

HAZARDOUS WASTE MINIMIZATION: PART VI

Waste Minimization in the Foundry Industry

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The foundry industry is a major consumer of waste materials (scrap). Unfortunately, the recycling of these waste materials can result in the generation of hazardous wastes that must be properly managed at a significant cost. This article focuses on two waste streams in the foundry industry; calcium carbide desulfurization slag and melt emission control residuals. The author presents an overview of how foundries have evaluated different waste management options with the ultimate goal of minimizing the generation of hazardous waste.

Although there may be differences in certain operations, basic foundry processes vary only slightly from one foundry to another. All foundry operations produce castings by pouring molten metal into molds, often consisting of molding sand and core sand. Once the casting has hardened, it is separated from the molding and core materials in the shakeout process. The castings are cleaned, inspected, and then shipped for delivery. Figure 1 is a schematic of a typical foundry process, showing both finished product and the types of air emissions and wastes generated.¹

Foundries are major consumers of waste materials. Scrap iron and steel are a major source of raw materials, amounting to 85 percent or more of the ten million tons of ferrous castings produced annually. Reclaimed copper, aluminum, lead, tin, zinc, and other metals are also recycled to a major extent in making castings. The recycled cast product is evident everywhere in the artifacts and machines which constitute man's material civilization. In addition, other residues from manufacturing operations, such as asphalts, pitches, sugars, resins, and cellulose

waste, are reused in the foundry processes.

Foundry Wastes

Foundry Solid Waste

An overall materials balance for a foundry is shown in Figure 2. Metal for melting and core and mold materials are the major input streams, while product and waste core and mold materials make up most of the output. Many foundries employ internal recycling of core and mold materials; however, these materials eventually lose their basic characteristics and are no longer suitable for use in the manufacturing process. They are then disposed in a landfill. Nonferrous foundries perform additional internal recycling because slags, dross and grinding residues may contain metal of sufficient value to be extracted in smelters. The reclaimed metal is then returned to the foundry as an ingot, thereby reducing metal loss.

Hazardous Waste

Certain foundry processes have the potential to generate hazardous wastes

within the plant. These processes include the following:

- Melting—To reduce the sulfur content of iron, some foundries use calcium carbide desulfurization in the production of ductile iron. The calcium carbide desulfurization slag generated by this process may exhibit the characteristic of reactivity.
- Melting—Melt materials which contain significant amounts of certain heavy metals—such as lead, cadmium, and chromium—may result in wastes which are classified as hazardous due to EP toxicity.
- Molding—Nonferrous alloy castings containing lead, such as certain brasses and bronzes, may generate system sand wastes which could be hazardous due to EP toxicity.
- Core-making—Some core-making processes use strongly acidic or basic substances for scrubbing the off-gases from the core-making process. Sludges from this scrubbing process may exhibit the characteristic of a corrosive waste.

Waste Management Options

The basic management options for minimizing foundry wastes are as follows:

- Reduce/alter product requirements
- Alter raw materials
- Improve production process control
- Recycle to the original manufacturing process
- Recycle/beneficially reuse in other processes
- Treatment

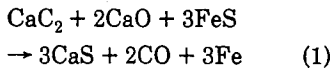


This paper will discuss how certain foundries have evaluated the application of these waste management options for calcium carbide desulfurization slag and melt emission control residuals.

Calcium Carbide Desulfurization Slag

Process Description

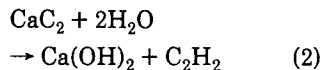
In the production of ductile iron, it is often necessary to add a desulfurizing agent in the melt because the charge materials contain excessive amounts of sulfur. One desulfurization agent commonly used is solid calcium carbide (CaC_2). Based on investigations by Talbala *et al.*,² the calcium carbide is thought to decompose to calcium and graphite. The calcium then reacts with sulfur in the melt to form calcium sulfide (CaS) (Equation 1).



The calcium carbide desulfurization slag is generally removed from the molten iron in the ladle and placed into a hopper. To ensure adequate sulfur removal, calcium carbide must be added in slight excess. Therefore, the slag contains both CaS and CaC_2 . The desulfurization process with calcium carbide is shown in Figure 3.

Waste Characteristics

One common practice is to treat the calcium carbide desulfurization slag with water.³ This is done to generate and release acetylene gas from the unreacted calcium carbide (Equation 2).



The other major reaction product is solid calcium hydroxide or lime.

Because this reaction is exothermic, a considerable amount of heat can be generated, which is particularly evident when only small quantities of treatment water are used. Under these conditions, acetylene can ignite during the wetting and mixing of the slag. Furthermore, upward convection currents and steam generation resulting from treatment reactions may cause the release of considerable amounts of fugitive dust.

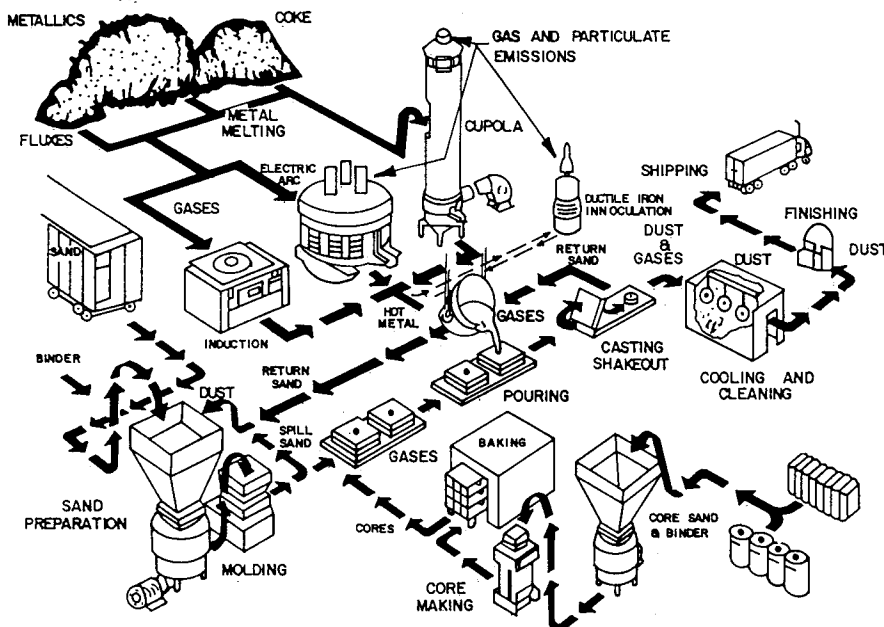


Figure 1. Typical foundry processes. (Source: EPA).

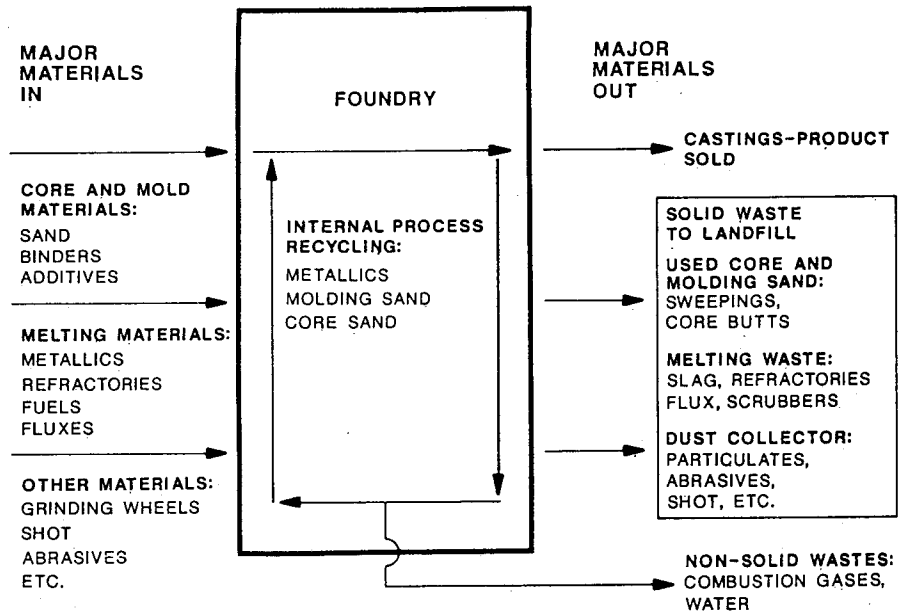
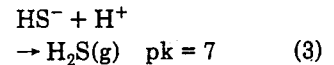


Figure 2. Foundry materials balance.

The calcium sulfide in the slag may release sulfide into solution in the treatment process water. This sulfide will remain in solution at high pH. However, in the neutral to acidic pH range, bisulfide (HS^-) is converted to hydrogen sulfide gas (Equation 3).

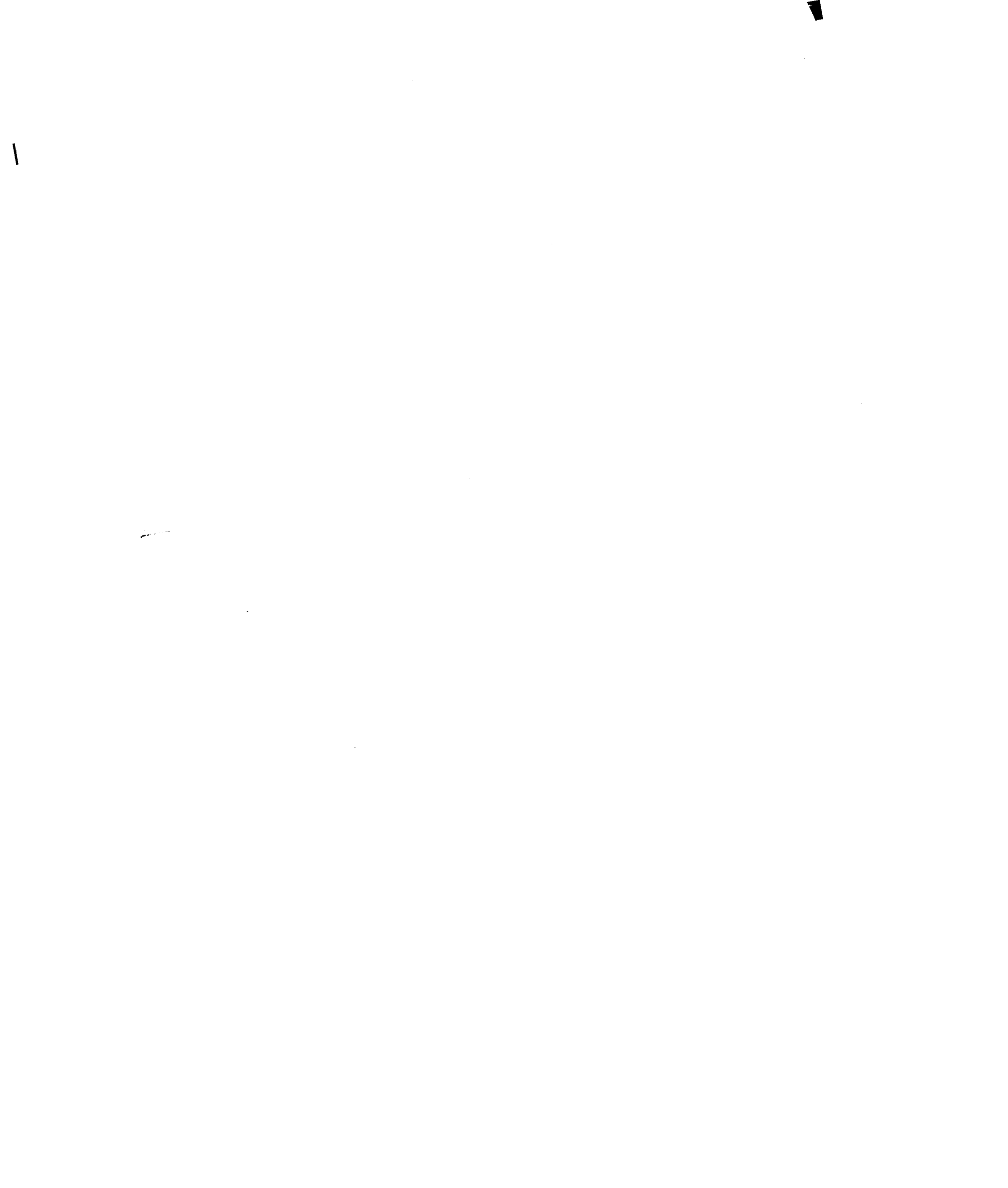


During typical treatment operations, the alkaline nature of the calcium carbide desulfurization slag prevents the pH from dropping to a point where hydrogen sulfide gas is formed. However, the treatment water contains bisulfide, and therefore has the potential for releasing H_2S if the wastewater is neutralized in a settling pond or wastewater treatment plant before the sulfide has been adequately diluted.

Calcium carbide desulfurization slag has a distinctive odor. Since pure acetylene is odorless, the odor must be produced by other trace constituents in the off-gases. A calcium carbide desulfurization slag sample from one ductile foundry was treated with water at a 1:1 solid-to-liquid ratio and the gas collected in a Tedlar bag for analysis by GC-MS. Several trace gases were identified:

- Arsine
- Divinyl sulfide ($\text{CH}_2=\text{CH})_2\text{S}$
- Ethanethiol (ethyl mercaptan)
- Methane
- Phosphine
- Carbon monoxide

The sum of measured volumes of these gases represented less than 1 percent of the total gas volume generated. However, the solubility of these gases in the reaction water was not accounted for. Any one of these gases (except



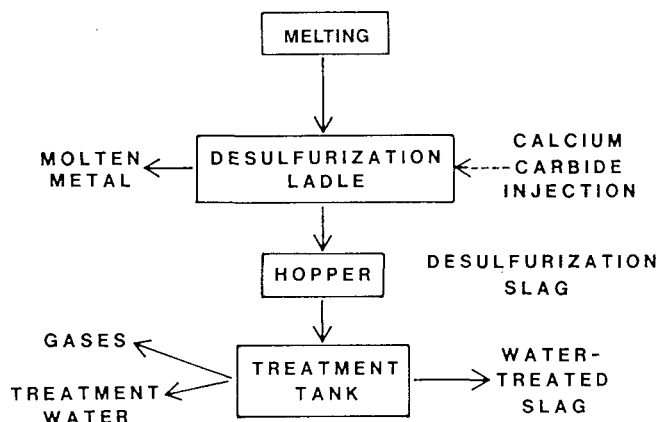


Figure 3. Process flow diagram.

methane and carbon monoxide), or a combination of them, could contribute to the observed odor. Furthermore, the reaction of the slag with water may give rise to potential health hazards if workers are exposed to excessive concentrations of these gases.

Field measurements were conducted at a foundry site where calcium carbide desulfurization slag was being treated with water. Arsine and/or phosphine and carbon monoxide were detected with Draeger gas detection tubes; and divinyl sulfide was identified by GC-MS from a grab sample in a gas sampling bottle. It is difficult to differentiate between arsine and phosphine using Draeger tubes. Sampling and analysis of off-gases using NIOSH methods P & CAM 265 and 216 showed that these substances, if present, were below the detection limits of these methods.

All three gases are of particular concern for human health reasons. The TLV (8-hour average) for carbon monoxide is 5.5 mg/m³, and the National Ambient Air Quality Standard (NAAQS) is 10 mg/m³. No standard for divinyl sulfide has been established in the United States. However, in the Soviet Union, where toxicological research on laboratory animals indicates that divinyl sulfide is a central nervous system depressant,⁴ a maximum allowable concentration (MAC) of 0.2 mg/m³ has been recommended.⁵

Regulatory Framework

Solid wastes can be classified as hazardous under the federal Resource Conservation and Recovery Act (RCRA) as either "listed" or "characteristic" wastes. One of the characteristics of a hazardous waste, as defined under 40 CFR 261.23, is reactivity. Calcium carbide desulfurization slag generated at ductile iron foundries may be

considered hazardous by this definition. Specifically, the calcium carbide slag reacts with water to form acetylene gas which may give rise to explosive mixtures as defined in 40 CFR 261.23(3). Also, with a neutral to acidic pH value, the calcium carbide desulfurization slag may emit hydrogen sulfide gas, which may result in its definition as hazardous under 40 CFR 261.23 (5). Other gases, which are potentially toxic at high concentrations, may also be generated during treatment of the slag (40 CFR 261.23 (4)). For these reasons, analysis and treatment of this type of waste is of great concern to the ductile iron foundry industry.

The ductile iron foundry industry has performed substantial studies and completed development work on each of the previously mentioned waste management options. A discussion of the results of that work follows.

Reduce/Alter Product Requirements

Like most specifications for products, the requirements for ductile iron have been developed with time and experience. The key property that differentiates grey iron from ductile iron is the sulfur content. There is a large body of information that relates the sulfur content of cast iron to the physical properties. Individual manufacturers of products have also researched the properties needed for their products, and have established specifications for sulfur content and other related properties so that product requirements are met.

However, often the material specifications for products have been established not on the needs for the product but on what the state-of-the-art technology is capable of producing. When this happens, a particular technology is actually being prescribed in a left-handed sort of way.

Some companies have found that they need to go back to square one and reassess the needs of the product to determine whether, for example, the sulfur content they have specified is too restrictive. Some companies have found that the product requirements can be adjusted without sacrificing the utility or the durability of the product.

What does this mean for calcium carbide desulfurization? It means that, if a higher sulfur content is acceptable, the foundry will not have to go to the far end of what the calcium carbide desulfurization treatment process will produce. Instead of having to add a 20 or 30 percent excess calcium carbide to the molten metal to ensure complete desulfurization, a lower dose could be used, resulting in far less unspent calcium carbide in the waste; therefore, the wastes may not be classified as reactive hazardous waste.

This is not a purely hypothetical option, but exists in reality within the foundry industry. Not all ductile iron foundries that employ calcium carbide desulfurization generate reactive hazardous waste. Whether the differences are due to more or less stringent product requirements cannot be determined for certain. The quality of the charge metal purchased and the design of the desulfurization process itself also affect waste characteristics. But it is clear that if large excesses of the calcium carbide reagent are not needed, and if the desulfurizing process equipment is efficient, the resulting calcium carbide desulfurization slag will be far less reactive, if not nonreactive.

Alter Raw Materials

Here, the ductile iron foundry industry has two basic options. The first is to eliminate the generation of the reactive desulfurization slag by substituting calcium carbide with some other material or materials. A few large foundry companies have made major advancements in new desulfurization technologies over the past two years. One such process involves the use of a mixture of calcium oxide, calcium fluoride, and two other materials. Their largest operating ductile foundry has completely converted to this process. The foundry reports that, not only is the product quality satisfactory, but the plant has eliminated the generation of a major problem hazardous waste, and the economics of the process are actually better than calcium carbide desulfurization. The process this company developed is proprietary and will likely be patented.

A second major option is to alter the charge metal by purchasing only scrap



that contains low sulfur content in the first place. This method is commonly used by steel foundries, since the products they manufacture and the processes they use generally require a higher grade of scrap with lower sulfur content. The purchase of high grade low sulfur scrap may or may not, however, work for production of high quality ductile iron. Even if it will work, the supply of high quality scrap varies and the economics may favor other options.

Improve Process Control

Since the unspent calcium carbide (i.e., the calcium carbide that is not used in the desulfurization process) is what causes the slag to be classified as reactive, a logical method of eliminating the hazardous characteristic would be to control the process better in order

to completely react the calcium carbide with the sulfur in the metal.

The problems here are twofold. First, the amount of sulfur in the scrap metal varies widely, so the metallurgist never knows exactly what dose is needed to just use up the calcium carbide. The second problem is that there is some inherent inefficiency in contacting the sulfur with the calcium carbide, and some metallurgists contend that an overdose will always be necessary, even if one could predict stoichiometrically exactly how much calcium carbide was needed to reach a desired sulfur content.

Typically, when a foundry begins using calcium carbide for desulfurization, the level of unspent calcium carbide in the slag is very high. This level decreases with time and experience, but often not to a level low enough so the

waste could be considered nonreactive. Recent innovation in process control for calcium carbide defulfurization include methods of introducing the material as well as forms of the material itself. The most common form of calcium carbide used is coarse granules. Some companies have experimented with very fine granules, coated granules, and solid rods made of calcium carbide in an effort to control the physics of the reaction more closely. Because there is no established EPA test procedure for some of the reactivity criteria that come into play with this waste, it is hard to claim clear success, but at least two calcium carbide manufacturers appear to have come up with important developments for this basic option.

Recycle to the Original Manufacturing Process

Often, calcium carbide desulfurization slag will contain from 10 percent to 50 percent metal. Because the slagging operations involve raking molten materials off a ladle of 3,000°F metal, it is common to find fairly high metal content in the slag. Sometimes, the metal comes in the form of large blocks or "pigs" of metal. Other times, it comes in the form of small granules of metal included in slag particles.

Several foundries have recognized for some time that there is a great deal of valuable material being wasted, and have sorted through desulfurization slag to reclaim chunks of metal for return to the melting furnaces. Several foundries have also experimented with recharging of the entire mass of the slag back into the melting furnaces.

When this is done, the calcium hydroxide is included in melting furnace slag, which is nonhazardous. Unspent calcium carbide is either used or oxidized in the melting furnace. However, little testing has been done to determine where the sulfur actually goes. Most of it may be included in the slag, but it may also be emitted to the air as sulfur dioxide, or, for foundries with wet emission control systems, it may be dissolved in the water.

Foundries which have tested this method have found that, with good control and metering of the recycle, the sulfur does not seem to concentrate in the metal, so the first hurdle—that of producing quality products—looks manageable.

Before, going forward with this option, a foundry needs to know the environmental effects on all media for this recycling operation. It needs to know what additional contaminants are being placed into the air, into the water,

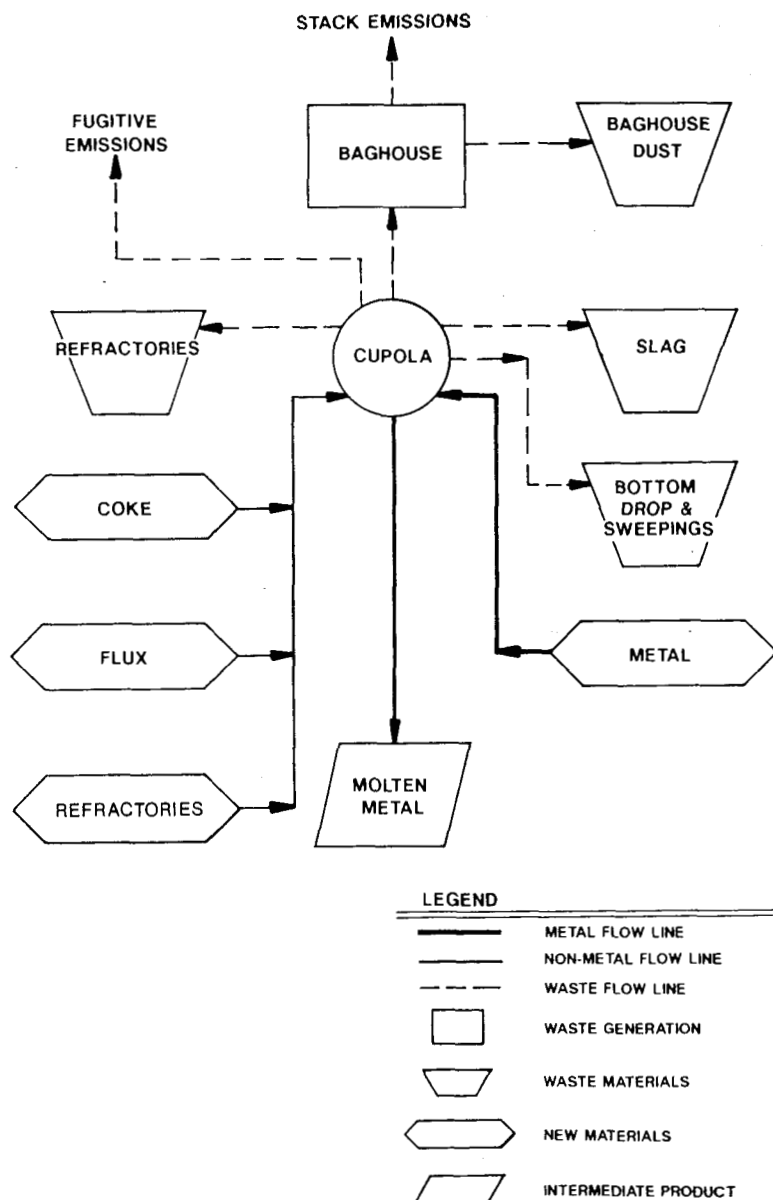


Figure 4. Foundry melt process schematic.



and into wastes from the process. But, given that those things are known and turn out favorable for the recycling, other major hurdles are the logistics of the recharge and regulatory constraints.

Recycle/Beneficially Reuse In Other Processes

Because the calcium carbide desulfurization slag contains lime, some foundries have determined that it can be useful in dealing with other problems that they may have. Since some foundries generate melt emission control residuals (e.g., furnace dust) that are classified as EP-toxic due to lead and cadmium leaching, they have found that by blending calcium carbide desulfurization slag with the melt emission control residuals in proper doses, the mixture is often non-EP-toxic. Because the majority of this treatment effect is accomplished through the lime content of the slag, one must be concerned about overdosing, since raising the pH of the furnace dust too high (above about pH 11.0) will cause lead to leach out. (Lead leaches at both low and high pHs.) RMT has experimented with treatment substances that, when mixed with calcium carbide desulfurization slag, will cause melt emission control residuals to be rendered non-EP-toxic, and will also ensure that the treated waste does not cause problems when disposed in a nonacidic environment.

Treatment

We have seen that the state-of-the-art methods for spraying or immersing the desulfurization slag in water have the potential to cause difficult air emissions and industrial hygiene problems. Several foundry companies and research groups have evaluated three different basic types of reactors for treatment of calcium carbide desulfurization slag.

The first, a reactor system involving immersion of the slag in water, is really a more controlled version of the methods commonly used by foundries at this time. The British Cast Iron Research Association has done work on these types of reactors over the past 10 years, and has developed prototypes for systems to introduce the slag into the water.

Some groups experimenting with these types of processes have experienced problems with gas control and fires or explosions. Since the latent heat from the desulfurization slag is slow to dissipate, potentially explosive conditions can develop where the per-

sonnel operating the treatment systems simply do not wait long enough to pay close enough attention to the condition of the slag before introducing it to the treatment systems. The prototype systems that have been suggested and tried deal with quantities of desulfurization slag, usually less than 200 pounds per batch, and require trained and knowledgeable people to operate. The foundry industry has generally shied away from water-based reactors for the desulfurization slag based on inherent problems with process control and dependency on personnel.

A second major type of reactor involves thermal destruction of the calcium carbide. At about 1,500°F, both calcium carbide and acetylene are thermally oxidized. Therefore, a system such as a rotary kiln could be used for thermal destruction of the reactivity characteristics. The additional benefit of thermal destruction is that it will also effectively deal with potential sulfide reactivity problems. Large chunks of metals often included in the desulfurization slag will tend to be a problem for many types of thermal units. Concern over air emissions and cost are other hurdles to the use of thermal systems for calcium carbide desulfurization slag.

Some efforts have been made to use the latent heat of the slag (the slag generally runs from 2,600 to 2,900°F when it is generated) by introducing a small flow of oxygen into the very hot slag. Little serious experimentation has been done for this method, since the system again involves a process that is different than what has been used in the past

and would appear to be personnel-dependent.

A third treatment method involves chemical reaction of the calcium carbide, the acetylene, the other potential off-gases, and the sulfide through use of strong oxidizing agents, such as potassium permanganate and hydrogen peroxide. These chemicals have been shown to be effective in reducing off-gases and in eliminating sulfide reactivity when introduced to the water that is used to treat the slag. However, the chemical doses for achieving all of those goals are very high, and full-scale systems would be very costly.

Improve Existing Treatment Methods

Some improvements that have been made to the crude methods normally used by foundries to treat reactive calcium carbide desulfurization slag include treatment of the waste in a tank rather than in a waste pile. The tanks, generally constructed with three vertical sides and a ramped floor on the fourth side, first involved placing the waste and spraying water into it. Later versions have involved deeper tanks with flat floors that will allow placing hoppers of slag in the bottom of the tanks and immersing them in water by a combination of spraying and flooding. Experiments have shown that, if the slag can be rapidly covered by water, as little as one foot of water over the top of the slag will act as a scrubber; and many of the gases, including acetylene, arsine, and phosphine, will largely be dissolved in the water. When chemical oxidants such as potassium per-

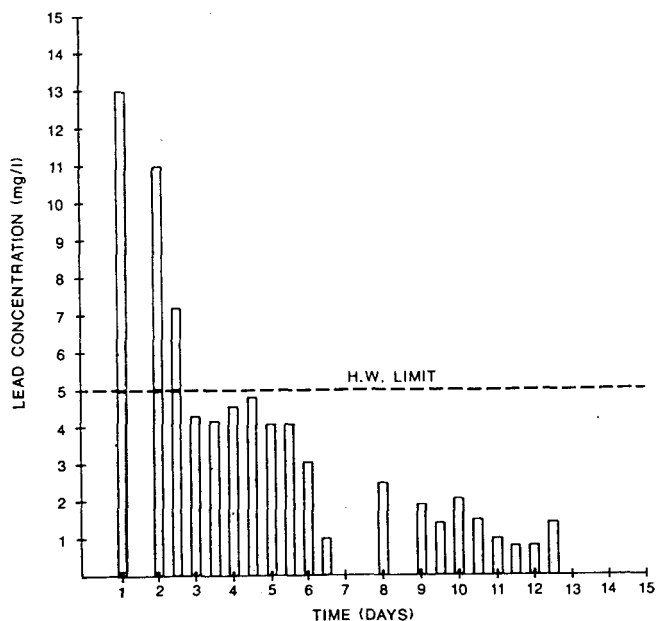


Figure 5. Foundry charge modification EP toxicity test results.



manganate or hydrogen peroxide are added to the water, the air pollution control effectiveness seems to increase.

However, the foundry must be concerned about dissolving large quantities of flammable and toxic gases as well as sulfides, since introducing this water to the plant's wastewater treatment system or to the sanitary sewer could cause the gases to be liberated again at some other point.

Also, there is serious question as to whether such a system would be capable of obtaining a RCRA Part B Permit to operate without formal air emission control systems. These open tank systems are designed to be crude but effective. When one begins to try to collect flammable and toxic gases over such open tanks and to allow access of fork lift trucks to deliver and retrieve hoppers of slag, the logic of the system falls apart very quickly and one returns to the reactor concept or other options.

Summary of Options

The best options for calcium carbide desulfurization slag management appear to lie in altering the raw materials, improving the process control, and recycling to the original manufacturing processes, assuming the product requirements cannot be modified enough to eliminate the generation of reactive desulfurization slag using calcium carbide. Several foundries and suppliers have made major advancements in each of these options, and the next two or three years will tell which of the options becomes most popular.

Melt Emission Control Residuals

Process Description

The production of iron castings requires that the metal be in a molten state so that it can be poured into the open cavity of the mold to produce the desired shape of the casting. Foundries which produce grey iron castings use one of the following three different processes to melt the grey iron:

- Cupola
- Electric arc furnace
- Induction furnace

The Clean Air Act set standards for the discharge of emissions into the atmosphere. Many foundries have been required to install air pollution control equipment over their melting operations to come into compliance with these regulations. Foundries typically use either a dry baghouse or some form of wet scrubber system (e.g., wet cap,

venturi, etc.) to collect the particulates for the melting operation.

A materials flow diagram for the melting operation within a typical foundry (with cupola melting) is illustrated in Figure 4. As illustrated in this figure, new materials into the melting operation include scrap metal, fluxes, coke (source of fuel for the cupola), and refractory material. Outgoing wastes generated by the process include spent refractories, slag, bottom drop and sweepings (for cupola operations), and either baghouse dust or a wet sludge depending on the type of emission control system. Typical pouring temperatures for grey irons range anywhere from 2,040°F to 2,700°F.

Waste Characteristics

Of all the waste generated by this process, the one that has been shown to be hazardous in some cases is the emission control residuals collected by the air pollution equipment. Whether or not the emission control residual is hazardous is largely a function of the incoming quality of the metal which is charged into the furnace. The inflow of tramp metals into the furnace from other new materials, such as coke or flux, is generally small in comparison to the contribution of such metals from the incoming scrap. Numerous "tramp" metals or minor constituent metals contained in the scrap which is charged into the furnace include copper, nickel, chromium, molybdenum, tin, aluminum, and lead. In general, the higher grades of scrap exhibit lower concentrations of these metals, while the lower grades of scrap exhibit higher concentrations of the tramp metals.

What grade of scrap is used by a given foundry is largely dictated by the quality of the casting being produced. For example, foundries which are producing counterweights for heavy machinery tend to use a much lower grade scrap than those foundries which are producing high grade industrial cast iron valves.

The reason the emission control residuals have sometimes exceeded EP toxicity hazardous waste limits for lead is because the melting point of grey iron is approximately 2,700°F, where the melting point for lead is only about 620°F. As the metal is melted, the lead will tend to volatilize and concentrate in the residual solid materials collected by either the baghouse or wet dust collection emission control system.

In a study conducted by the American Foundrymen's Society in conjunction with the University of Wisconsin and EPA,⁶ leaching tests were conducted on cupola emission control dusts and sludges from 21 different foundries. The results of this study indicated that 9 out of the 21 foundries generated emission control residuals which would be considered as a hazardous waste on the basis of EP toxicity for lead. Two other foundries generated emission control residuals which would be classified as hazardous on the basis of EP toxicity for cadmium. The range of lead concentrations in the EP toxicity test for the 21 foundries ranged from less than 0.6 mg/L to 130 mg/L. The mean lead concentration for the EP Toxicity test was 12.8 mg/L and the median was 0.8 mg/L. This type of variation in the characteristics of emission control sludge from different foundries is indicative of the variability of the incoming scrap lead content.

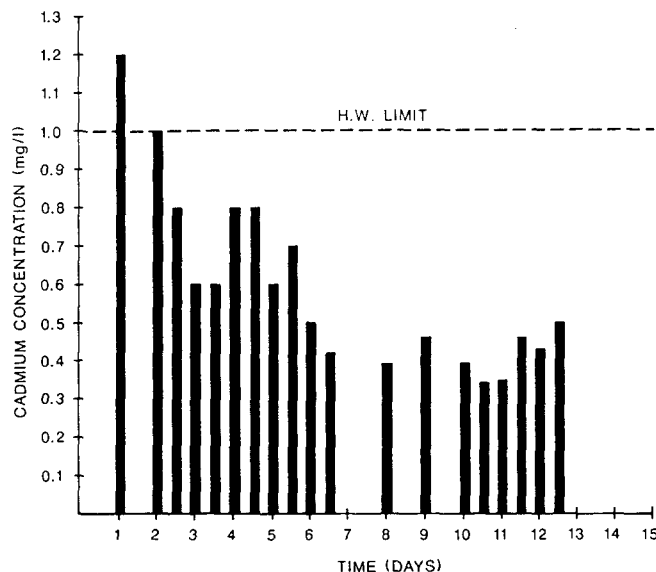


Figure 6. Foundry charge modification EP toxicity test results.



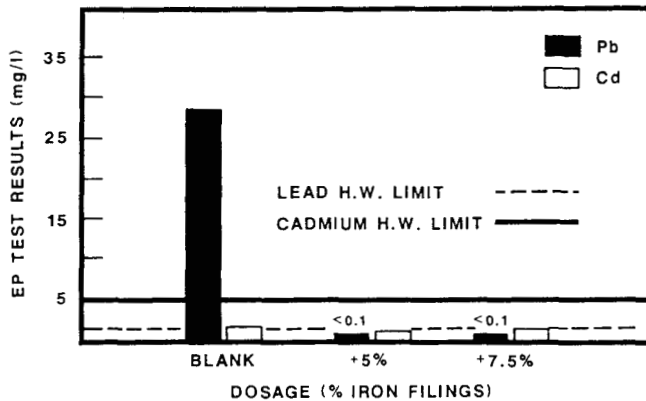


Figure 7. Lead and cadmium leachate concentrations from cupola emission control sludge treated with metallic iron.

Regulatory Framework

At this time, EPA has not "listed" emission control residuals from grey iron foundries as hazardous. It is unlikely that these wastes meet the characteristic of ignitability, corrosivity, or reactivity. However, it has been demonstrated in previous research that certain foundries do generate emission control residuals which meet the characteristics of EP toxicity. Those wastes which are classified as a hazardous waste on the basis of the EP toxicity criteria, must be managed according to the hazardous waste management regulations promulgated under RCRA.

Reduce/Alter Product Requirements

The key issue in reducing or altering product requirements relative to minimizing the generation of EP-toxic emission control residuals is that the chief source of contamination, namely lead and/or cadmium, is not required in the production of grey iron. These materials are in fact "tramp metals" that are present in the scrap materials which are being recycled by the foundry industry to produce their castings. In fact, elevated levels of lead in grey iron can cause negative structural affects on the cast iron. Therefore, while it would be fundamentally sound to attempt to reduce or alter lead content product requirements, in reality, lead is not even required for casting production. Therefore, this management option has little usefulness in the minimization of waste generation.

Alter Raw Materials

A predominant source of lead that is contained in the emission control residuals from foundry melting operations, is contained within the scrap ma-

terial itself. It is true that other new materials such as coke and certain fluxes may also be sources of incoming lead. However, generally these sources contain much lower quantities of lead than does the incoming scrap.

The first step in altering raw materials to successfully minimize the generation of hazardous wastes from emission control residuals, is to identify the incoming source or sources of lead and cadmium. Although the incoming scrap is generally the primary source of lead, all incoming sources should be evaluated on a preliminary basis to verify this assumption. It has been the authors' experience that, in some cases, even the soil that has adhered to the scrap coming from the scrap yard may be a source of lead. In one case, this soil material was subjected to the EP toxicity test by the author and found to exceed the hazardous waste criterion for lead in the EP toxicity test. To eliminate this source, the foundry in question placed pallets at the base of the charge bins and had to

manually clean incoming loads of dirty scrap to eliminate this contamination source.

Once the sources of lead have been identified, the next basic step is to make purchasing arrangements to acquire alternative sources of new materials which contain lower concentrations of lead and cadmium. Once these sources have been obtained, a charge modification program is developed and implemented using the new sources of raw materials. It is advisable to first purge the emission control system of residual waste material prior to implementing the charge modification program. In general, carryover from existing waste in the emission control system can mask the true results of the charge modification program unless proper precautions have been taken to purge the system.

Figure 5 and Figure 6 illustrate a reduction in lead and cadmium concentrations from the EP toxicity test on emission control residuals collected during a two-week charge modification program at a large foundry. In Figure 5, a drastic reduction in lead concentration with time can be seen over the first two or three days of the charge modification program. This is typical of other charge modification programs which have been conducted, assuming adequate purging of the system has been performed prior to the charge modification program. According to Figure 6, the reduction in cadmium concentration with time does not show the same drastic reduction experienced with lead. However, the charge modification program for this foundry was also successful in reducing cadmium levels to below the hazardous waste limit in the EP toxicity test.

Altering raw materials has been

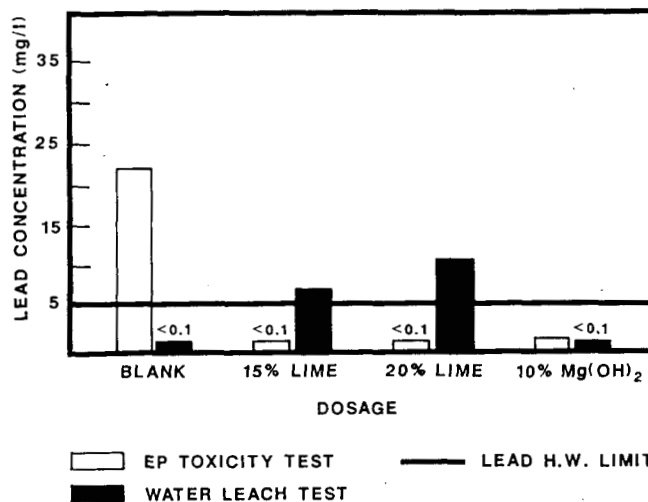


Figure 8. Lead leachate concentrations from brass foundry solid waste treated with lime or magnesium hydroxide.



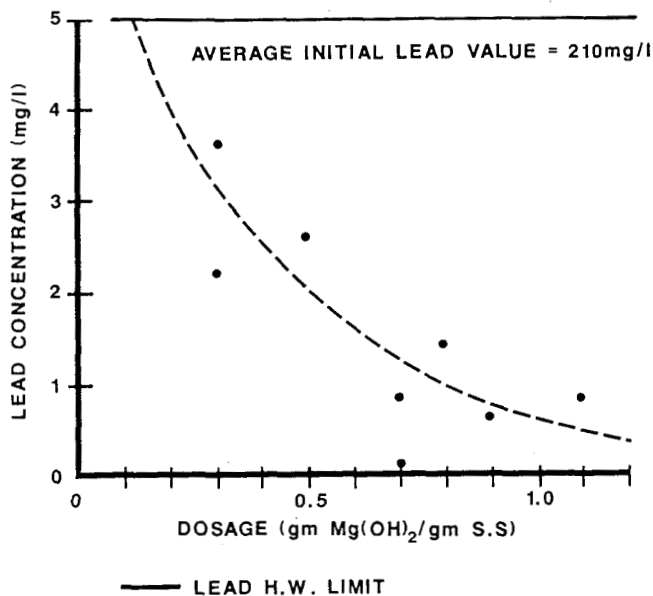


Figure 9. Lead leachate concentrations from cupola emission control sludge from wastewater treated with magnesium hydroxide.

shown to be a successful way to minimize the generation of hazardous emission control residuals in the foundry industry. However, while charge modification programs have been successful, it is generally not economical for a foundry to continue to melt the higher grade scrap and still remain competitive. In many cases, foundries have conducted successful charge modifications only to realize that the economics of the higher grade scrap preclude its continued use in the foundry; therefore, the charge modification program is abandoned.

Improved Process Control

The reason hazardous wastes are sometimes generated by the foundry industry is because airborne particulates, which prior to the Clean Air Act would have been released to the atmosphere, are now required to be captured through air pollution control equipment. Some foundries have chosen to switch to induction melting furnaces to melt grey iron. One of the advantages of the electric induction melting furnace is that, in general, air pollution control equipment is not necessary for the emissions from this operation. This assumes, however, that relatively clean materials, (e.g., clean metal scrap) can be used in the melting process. Obviously, the elimination of the need for collecting emissions over the melting operation eliminates the generation of air pollution control residuals. When this can be done, it is an effective way to minimize waste generation.

Recycle to the Original Manufacturing Process

The recharging of the emission control residuals is a common practice in the steel-making industry.⁷ This has been done in some cases to supplement alloy materials which are added to the melting operation. The practice of recharging foundry emission control residuals has been investigated by some foundries with varying degrees of success. Materials handling and the metallurgical considerations will definitely impact the feasibility of such an alternative. This method for hazardous waste elimination is generally not used by a majority of foundries.

Recycle/Beneficially Reuse

Another reuse alternative would be to reclaim the lead and cadmium which

have concentrated in the emission control residuals. The feasibility of this reclamation outside of the original production process largely depends on the following:

- Concentration of metals within the emission control residual.
- Cost of recovering the metals.
- Market price for the product.

While recycling of these materials outside the original production process has been used in the nonferrous foundry industry (i.e., brass foundry), its application within grey iron foundries is extremely limited.

Treatment. Various chemical means have been used to reduce the leaching potential of toxic metals. The four types of chemical treatment applicable to emission control residual waste which are EP-toxic for either lead or cadmium include the following:

- Precipitation
- Absorption
- Chemical reduction
- pH control

This paper will highlight two of the four chemical treatment methods which have been used quite extensively in the foundry industry.

Chemical reduction. Chemical treatment using metallic iron added to hazardous wastes has proved effective. Figure 7 shows that at a dosage of 5 percent (by weight) iron filings, lead leaching from a cupola emission control sludge was reduced from 28.6 mg/L to less than 0.1 mg/L.⁸ At a dosage of 7.5 percent (by weight) iron filings did not significantly increase treatment effectiveness. Cadmium leaching was virtually unaffected by treatment at these dosages. The mechanism proposed to explain the observed decrease in lead

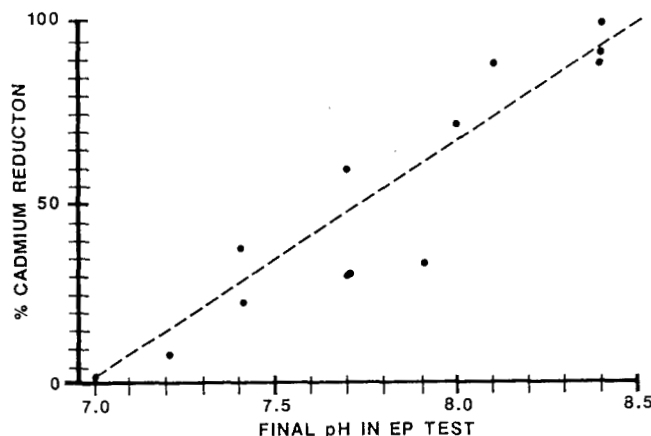


Figure 10. Percent reduction in cadmium leachate concentration vs. final pH in EP toxicity tests on cupola emission control sludge from wastewater treated with magnesium hydroxide.



leaching is a redox reaction whereby metallic iron reduces divalent lead to metallic lead.⁸

Evidence for a redox mechanism is found in EP toxicity test results. The addition of iron filings resulted in a final pH in the EP toxicity test slightly higher than untreated samples, indicating that the hydrogen ion may have been neutralized by chemical reduction.

Some success has been achieved using metallic iron to treat wastewater directly. An advantage of using metallic iron instead of iron hydroxide is that less sludge volume is generated. The presence of oxidizing agents in the wastewater can limit the effectiveness of metallic iron treatment.

pH control of solubility. Another method of chemical treatment involves the pH of the waste so metals will not be soluble when exposed to acidic conditions. Since the solubility of many metals, including lead and cadmium, is pH dependent, waste classified as EP-toxic can sometimes be rendered non-hazardous by adding a material that will maintain a neutral or slightly alkaline pH during leaching with an acidic liquid, so the metals will not dissolve.

One of the simplest and most cost-effective additives for this purpose is slaked lime ($\text{Ca}(\text{OH})_2$). It is well-known that lime is effective in precipitating lead and cadmium as insoluble hydroxides. However, excess dosages of lime can result in pH values high enough to redissolve lead. The addition of 15 percent by weight lime to brass foundry solid waste reduced lead leaching from 22 mg/L to <0.1 mg/L (final pH in EP toxicity test of 7.8). However, when a water leaching test with no acid added was used, the pH was 11.6 and lead leached at 7.2 mg/L (Figure 8). This can pose a limitation to the use of lime because most leaching at disposal sites for treated foundry wastes is likely to be under leaching conditions with close to neutral pH. Similar results were presented by Nagle *et al.*⁷

Because of the problem of dissolving lead at higher pH values, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) is a more desirable material for pH control than lime.⁹ Magnesium hydroxide is buffered at a maximum pH of approximately 10.5; therefore, the potential for dissolving lead at higher pH is minimal even if an excess of $\text{Mg}(\text{OH})_2$ is added. Adding 10 percent $\text{Mg}(\text{OH})_2$ by weight as a 55 percent slurry to the same brass solid waste reduced lead leaching to 0.3 mg/L (final pH of 8.5 in EP toxicity test). Less than 0.1 mg/L of lead leached in the water leach test (Figure 8).

Magnesium hydroxide slurry has been tested on wastewaters from three

foundry cupola emission control systems. Doses ranging from 0.3 to 111 grams of $\text{Mg}(\text{OH})_2$ per gram of suspended solids resulted in a reduction in lead leaching from the resulting sludge to well below the hazardous waste limits (Figure 9). Reduction of cadmium leaching is dependent on the final pH of the leaching medium in the EP Toxicity test. Data for the $\text{Mg}(\text{OH})_2$ treatment tests indicate that a final pH of eight or more is required for significant reduction in cadmium leaching (Figure 10).

Although magnesium hydroxide is more expensive than lime, it is preferable to lime because it has the benefit of easier pH control, thereby reducing process control requirements. The results of testing show that, while in many cases adding lime or magnesium hydroxide is effective in rendering a hazardous waste nonhazardous, knowledge of the leaching characteristics of the waste material and the treated waste mixture is important to ensure effective treatment and proper disposal. Also, while pH control of solubility appears to be an effective treatment method in the short-term, long-term characteristics of the chemical additive should be evaluated to ensure that the waste will remain nonhazardous over time.

Summary of Options

The best option for emission control residual management appears to be either altering the raw materials (i.e., charge modification) or the use of electric induction melting without air pollution control equipment. When these options are not feasible from an economic standpoint, the only remaining option, other than hazardous waste disposal, is to treat the waste using an appropriate form of chemical treatment.

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