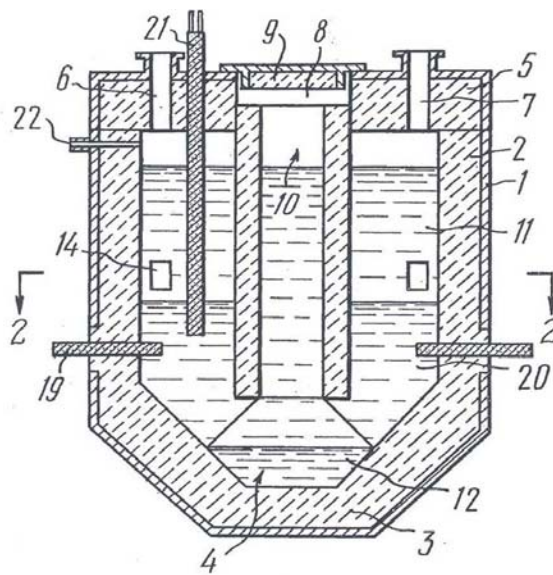

Fig. 4 – Vertical partitions for continual refinement of magnesium scrap[11].

peripheral chambers, containing the magnesium, stay closed during the sludging process. However, it is conceivable that some of the sludge could accumulate in the peripheral chambers, causing the entire furnace to be shut down.

Inert Gas and Filter Refining

The emergence of salt-free melting technology for magnesium refining has lead to the production of very pure magnesium alloys. In order to avoid oxidization of the liquid magnesium, a protective gas is used to cover the magnesium. The first cover gas used in the early development of the magnesium industry was sulfur dioxide (SO_2) which is toxic, dangerous to the environment, and potentially explosive (sulphur-dome effect). Problems with SO_2 lead to the development of sulphur hexafluoride (SF_6) - a nontoxic, odorless, and stable gas used extensively today in most fluxless magnesium operations. It is generally believed that the fluoride in the gas interacts with the magnesium oxide film to form a thin, continuous layer of magnesium oxyfluoride (MgF_2) on the surface of the liquid[11,13]. This inhibits the interaction between the magnesium and the oxygen in the air and thus prevents burning. This effect is achieved at very low levels of SF_6 (0.02 to 0.1%) and is always mixed with dry air and a less expensive gas such as carbon dioxide, argon, or nitrogen. Melt protection can also be achieved by alloying a small amount of beryllium (5-10 ppm)[14]. There is presently a drive to replace SF_6 with a more environmentally friendly gas (SF_6 has a global warming potential of 24 000). 3M, working with Noranda Inc., has recently experimented with a fluoroethylketone as a replacement.

In this particular method, clean, compacted magnesium scrap (Class 1) is charged into the melting furnace. A steel plate, with systematically placed ports for charging and refining equipment, is put over top of the crucible, separating the melting apparatus from the rest of the unit. The entire unit is closed and tightly sealed to avoid oxygen penetration. An SF_6 mixture is used to protect the surface of the magnesium from burning. Once the magnesium is molten, a metallic additive, usually $MnCl_2$, is mechanically stirred into the liquid. The compound decomposes and interacts with iron contaminates in the melt to form an intermetallic. The intermetallic is then precipitated out of the magnesium. Using a siphon tube, the molten metal is pumped from the melting furnace to the casting furnace.

The casting furnace is similar in structure to the melting apparatus. The entire furnace is enclosed, tightly sealed and an SF_6 cover gas is fed overtop of the melt surface. Two refining steps are used in the casting furnace to remove many of the small impurities within the magnesium. First, argon gas sparging aids in floating impurities to the top of the melt. The impurities are periodically removed from the melt surface, along with dross, by skimming.

In the series of pilot plant tests, the affects of argon gas sparging and filtering were studied on recycled magnesium scrap. The volume of the scrap, consisting of engine valve covers, small pump and carburetor bodies, spurs and risers, was first reduced. The furnace pot was filled with scrap, mechanically stirred, and protected from oxidation by an SF_6 gas mixture. Once molten, the sparger was introduced into the melt and periodically moved around for approximately 25-30 min. The top of the melt was skimmed regularly. After sparging was complete, the magnesium was pumped through a filter (illustrated in Fig. 5) and into a mould[6]. The filter tested was a 410 stainless steel, cylindrical, Johnson wedge-screen with openings of 0.114 cm.
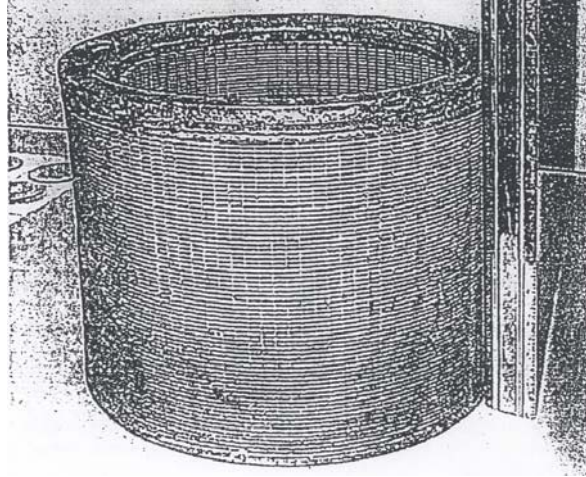
Fig. 5 – Filter for removal on inclusions from molten magnesium scrap alloys[16].

The same type of screen (but flat) was used for the bottom of the filter. To allow the magnesium to exit the filter, a trap door in the bottom of the filter was used.

It was determined that argon sparging alone, using the above sparger, produced a magnesium melt with an inclusion content of $100/cm^2$. This represented an 88% inclusion removal rate. Of the remaining impurities, it was found that argon sparging alone consistently floated only the smallest (<0.008 cm). However larger impurities (>0.08 cm) were not taken out of the magnesium.

It was also concluded that the filter successfully removed non-metallic inclusions 0.08 cm in size and greater. The resulting count of non-metallic inclusions 0.08 cm in size and greater was on average less than $0.05/cm^2$. However, the use of the filter did not have the same profound effect on smaller inclusions (0.008 cm and smaller). It was discovered that any reduction in mesh size resulted in plugging of the filters and cut the flow of magnesium. More information on filtration theory and different types of filters used for molten metal refining is provided in Appendix D.

Since argon gas sparging effectively removed smaller inclusions, and filtering effectively removed larger ones, Dow used both refining techniques to produce a very clean magnesium melt. The resulting inclusion count was $65/cm^2$. It was also noticed that the application of argon sparging reduced the level of dissolved gases in the magnesium melt. Dissolved gases enter into the scrap melt through a number of paths and contribute to microporosity during casting or solidification. Two major paths of entry are lubricants and moisture present on the scrap during charging. This is a major advantage since it reduces the need for an additional processing step before casting.

The primary benefit of the process is that the initial investment cost is low since only a mixer, filter, and sparger need to be acquired. This allows in-house recycling. Proper handling and cleaning can maximize the life-span of the equipment. For example, placing the pump and filter into a protective environment after removing it from the melt can reduce burning, which deteriorates the steel. A weak acid solution is then employed to clean the filter of any solidified magnesium and render it reusable. Since the process does not contain salts, it is capable of

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producing high-purity magnesium alloys at fairly high recovery rate. Also, good adjustment of chemical composition can be performed.

Only Class 1 scrap can be refined using this technique since the addition of large inclusions can plug the filter relatively quickly. This would cause regular stoppages to occur and decrease the life-span of the filtering equipment, thus increasing processing costs. Also, sulphur dioxide or hexafluoride-bearing gases need to be used to protect the surface of the magnesium.

Dow now uses these two methods for refining most of its die-casting scrap (Class 1) in a furnace shown in Fig. 6. In this system, magnesium scrap is shredded, preheated, and charged into an enclosed crucible for melting. The magnesium melt is refined using argon sparging, settling, and filtering. It is then filtered as it is pumped from the crucible to the casting area. An SF_6 mixture is used to protect the melt from oxidation.

Rauch's recycling furnace (Fig. 7) is another example of a fluxless approach, using gas sparging and filtration to manufacture clean magnesium from recycled die-casting scrap. The gas used to protect the melt surface is a combination of 0.2-0.5% sulphur dioxide and nitrogen gas[15]. The actual furnace is gas-fired and consists of three main chambers. The first chamber constitutes the area for melting the scrap magnesium, while the second and third chambers represent the refining areas. Nitrogen or argon sparging, settling and filtering are the three refining techniques used to rid the magnesium of impurities. To help avoid oxidation of the magnesium in the sealed furnace, the scrap is preheated to remove moisture, and fed through a paddle during charging.

Vacuum Distillation Refining

An interesting alternative for recycling all types of scrap magnesium is vacuum distillation. This method aims at refining magnesium scrap into very high-purity magnesium (99.999%) to be
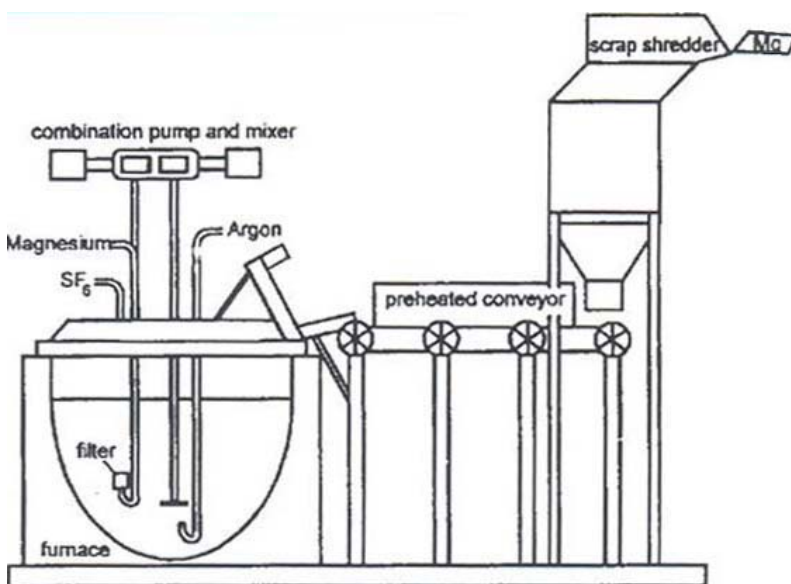

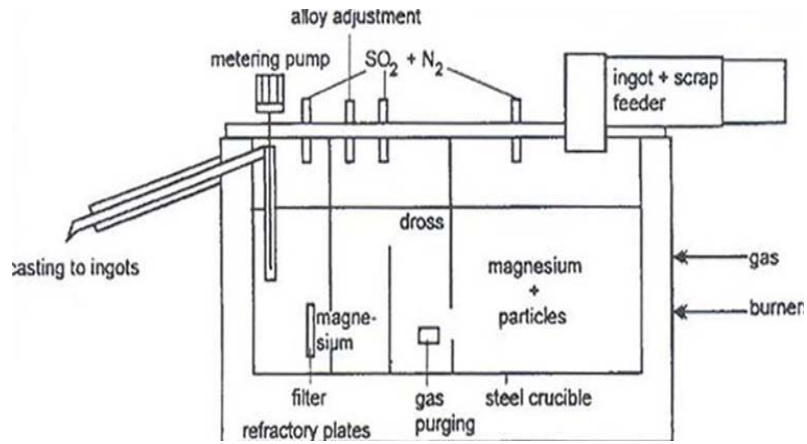Fig. 6 – DOW chemical plant for fluxless refining of magnesium die-casting scrap[15].
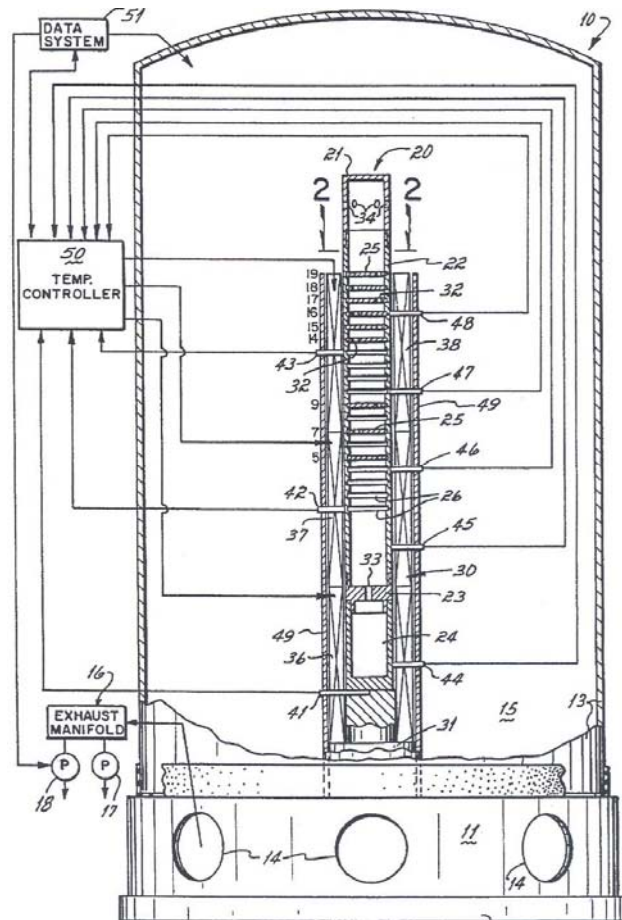
Fig. 7 - Rauch's in-house recycling furnace[15].

Fig. 8 - Patented vacuum distillation apparatus[16].

used in the semiconductor industry[16]. One particular application of high-purity magnesium is in blue-light laser diodes. It has been cited that this particular apparatus can improve the purity of the metal by roughly five hundred times in just one additional step[16]. The distillation apparatus can be seen in Fig. 8. A description of the reference numbers in Fig. 8 is provided in Appendix E. The column, crucible and vertical condenser with horizontal running high-grade graphite baffles at a number of different levels are all constructed from high-grade graphite. Steel can be used instead of high-purity graphite for the column, but that can result in slightly less pure magnesium. The column is contained in a three-zone resistance furnace. One zone is responsible for evaporating the magnesium within the crucible, the second zone heats the condenser above the boiling point of the magnesium, and the third zone controls the temperature of the column below the boiling point of magnesium. It is desirable for the temperature to decrease with the height of the column. The baffles are responsible for lowering the speed of the vapours so that the different condensation conditions can be reached on each baffle. Each condition has the ability to condense either purified magnesium or selective impurities. The magnesium will then condense onto the baffles to produce a high-purity product. The condenser is made up of two vertical parts so that the magnesium is accessible and the baffle locations can be altered. The column is then put under vacuum.

The crucible is heated until either the boiling point of the magnesium is reached or the vapour pressure of the magnesium is higher than the vacuum pressure within the chamber. For example, a vacuum pressure of 10^{-7} torr requires a melt temperature of 700ºC. The bottom and upper parts of the condenser are maintained at temperatures of 600ºC and 450ºC, respectively. The two baffles at the extreme ends of the condenser control the flow of the magnesium vapours while the baffles in-between collect much of the condensed material. Once the vapour drops below the vapour pressure of the magnesium, the metal condenses out of the gas. The higher-purity magnesium (>99.999%) is found at the ninth position and represents 55.5 wt % of the metal charge[16]. Zinc is by far the most common impurity at roughly 6 ppm[16]. Since zinc has a vapour pressure below that of magnesium, it will tend to condense more on the baffles located higher in the condenser. Most of the other impurities have a lower vapour pressure and will either deposit on baffles situated lower in the condenser or remain in the crucible.

In general, vacuum distillation processes are discontinuous and have a low output. The condensed fine magnesium is also highly pyrophoric rendering this process impractical for applications in the recycling industry. However, distillation under standard pressure is less complicated; it is a continuous process and has a much higher productivity, but a higher temperature is required to vaporize the magnesium. This is shown clearly in Table 1. Nonetheless, distillation is still being considered as a future alternative for refining all types of magnesium scrap. The less pure magnesium product can be sold to the steel industry for desulphurization purposes, while the high-purity product can be sold back to the die-caster as a magnesium-zinc alloy. This metal would have to compete with Pidgeon Process magnesium that is also produced under vacuum. This method accounts for half the world's magnesium production (coming out of China and 9000 tonnes from Timminco in Canada). The major impurities result in oxidation of the magnesium crowns or during remelting. Hence, downstream handling of the magnesium (treatment, casting) requires a high level of care to prevent oxidation of the melt.

A possible magnesium recycling procedure utilizing distillation is shown in Fig. 9 for treatment of automotive magnesium scrap. The magnesium scrap is first shredded into very small pieces

Table 1 - Vapour pressure of magnesium at various temperatures.

Temperature (°C)	Pressure (atm)
600	0.0013
650	0.0039
700	0.0094
750	0.021
800	0.043
900	0.152
1000	0.432
1050	0.684
1095	**1.00**
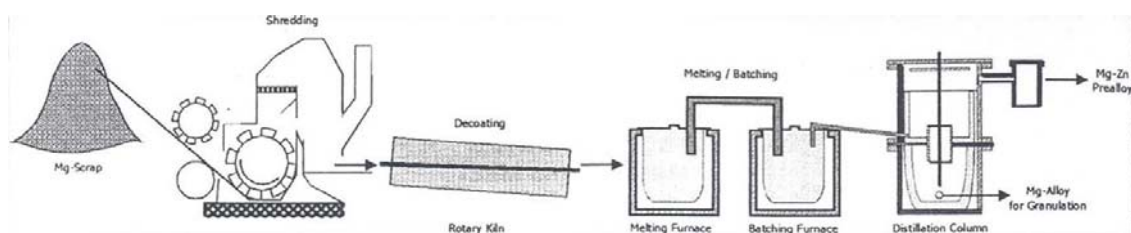
Fig. 9 - Innovative recycling path for future treatment of automotive magnesium scrap[5].

to improve decoating and charging efficiency in the rotary kiln and melting furnace, respectively. The decoating process nearly eliminates all coatings, such as paints and lubricants, on the surface of the magnesium. This improves the purity of the feed material. The preheated magnesium is then melted in an enclosed furnace under a protective atmosphere. It is likely that all chemical adjustments and crude refinements will be performed in the melting furnace. The molten magnesium will then be pumped directly to the batching furnace that serves solely as a storage area, until the magnesium is ready to be completely refined in the distillation column.

OTHER

Hydrometallurgy

A hydrometallurgical process for recycling used slags and drosses has been recently patented by two companies in Germany. The technique involves a reaction between aqueous hydrochloric acid and either the slag or the dross, and it produces chlorides of magnesium and other alloying elements. The magnesium is recycled by feeding the magnesium chloride back to the electrolytic cells while the more valuable alloying elements can be recovered and sold. The advantages of this treatment are that it can process dirty magnesium waste manufactured in primary and secondary magnesium industries and it allows recovery and sale of valuable metals. The main disadvantage is that the processing costs are high, making the treatment uneconomical if the waste product contains an insufficient amount of valuable metal. Also, the value of the magnesium is lost since the Mg units must be returned to the electrolysis cell as $MgCl_2$.

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APPENDIX A - CLASSES OF MAGNESIUM SCRAP[5]

Mg Scrap Class*	Characterization
Class 1A	High grade clean scrap without impurities (e.g., scrap castings, biscuits etc.)
Class 1B	Clean scrap with a high surface area in proportion to the weight
Class 2	Clean scrap with aluminum or steel inserts. No copper or brass impurities
Class 3	Clean, dry, and uncontaminated turnings and swarfs
Class 4	Flux-free residues (e.g. dross, sludge)
Class 5	Painted or coated scrap with/without aluminum or steel inlays No copper or brass-impurities
Class 6	Oily and/or wet turnings and swarfs
Class 7	Unclean and contaminated metal scrap (e.g. post consumer scrap) may contain: 1. Silicon (Al alloys, shot blasting) 2. Cu-contaminated alloys 3. Ni coatings 4. Non-magnesium sweepings
Class 8	Flux-containing residues from Mg-recycling

*Note: Other classification systems do exist. The above classification system was produced by Hydro Magnesium. Magnesium Elektron has a similar classification but it is based on a 6-class system.

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APPENDIX B - PRETREATMENT STEPS REQUIRED FOR SCRAP CLASSES 2-8 BEFORE REFINING[5]

Scrap Class	Pretreatment Steps
2	Magnetic separation, if necessary intermetallic compound formation and/or diluting
3	Compacting, increased flux quantity, if necessary intermetallic compound formation and/or diluting
4	Increased flux quantity if necessary intermetallic compound formation and/or diluting
5	Shot blasting, thermal decoating, if necessary intermetallic compound formation and/or diluting
6	Thermal treatment, chemical treatment, compacting, and increased flux quantity
7	Magnetic separation, shot blasting, thermal treatment, chemical treatment, intermetallic compound formation, diluting, and distillation
8	Extensive hydrometallurgical processing processes current not realized

APPENDIX C – PART NUMBER DESCRIPTION FOR FIGURE 4

Part No.	Description
1	Refractory lining
3	Furnace bottom
4	Basin
5	Roof
6	Roof opening #1 - for charging magnesium scrap
7	Roof opening #2 - for removing refined magnesium
8	Roof opening #3 – for removing slime
9	Cover for roof opening #3
10	Closed central chamber
11	Magnesium layer
12	Accumulation of slime
14	Outflow of magnesium in the direction of the process flow
19	Electrodes for producing heat
20	Salt layer
21	Tubular electric heaters for additional heating
22	Inert gas source for protecting magnesium metal

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APPENDIX D - FILTRATION THEORY

Filtration of particles out of a liquid stream occurs by either cake filtration or depth filtration. The mechanical removal of impurities by the surface of the filter is referred to as cake filtration, and it has been found that inclusions greater than 0.03 cm are easily removed using this method[3]. As the inclusions build up over time on the surface of the filter, they tightly pack together and form a filter cake on the filter surface. This formation increases the filtering capabilities of the filter as more metal is pushed through. One particular type of filter that largely depends on cake filtration is a ceramic foam filter. On the other hand, depth filtration is the most common filtering mechanism used in standard industrial filtration practices. This type of filtration can easily remove inclusions smaller than 0.03 cm since the filtration path is much longer and more rigorous, thus increasing the likelihood of the inclusions attaching to the filter. Particles that come in contact with the sides of the filtering apparatus may fasten to, or be held by, one or more of the following five mechanisms:

1. gravity, friction
2. physical confinement
3. chemical bonds
4. Van der Waals forces
5. electrostatic forces

The actual cause of chemical bonding is now receiving more attention as researchers have found that some ceramic surfaces exhibit a chemical interaction with certain types of inclusions.

The degree of efficiency of a filter largely depends on the properties of the molten metal being refined. These properties include the type, size, shape, number and distribution of the inclusions throughout the melt. Other factors that affect filtering efficiency include the flow rate of the metal, the surface area of the filter, and the depth of the filter. Slower flow rates generally result in greater filtration efficiency because of the increased opportunity for entrapment. Larger filter surfaces also increase the possibility of particle confinement on the mesh, resulting in better inclusion removal. The longer the path for particle transport, the more likely the particle will contact the filter medium and settle out of the liquid. Moreover, filters that depend on both cake and depth filtration and not just one mechanism will produce a better-filtered product. However, a large degree of cake filtration should be avoided since it leads to a dramatic reduction in metal flow. To reduce filtration, the metal being filtered should be as clean as possible.

There are many different types of filters used in the nonferrous molten metal processing industry. A summary of each type is illustrated below.

Strainer cores are the basic type of filter used mainly in down spurs in standard sand castings. The main purpose of these filters is to control the metal flow by slightly plugging the metal. However, in doing so they stop particles from passing by mechanical confinement and a small amount of cake filtration.

Metal or fiberglass screens effectively filter particles greater than 0.1 cm in size. Steel mesh and fiberglass cloth are usually used to filter aluminum melts while molybdenum mesh is commonly used for copper. These types of filters are planar and are rarely used more than once.

Bed filters are made up of tabular aluminum oxide (Al_2O_3) and are used mostly for high-volume filtration of casting or mill products. These filters are recognized as the most efficient way of eliminating or reducing fine inclusions in metal melts. However, their size, expense, and single alloy use make them impractical and uneconomical for large-scale use in most foundry applications. Also, bed filters can lead to turbulent flow, which increases the formation of oxides during casting.

Bonded particle filters are refractory grains of either aluminum oxide or silicon carbide reacted together to produce a rigid structure. This structure causes the molten metal filtration path to be long and complex, resulting in good depth filtration. Bonded particle filters contain approximately 38% porosity of varying sizes. Other advantages include long service lifetime, low temperature gradients, and reusability. These filters are used vertically, between melting and holding furnaces, and have been successful in many mill product, foundry and die-casting operations. The average durability of the filter is 500 tonnes[3].

Cartridge filters are identical to a heat exchanger as they consist of a shell and tube construction, employing a large surface area for physical contact with melt inclusions. The pore size is usually small, resulting in very low flow rates. However, the purity of the resulting melt is high making cartridge filters a vital method for manufacturing high-quality metal for the airline and electronics industry. Inclusions smaller than 0.005 cm in size have been removed with an efficiency of 95% or greater using this type of filter[3].

Ceramic foam filters are the most popular filters used in refining nonferrous castings. The filters are manufactured by coating reticulated polyurethane cellular foam with slurry, followed by drying and firing to eliminate the foam[3]. The final product is a ceramic shell of the original foam. Ceramic materials used for foam filters are alumina, zirconia, mullite, and sometimes chromic oxide. The porosity of the filter is approximately 75%, and pore size ranges throughout the filter[3]. The main mechanism of filtration is believed to be cake, however some depth filtration does occur. These filters are used in singular or multi-layered planar forms and can be found in the die-casting and foundry industries.

APPENDIX E - PART NUMBER DESCRIPTION FOR FIGURE 8

Part No.	Description
10	Entire vacuum distillation apparatus
11	Feed through collar or base
12	Base plate or support
13	Quartz chamber housing
14	Vacuum feed through ports
15	Vacuum chamber
16	Vacuum exhaust manifold
17	High volume mechanical port
18	Cryogenic high vacuum pump
20	Distillation column
21	Top condenser cap
22	Vertically disposed cylinder condenser
23	Bottom cap
24	Crucible
25	Plurality of bafffles (9 Total)
26	Baffles spaced vertically along height
30	Furnace assembly
31	Block to rest crucible
32	Circular hole in each baffle
33	3/16 central hole
34	Six circumferentially spaced holes in 21
36	Lower heater
37	Middle heater
38	Top heater
41	Thermocouple for lower heater
42	Thermocouple for middle heater
43	Thermocouple for top heater
44	Thermocouple
45	Thermocouple
46	Thermocouple
47	Thermocouple
48	Thermocouple
49	Open ended cylindrical alumina tube
50	Temperature controller
51	Data system for compiling data

APPENDIX F - ABILITY TO RECYCLE DIFFERENT SCRAP CLASSES

CLASS 1

Class 1 scrap is broken down into two different types: denser and high-surface-area scrap. This is done for two reasons:

1. the scrap's bulk density can differ remarkably which can influence transportation costs and thus the final cost of external recycling, and,

2. high-surface-area scrap (surface area to volume ratio up to 25 times larger) will have a greater increase in oxide added to the melt. This requires extra refining to remove the oxide, and can reduce the recovery rate of the alloy from the melt[17].

However if proper care is taken, both types of Class 1 scrap can be recycled effectively by either in-house or external recycling. Generally, Class 1A scrap can be refined using both flux and fluxless processes, depending on the desirable quality of the metal. On the other hand Class 1B can only be recycled using flux processing because of the high oxide content.

CLASS 2

Since this classification of scrap contains inserts, it cannot be recycled directly by the die caster. Therefore, it is suggested that an external recycler with a batch treatment facility should process this class of scrap to manufacture a quality ingot. Any castings that contain nickel or copper inserts cannot be recycled into die-casting level materials but can rather be recycled into alternative products by an external operation. The value of scrap with Ni and Cu inserts is very low.

Scrap that is painted must be scrubbed extensively before it is remelted to reduce the various emissions including dioxins. Thus, it has to be recycled by an external operation before it can be sent to the die-casting foundry. Because of the additional treatment, the cost of painted scrap is much lower than other types.

Due to variations in the scrap input, it is recommended that a batch treatment be used to recycle this class of magnesium scrap. This is because it allows the flexibility of making adjustments to major element composition and impurities on a melt-by-melt basis.

CLASS 3

This type of scrap is mainly spillage or leakage from the die-casting machines and is usually oily and/or wet. Since the scrap contains oily magnesium, it is listed under the Basel Convention for trans-shipment of waste. It is therefore subject to pre-notification procedures, and the use of approved transport and other regulations, increasing the final cost of recycling[17]. Also, before it can be remelted, an additional processing step is required to remove the oil from the scrap and to ensure it is dry thus, further increasing the overall cost.

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Because of the additional processing costs, it is likely that the total cost will exceed the value of the metal recovered, making the recycling of this material a net loss. However, there is no other environmentally acceptable long-term alternative. Due to tighter environmental regulations, the cost of landfilling is rising, and, added to the burden of future liability, this has made recycling Class 3 scrap seem much more necessary for die casters.

CLASS 4

This scrap class incorporates all forms of chips, swarfs, and small machinings. The size of this scrap can vary dramatically from chips to small flakes. The difficulty in handling smaller pieces not only increases the cost of recycling but it also reduces the recycling efficiency. However, some of the recycling companies in Japan are using a relatively new technology to address this problem. A mechanical press is used to briquette small pieces of magnesium scrap into small disks for remelting[18]. However, the type of treatment that can be used mainly depends on whether the scrap is dry (4A) or wet (4B & 4C).

Dry, clean Class 4 scrap is an easily recyclable material and has high commercial value. If the scrap is oily, then extra treatment is required. If the lubricant is a mineral oil, then it can easily be removed from magnesium pieces by using an aqueous alkaline degreasing solution in a wash, centrifuge, and drying system. However for high-speed machining, the die-casting industry is moving more towards an aqueous emulsion type of lubricant. This type of oil is much harder to remove and will require modifications to commercial cleaning solutions in order to achieve clean magnesium scrap.

As is the case with Class 3 scrap, the cost of processing the magnesium will probably exceed the value of the magnesium produced and will be a cost to the die caster rather than a recovery. Oily or wet turnings are classified as hazardous material and require storage and transportation in approved steel drums. On the other hand, dry turnings can be moved in large, flexible Intermediate Bulk Containers (IBCs).

In order to lower the cost of recycling, dry machining should be used whenever possible. Also, dry scrap should always be separated from wet scrap to take advantage of the higher commercial value.

CLASS 5, 6 AND 7

Flux-free residues, including dross and sludge, are not classified as hazardous waste and can be transported in IBCs. However, any residue that contains flux is considered a hazardous material and requires costly storage and transportation in UN-approved steel drums.

Most of the techniques used to recover magnesium from these residues are flux-based recovery processes. Most of the magnesium can be recovered, and remaining residues can be further processed using leaching techniques and then landfilled on government-approved sites.

The cost of recycling these classes of scrap would equal the value of the metal recovered if the residues contained at least 50% magnesium. Any residues with a metal concentration lower than 50% are unprofitable[17].

Any material containing less than 20% metal would not be economical and would be better dealt with by the die caster. One option for the die caster is to digest the material in water, creating a reaction with the magnesium, and follow local disposal guidelines[17].

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APPENDIX G - RECYCLING CONCERNS

In magnesium recycling, the shape and cleanliness of the returns are the two most important factors. Class 1 scrap, including biscuits, runners, and reject parts, can vary greatly in shape due to the different processes used and the item being produced. For the recovery rate to be high, some sort of consistency of the scrap must be maintained so that sorting is avoided, the bulk density is high, the dimensions of the scrap are to specifications, there are no dirty or oily returns, and there is no excess flashing[19]. If there is no consistency then the following can occur:

1. The heat generated when oil burns off the scrap can affect the melting scrap rate. This is more of a concern when the returns are very fine.

2. Differences in volume-to-surface ratio can greatly affect the melting rate. For example, large biscuits would have a higher surface-to-volume ratio then a large ingot.

3. Scrap with a higher surface-to-volume ratio would contain more magnesium oxide, thus, the magnesium oxide would not melt and would form sludge.

4. Any moisture present on the scrap will decompose in the furnace and produce hydrogen, which is a major contaminant of magnesium melts. Also, hydrogen gas can form and cause small explosions.

The presence of elemental hydrogen in molten magnesium is disastrous because it causes microporosity and microshrinkage in castings. There are many possible sources of hydrogen in magnesium recycling including hydrocarbon residues from various lubricants left on scrap, chemically bound water in hygroscopic fluxes, and a humid atmosphere. Inert gas sparging is the most common technique used to eliminate hydrogen from magnesium melts.

To help improve the recovery rate of magnesium, degreasing and crushing the scrap should be considered. Degreasing will lower the possibility of hydrogen contamination and reduce the pollution (smoke and soot) in the melting facility. Crushing should be used to improve the bulk density of the scrap. Also, faster additions and melting of the scrap would help minimize burning and oxidation. In order to improve the melting rate, compact, preheated scrap and stirring would be necessary.

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