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**SUMMARY OF DATA ANALYSES AND EXPERIMENTAL DESIGN
FOR INVESTIGATION OF IRON CHEMISTRY
IN LEAD-CONTAMINATED MATERIALS**

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ABSTRACT

This effort summarizes and analyzes existing data and equilibrium chemical interactions between the metals in wastes and the iron filings used to stabilize the waste. Applications data and basic chemical equilibrium data have been compiled and analyzed to improve the understanding of the reaction(s), identify data gaps and issues, and help suggest the appropriate experimentation. Additionally, other types of treatment have been evaluated for their ability to sequester lead and remediate foundry sand.

Literature and industry contacts served as sources. The main emphasis has been on lead (Pb) chemistry in association with iron (Fe). The characteristics, use, and reuse practices for sand as a foundry mold constituent have been studied. Data collected for the study have identified an emphasis in the foundry industry on process changes to eliminate the source of lead in the foundry sand, maximize sand reuse within the foundry, and identify beneficial reuse options where possible. These process changes, although not directly in the scope of this project, can alter the characteristics or volume of the foundry sand being treated. Therefore, the waste minimization efforts for foundry sand are summarized.

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1.0 INTRODUCTION

1.1 BACKGROUND

Lead-contaminated foundry mold sand wastes generated by bronze and brass foundries and product manufacturers have been treated by addition of metallic iron filings such that the waste passes the Toxicity Characteristic Leaching Procedure (TCLP) analytical method (40 CFR Part 261, Appendix II). The American Foundrymen's Society (AFS) has published several studies which illustrate this treatment. However, the studies do not provide information on the reactions involved or the long-term effectiveness of the treatment. It may be that the iron filings merely bind the lead temporarily and thus "mask" the TCLP analytical method. If so, further chemical changes in the environment could cause lead to be released from the mold sand to the environment. The long-term efficacy of this lead treatment approach is of concern and needs to be addressed.

1.2 SCOPE OF STUDY

The purpose of this effort is to summarize and analyze existing data and equilibrium chemical interactions between the metals in these wastes and the iron filings used to stabilize the waste. Applications data and basic chemical equilibrium data were compiled and analyzed to improve the understanding of the reaction(s), identify data gaps and issues, and help suggest the appropriate experimentation. Additionally, other types of treatment were evaluated for their ability to immobilize lead and remediate foundry sand.

Information in this report is developed from a review of foundry sand uses and treatment methods. Both literature and industry contacts were used as sources. The main emphasis was on lead (Pb) chemistry in association with iron (Fe). Efforts also were made to identify other potentially reactive materials. Thermodynamic analysis was performed to describe possible reaction mechanisms involved and the potential long-term stability of the reaction products when released into the environment.

The characteristics, use, and reuse practices for sand as a constituent in foundry molds are outlined to help define the waste conditions. Efforts to collect data for the study also identified an emphasis in the foundry industry on process changes to (1) eliminate the source of lead in the foundry sand, (2) maximize sand reuse within the foundry, and (3) identify beneficial reuse options where possible. These process changes do not fit directly within the scope of this project. However, these changes can alter the characteristics or volume of the foundry sand being treated. Therefore, waste minimization efforts for foundry sand are summarized.

The significant volume of literature on the use of iron filings to reduce Pb solubility from contaminated sands, waste materials, and earthen materials has not been summarized as an aggregation of knowledge. Data are available in Joint Army, Navy, Air Force (JANAF) thermochemical data tables, literature sources, and commercial thermodynamic calculation programs to describe the reaction mechanisms and indicate the long-term stability of the reaction products. Where data are

unavailable or difficult to interpret, studies of the equilibrium chemistry of systems containing metal contaminants and iron were applied to improve understanding of the reaction mechanism(s).

Description of brass and bronze foundry sand characteristics and analysis of the chemistry of possible treatment options allowed the development of proposed experiments to confirm the reaction mechanism(s) and to evaluate the long-term stability of the products.

2.0 CHARACTERISTICS AND USE OF FOUNDRY SAND

This section summarizes the types of sand and binders used in the casting industry and past, current, and future methods for cleaning and reusing foundry sand. The main emphasis is on defining the properties of the waste stream to be treated by iron addition or other methods to reduce lead solubility.

2.1 GENERAL CHARACTERISTICS AND APPLICATION OF FOUNDRY SAND

Foundries produce metal shapes by pouring molten metal into molds. Molds used in the foundries are typically made from sand. The sand grains in the molds are held together with additives called binders. After use, the external mold and internal core, if any, is physically removed by a shakeout process. Traditionally, the casting molds and cores for shapes were formed from various types of sand formed with clay-based binders. Current molding techniques often apply more complex binder systems such as silicates or organic resins made from phenolic-urethane polymers.

Sand used in the molds is mined from deposits that were formed by natural forces that resulted in the disintegration of rocks. In all, SiO_2 is the principal ingredient. Some sand deposits contain clay, which may be present in varying percentages, while other sand deposits are virtually pure SiO_2 . In the past, sands from the clay-containing deposits were used to make molds since the clay acted as a binder (Miske, 1992). These sands that were used "as mined" are referred to as "natural sands." Before 1900, nearly all metal casting molds produced in the United States were made from natural sands. One of the most commonly used types was Albany sand, which occurs along the Hudson River from the Adirondacks southward. That type of sand was the backbone of the industry until fairly recently. It was in common use, particularly in the east, until the 1950s and even 1960s.

"Synthetic sand" refers to molding sand that is mined as nearly pure silica then is compounded with clays such as bentonite and/or other ingredients. Use of "synthetic" sands is now nearly universal. This change occurred for several reasons. First, natural sands are difficult to control in operations because the "as-mined" ingredients (clay or otherwise) vary considerably. Synthetic (or compounded) sands can be controlled to provide the desired characteristics and molding sand is one of the most critical variables in foundry operations. By the close of the 19th century, in response to increased demand for castings, machine molding appeared increasing the demands for molds. As casting runs increased and specifications for surfaces and tolerances tightened, firmer control became essential. Given the vagaries of natural sand, foundrymen increasingly turned to synthetic sand systems. Supplies of pure sand were huge and mixes could be controlled and adjusted. Table 1 presents a comparison of the properties of various types of sands.

Silica sand (SiO_2) is used predominantly for green sand molding for economic reasons. Silica sand is characterized in terms of its origin, particle size, size distribution, and grain shape. Terms such as "lake" or "bank" sands refer to the nature of the sand outcropping where the sand is mined. The sand grain size is a calculated number based on a weighted percentage of the sand screen size distribution. Sands with a five-screen distribution are preferred to achieve good sand strength

TABLE 1. COMPARISONS OF FOUNDRY BASE SANDS

	Silica	Olivine	Chromite	Zircon	Zircon/Aluminum Silicate	Staurolite
Origin	USA	USA (Washington, N. Carolina)/ Norway	Republic of South Africa	USA Australia	USA (Florida)	USA (Florida)
Color	White/light brown	Greenish-gray	Black	White/brown	Salt & pepper	Dark brown
Hardness (MOHS)	6.0 - 7.0	6.5 - 7.0	5.5 - 7.0	7.0 - 7.5	6.5 - 7.0	6.5 - 7.0
Dry Bulk Density (lb/ft ³)	85 - 100	100 - 125	155 - 165	160 - 185	155 - 168	143 - 146
Specific Gravity	2.2 - 2.6	3.2 - 3.6	4.3 - 4.5	4.4 - 4.7	3.2 - 4.0	3.1 - 3.8
Grain Shape	Angular/rounded	Angular	Angular	Rounded/angular	Rounded	Rounded
Grain Distribution	2-5 screens	3-4 screens	4-5 screens	2-3 screens	3 screens	3-4 screens
AFS Grain Fineness number ranges	25 - 180	40 - 160	50 - 90	95 - 160	Approx. 80	Approx. 70

Source: Adapted from report of AFS Molding & Core Aggregate Committee 80-j.

and compactability. Most brass and bronze foundries use a sand with an American Foundrymen's Society Grain Fineness Number (AFSGFN) between 60 and 90 to achieve an optimum balance between casting surface finish, mold permeability, and sand molding properties. Both round-grain and subangular-shaped sands are used. Round-grain sands generally promote sand strength properties and subangular lake sands tend to improve mold permeability.

Other specialty sands, such as olivine, zircon, or chromite sands are occasionally, but infrequently, used as a thin layer or "facing sand" at the casting surface when needs arise for modified thermal properties or improved surface finish. In a chromite faced mold, silica sand is still used as the mold backing to provide strength while remaining sufficiently permeable to allow heat and gases to escape. The surfaces that contact the hot metal are faced with chromite sand to resist the high temperatures and promote chilling of the molted metal. The proportion of chromite to silica sand depends on the foundry practices and the size and shape of the part being cast. The chromite sand content of a mold may be as high as 50 wt% or as low as 1 wt%, with a typically average of 2 to 15 wt% (Hwang et al., 1992).

One of the primary types of synthetic sands is referred to as "green sand." Green sands contain at least three ingredients, with clay, water, and SiO_2 being the primary ingredients. Other materials can be added to enhance the basic desired properties discussed above. Clay is the essential bonding addition and can consist of bentonites (montmorillonites), fireclays (kaolinites), or special clays. Other ingredients are commonly added, including cereals, pitch, seacoal, wood flour, silica flour, and iron oxide. With the proliferation of high-speed automatic molding, even in many small job shops, the composition of synthetic sands became increasingly critical. Different types of metals, differing casting weights and configurations, and the requirements of the various mechanical systems all influenced composition.

Clays used in foundries, regardless of type, are hydrous alumina silicates, and their properties provide cohesion and plasticity in the green state and high strength when dried (Peters, 1993). Bentonites are the most useful clays for foundry work and occur naturally in two forms — sodium bentonite (Western) and calcium bentonite (Southern). Sodium bentonites swell strongly when mixed with water and the volume increases as much as 10 to 20 times. The main features of sodium bentonite clays in green sand are (1) high dry strength, which lowers the risk of erosion; (2) better tolerance of variations in water content than other types of clay; and (3) high resistance to burnout, which reduces clay consumption. Calcium bentonites do not swell or form gels when mixed with water. Their properties are improved substantially by chemical treatment with soda ash (sodium carbonate) to form sodium bentonite. The treatment process is called activation, and it changes the nonswelling bentonite to a swelling bentonite with properties approaching those of natural sodium bentonite. Soda-activated clays are used extensively through the ferrous and nonferrous foundry industries. They have high green strength, a wide moldability range, moderate dry strength, and a good resistance to scabbing and expansion defects.

A blend of clays often is used to achieve the desired sand properties. Clays are hydrous aluminosilicates. Western bentonite, Southern bentonite, and fireclay are the most common forms of foundry clays. Bentonite clays typically are at least 80% montmorillonite. Western bentonite contains monovalent sodium ions (Na^+) and thus is referred to as sodium bentonite. Western bentonite is used to prevent premature drying of the mold surface, to reduce sand expansion defects, and to reduce mold erosion during pouring that can lead to sand inclusions in the castings. Southern bentonite contains divalent calcium ions (Ca^{++}) and is referred to as calcium bentonite. Southern bentonite requires less water and mulling energy than Western bentonite and is used to reduce sand lumps during shakeout and to reduce hot tear defects in alloys having wide solidification ranges. Fireclay (kaolinite) requires more water and attention to mulling than bentonite clays, but occasionally is used because of low cost and the ability to withstand high temperature.

By the 1980s, machine molding had become considerably automated, with lines producing up to 400 molds per hour as much as 4 ft square, magnifying the importance of the green sand mix. The universal requirement for machine molding, especially when it is automated is a sand that exhibits consistent properties — green strength, compactability, dry strength, hot strength, permeability, refractoriness, flowability, collapsibility, etc. Each type of machine mold imposes its own sand requirements.

In the 20th century, alternatives to green sand molding proliferated, many being developed originally as coremaking processes. One was the Croning process, which was brought out of Germany after World War II and renamed the shell mold process. It involves sand and phenolic resin mixtures formed into shells and cured in heated metal patterns. The shells are then bolted or otherwise joined, backed by a medium such as sand or shot, and poured. The process excited great interest in the 1950s and 1960s, declined for a while, but seems to be regaining some popularity.

Today, more important are the chemically bonded, self-setting molding and coremaking processes, which involve both organic and inorganic chemicals. They harden the sand mixture at room temperature in coreboxes or in contact with patterns. A number of these processes require injection of a gas (sometimes toxic) into the sand mixture to bring about the chemical reaction.

Introduction of these types of sands precipitated the development of a whole new category of mixing and/or delivery systems. Most originally were slow-curing resins with long bench lives, but the systems available increasingly became reactive, thus speeding up the hardening process.

The effect of chemically bonded sands has been to permit significant increases in capacity in relatively small foundries in part because of the elimination of complex sand preparation equipment but sand reclamation can be a problem. The advantages and considerations associated with the various types of chemical binders are discussed in Table 2.

Binderless sands are another option. They require more handling than preparation. The expendable pattern casting process uses a polystyrene pattern that can be made automatically, like a diecasting. The pattern is placed in a box (flask) and surrounded by unbonded sand of the appropriate fineness for the casting. When the mold is poured, the polystyrene evaporates as the cavity fills with metal. The pattern is coated to produce a good surface and the resultant casting is similar to an investment casting in that it has no parting line. This process is finding growing acceptance today for both nonferrous and ferrous castings. Problems include surface finishing and the economics of pattern production when castings are complex and pattern parts must be glued together. Every casting requires a new pattern, but sand preparation economies compensate for much of that cost. Another binderless process is the vacuum process, although it is not widely used. It combines binderless sand, a sheet of plastic, and a flask designed to pull a vacuumized mold. Sand preparation is simple, but the costs of the plastic and the special flasks offset this cost. The process reduces machining and can produce excellent castings, especially when large and flat.

Core molds often use different binder mixtures than those used for the outside molds. These molds are usually chemical binders. Several types of coremaking include cold box, no-bake, hot box, warm box, shell, and core oil coremaking. Table 3 presents a summary of the various resin-based processes available.

"Cold box" is a generic term originally understood to mean the phenolic-urethane-amine process, although it has recently come to describe any core binder process that uses a gas or vaporization catalyst to cure resin-coated sand while it is in contact with a room temperature pattern. All cold box processes use the typical blow, gas, purge, and strip steps in the coremaking sequence, except that the silicate-CO₂ system does not include a purge cycle. Cold box binders provide a flowable sand mix that easily is blown into intricate shapes. Tooling can be of wood, metal, or plastic. The size of cores and molds produced in the cold box process is limited only by machine handling capacity. A gassing system is used to meter out a predetermined quantity of liquid, change it to a gas, combine it with a

**TABLE 2. SUMMARY OF CHEMICAL BINDER ADVANTAGES
AND CONSIDERATIONS**

Acid-Catalyzed No-Bakes

Furan	<p>Good strength development Excellent hot strength Color change during cure Various N₂ and H₂O levels Very sand sensitive 10- to 60-min strip 4-hr minimum pouroff Resin shelf life (silane degradation) Acid handling Slow through-cure</p>
Phenolic	<p>Zero to low N₂ content Good strength properties Color change during cure 15- to 60-min strip Sand sensitivity 4-hr minimum pouroff Strong acid catalyst required Slow through-cure</p>

Urethane No-Bakes

Alkyd oil	<p>Excellent stripping Least sensitive to control Water free Low N₂ No unpleasant fumes Wide strip time range Good through-cure Moderate unbaked hot strength 18- to 24-hr cure before pouroff (without baking) 15- to 140-min strip</p>
Phenolic	<p>30-sec to 2-hr strip Low sand sensitivity Excellent flowability 10-min pour-off Excellent through-cure Zero retention mixer Process layout Iron oxide for steel Release</p>

Inorganic No-Bakes

Sodium silicate	<p>Environmentally friendly Decreased cost Low sand sensitivity Low gas evolution Low water Slow cure characteristics Poor shakeout Wet reclamation low strength Humidity sensitive</p>
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**TABLE 2. SUMMARY OF CHEMICAL BINDER ADVANTAGES
AND CONSIDERATIONS (Continued)**

<u>Inorganic No-Bakes (continued)</u>	
Cement	Environmentally friendly Very low cost Non-sand sensitive Slow cure characteristics Poor shakeout and reclamation High cement and H ₂ O additions; release (rigid cure)
Aluminum Phosphate	Environmentally friendly Low sand sensitivity Low gas evolution Low water Good shakeout and reclamation Slow cure characteristics Low strength Humidity sensitive
<u>Vapor-Cured Systems</u>	
Furan/SO ₂	Fast cure Long bench life Good hot strength Color change during cure Good shakeout Material handling Closed system gassing Corrosive Sand sensitive Resin buildup on pattern
Phenolic urethane/amine	Very fast cure Low sand sensitivity High productivity Medium bench life Iron oxide for steel Closed system gassing
Sodium silicate/CO ₂	Environmentally friendly Low sand sensitivity Decreased cost Low gas evolution Nonhazardous gas Poor shakeout and reclamation Low strength Humidity sensitive

Source: Adapted from Peters, 1993.

carrier gas in the correct ratio, and deliver it to the core box for use. A scrubber system is used to prevent discharge of vapors into work areas or to the atmosphere outside the plant.

No-bake processes are designed around a continuous mixer that mixes binder with the sand, adds catalyst, and disperses the mixture into the corebox. A no-bake binder system begins to cure the instant it comes into contact with the catalyst. How fast it cures depends on (1) type of

TABLE 3. SUMMARY OF RESIN-BASED CORE BINDERS

Cold Box	No Bake	Heat-Activated
Phenolic/Urethane/Amine	Furan/Acid	Shell
Silicate/CO ₂	Phenolic/Acid	Core Oil
Furan/SO ₂	Phenolic/Ester	Phenolic Hot Box
Epoxy/SO ₂	Oil Urethane	Furan Hot Box
FRC/SO ₂	Silicate/Ester	Warm Box
Phenolic/SO ₂	Alumina Phosphate	Airset
Phenolic/Ester	Phenolic Urethane	
	Phenolic/Ester	

Source: Peters, 1993.

resin, (2) sand chemistry, (3) percent and type of catalyst, and (4) temperature. The sooner resin-bonded sand is formed after the resin and catalyst are mixed, the stronger and better core or mold it will make. Operating in the optimum temperature range of 75 to 85°F reduces the amount of catalyst use and may permit use of less resin, which in turn improves flowability and strength.

Hot box binders cure uniquely. After sand has been coated, it is blown into a heated corebox. The wet mix begins to cure as soon as it comes into contact with the hot pattern (typically 450 to 550°F). Warm box coremaking uses the same coating equipment, processing procedures, and production techniques as conventional phenolic hot box and furan. However, pattern temperatures typically range from 300 to 450°F. The shell process for coremaking consists of five steps: blow, invert, drain, cure, and strip. The shell resin-curing mechanism involves the transition from one type of solid plastic to another — thermoplastic to thermosetting. Core oil binder is used in combination with water-activated cereal to produce a sand mix that has green strength.

2.2 TYPICAL BRASS AND BRONZE FOUNDRY OPERATIONS

This section focuses more specifically on the sand molding materials and sand systems used by modern, high-production foundries producing leaded-brass and bronze castings. Typical sand molds are horizontally parted with a top half (cope) and a bottom half (drag). Sand cores are used to form internal passageways in the cast part. For economic reasons, most high-production brass and bronze foundries use automated green sand molding lines to produce molds at a rate of 200 to 300 molds per hour. Multiple cavity molds are typical, with four to eight castings per mold being common. As discussed above, variety of organic and inorganic chemical binders systems have emerged that can be used as alternatives to green sand molding (Miske, 1992; Peters, 1993). However, these binders have not found widespread acceptance in high-production brass and bronze foundries because of economic considerations and the relative difficulty in reclaiming the sand for reuse compared to the ease of reclaiming green sand.

Green sand as used in high-production casting is a synthetic sand mixture composed primarily of silica or other type of sand and includes water (typically 2 to 4 wt %) and clay (typically 5 to 8 wt %). The term "green sand" refers to the moisture in the sand rather than the color of the sand mixture, which typically becomes black as it is recycled. When this mixture is blended or "mulled," the water plasticizes or "tempers" the clay, which then acts as a bonding agent for the sand. The sand mixture may be compacted using automated molding equipment against a metal form

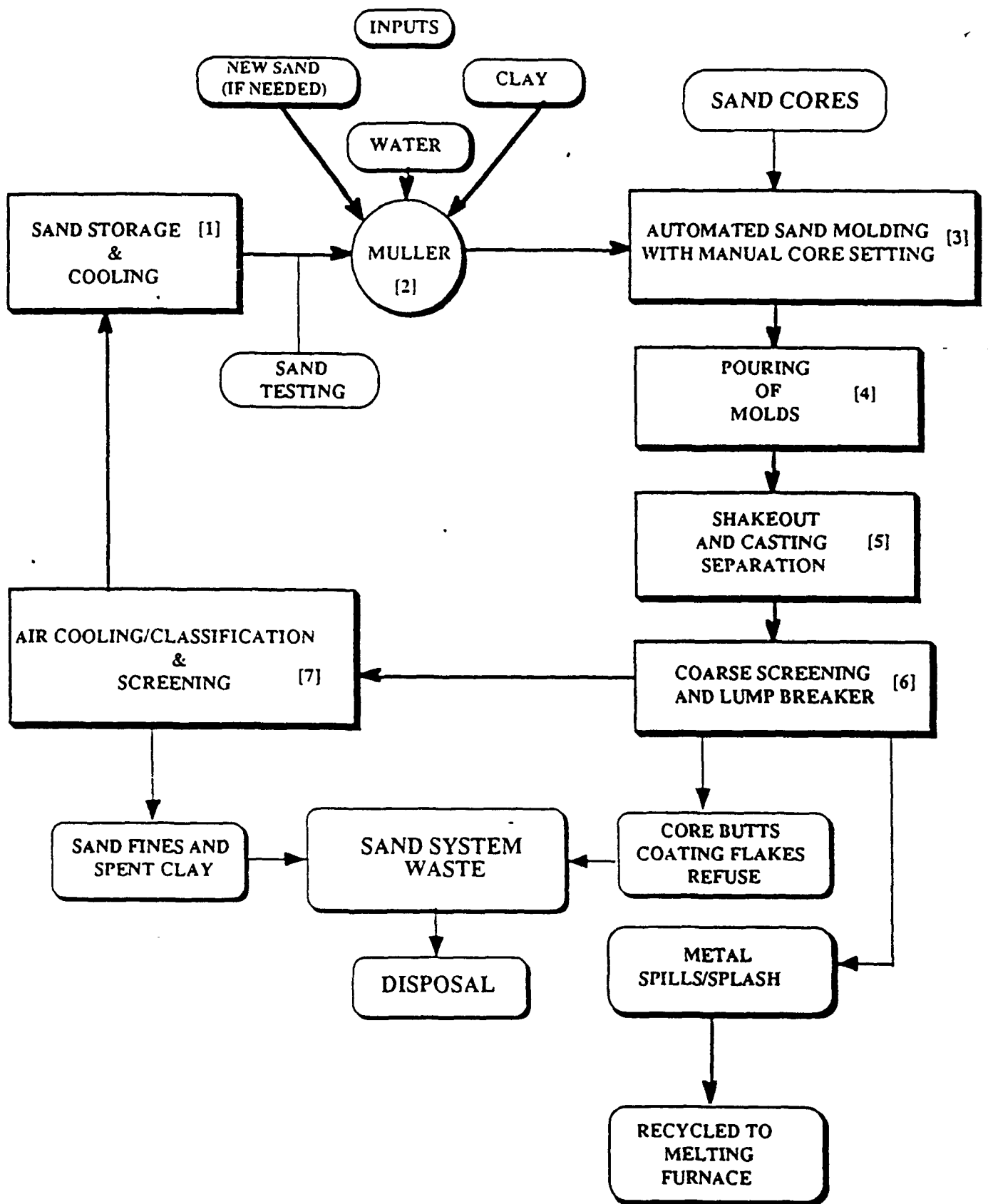


Figure 1. Schematic of a system for recycling green casting sand.

Sand molds are produced using high-speed, automated molding equipment [3]. The sand cores are inserted into the mold prior to closure of the mold halves. It is desirable for the core sand to be of the same type as the system sand, because most of the core sand is entrained into the system sand at shakeout. The mold assemblies are conveyed to a pouring station [4], which may be in linear or carrousel-type configuration, and the molds are poured with the molten alloy normally at 2100 to 2200°F (1149 to 1204°C). After cooling for approximately one-half hour, the castings are removed from the molds at the shakeout station [5]. Various schemes are used to recover the sand for reuse. Whether shakeout is performed in a single piece of equipment such as a rotary shakeout drum or at separate work stations, the essential operations include:

1. Separate the castings from the sand mold.
2. Break up large sand mold pieces and roughly screen.
3. Recover metal values such as spills and splashes for remelting or smelting.
4. Cool sand and reclassify by size using air classification or screens.
5. Remove system fines.

Finally, the sand is returned to the storage system for additional cooling and reuse.

2.3.2 Waste Characteristics

The amount of molding sand and core sand used during each casting cycle can be expressed as a ratio of the sand to the casting weight. The actual ratios depend greatly on the casting geometry and the individual foundry operation. Typical values for the molding sand-to-casting weight range from about 10:1 to 20:1. Casting weight-to-core sand ratios are normally in the range of 5:1 to 10:1.

The amount of foundry waste generated during each cycle is a small fraction of the sand used in a given mold and typically on the order of 1 to 2% of the combined molding and core sand weight. Annual foundry sand system wastes, including those contributed by the blast cleaning screens and baghouse, may weigh as much as 20% of the annual weight of castings poured in the foundry. Aggressive solid waste recycling practices can reduce this amount to about 2.5% (Davis and Baker, 1990; Smith, 1992). The wastestream has a variable composition even within a given foundry operation, but normally includes:

- Sand fines (mostly finer than 100 mesh)
- Dead or calcined clay fines
- Core butts (sections of the sand cores that did not receive sufficient thermal energy to cause complete breakdown of the core binder)
- Flakes of any coating used and miscellaneous refuse from core adhesives or molding aids
- Small quantities of metal particulate that were too fine to be screened for recycling.

Although not common, the quantity of sand entering the system from sand cores may be quite high in some operations, and some fraction of the system sand must be disposed of periodically to maintain a constant sand balance. Castings that are further processed by blast cleaning often have

a thin layer of adherent or burned-on sand. This sand is removed during the blast cleaning and frequently is combined with the waste fines from the system sand.

2.4 LEAD CONTAMINATION OF FOUNDRY SAND WASTES

Although lead is below its boiling point 3171°F (1744°C) at the normal pouring temperature used for leaded brass and bronze castings (about 2100°F or 1149°C), it has a significant vapor pressure of about 10 torr (Chemical Rubber Co., 1969). After molds are filled with molten leaded brass or bronze alloys, lead vapors penetrate into the permeable sand layers adjacent to the casting surface and condense on the relatively cooler surfaces of the sand grains. Revolatilization and later condensation of lead may occur as the thermal front advances through a sand mold during cooling.

Ostrom, Trojan, et al. (see various references in Annotated Bibliography, Appendix A) investigated the sand interface reactions with leaded copper alloys and confirmed that lead not only reacts with bentonite to form lead-aluminum-silicates but also forms a complex copper-tin-lead oxide at the surface in direct contact with the molten metal. Mondloch et al. (1987) further determined that small elemental lead nodules deposit preferentially on zinc oxide-coated sand grains located within a few millimeters of the casting surface.

The sand layers immediately adjacent to the casting surface are those most likely to fracture from thermal stresses and also to be carried into the blast cleaning operations. Thus, shakeout fines and blast cabinet wastes are prone to higher lead contents than the system sand in its entirety.

During solidification and cooling of leaded copper-base castings, the immiscible lead phase remains molten until the casting has cooled below the melting point of lead (621°F or 327°C). As a result molten lead migrates to internal shrinkage voids in the casting, effectively performing a sealing or pressure-tightness function. However, some lead also may segregate or "sweat" to both the external and internal casting surfaces. Thus, liquid lead is present at some portions of the casting surface and may contribute to contamination of the adjacent sand surfaces if wetting occurs.

Limited data are published on the lead content in various foundry sand wastestreams. Table 4 indicates the metallic content of several common brass foundry wastestreams (Davis and Baker, 1990).

TABLE 4. METALLIC CONTENT OF BRASS FOUNDRY WASTESTREAMS^(a)

Waste Material	Lead (weight %)	Copper (weight %)	Zinc (weight %)
Shotblast baghouse	3.85	25.5	8.00
Shotblast discharge	1.18	12.0	2.24
Dust collector	0.32	0.29	2.46
Furnace baghouse	2.31	0.30	60.0
Molding sand	0.17	0.28	1.38

Source: Davis and Baker, 1990.

3.0 WASTE MINIMIZATION AND TREATMENT OPTIONS FOR FOUNDRY SAND

3.1 SAND RECLAMATION

Some foundries are exploring sand reclamation to increase the life of casting sand and further reduce the volume of waste. Reclamation is a processing to restore waste sand to near its original condition. For the purpose of this discussion, reclamation may be distinguished from recycling in that reclamation involves reconditioning the sand to substitute for new sand additions as opposed to recycling where the waste sand is reused with minimal processing to remove core butts, metal particles, and fine particles.

Many foundries employing organic chemically bonded sand molds and cores find sand reclamation to be an economic necessity. A variety of reclamation techniques may be used including dry, thermal, wet, or hybrid reclamation units. Dry reclamation using mechanical or pneumatic systems is the most common, although thermal and mechanical/thermal hybrids are becoming more popular. Wet reclamation systems have not gained widespread acceptance due to the high energy costs associated with drying the sand after reclamation and the generation of a wastewater stream.

Sand reclamation is not commonly associated with green sand molding. Green sand mixtures are inherently recyclable by virtue of their ease of reconditioning for reuse. However, thermal and mechanical reclamation of waste shakeout sand has been demonstrated as a technique to offset the costs of new sand additions and shakeout sand disposal. Mechanical reclamation offers an advantage in terms of recovery of the active portion of clay that is present in the shakeout sand. Thermal reclamation above 1200°F (649°C) is required to completely calcine and remove all clay, if the objective is to restore the properties of the sand to those similar to raw, unbonded sand. To date, conventional reclamation techniques have not proven to be entirely feasible for converting hazardous brass foundry sands to nonhazardous waste on a commercial scale. An additional consideration is that care must be exercised to avoid casting and molding problems when reusing the reclaimed sand if its processed condition is largely sand fines.

Process development is on-going at the Michigan Technology University. Mechanical scrubbing and thermal reclamation were tested for binder removal. The binder removal efficiency for mechanical scrubbing was not as high as that for thermal treatment, which was found to give satisfactory results. Magnetic separation, electrostatic separation, fluidized-bed separation (pneumatic tabling), and wet tabling were tested for their ability to separate chromite from silica sand. Dry magnetic separation followed by wet tabling was identified as the optimum sand separation process (Hwang et al., 1992).

The Electric Power Research Institute (EPRI) is researching methods to recover casting sand from either resin-bonded or clay-bonded molds using thermal treatment. Their research indicates that resin-bonded sand can be treated for reclamation at 540°C (1000°F) by gas-fired or electrical resistance heaters. Thermal processing of clay-bonded casting sand requires higher temperatures (Douglas and McDonough, 1991).

Mechanical scrubbing of brass foundry mold sand has been studied. Tests are reported to indicate that the leachable lead and cadmium levels can be reduced, but the resulting materials still

exhibit TCLP toxicity. The report concludes that further development of scrubbing systems to recover brass foundry sand would be required but might prove successful (Nagel et al., 1983).

3.2 RECOVERY OF METALS FROM FOUNDRY SANDS

Davis and Baker (1990) report the successful reclamation of metal values from brass foundry solid wastes using a ball-milling operation. Shotblast baghouse and shotblast discharge dusts are sold for their copper content, and the furnace baghouse dust is sold to a smelter for its zinc content.

Cyprus Miami Mining is a primary copper smelter that processes complex sulfide ores (LaChapelle and Dyas, 1993). The smelter produces copper as its main product but also produces gold and silver. Volatile metals such as lead, arsenic, and mercury are captured by acid scrubbing and sent to other facilities for recovery. They are reported to be an exempt recycling facility with the capability to accept D002 through D011 characteristic waste and F006 listed waste. The facility accepts selected metals, metal sludges or filter cakes, and incinerated ashes containing copper, silver, or gold. Processing ash from incineration of municipal wastewater treatment sludge provides silica as a flux and allows recovery of the trace quantities of gold and silver in the sludge. The plant also processes used foundry sand and lime residues from boiler cleaning. These materials also provide fluxing agents and allow metal recovery.

3.3 RECYCLING/WASTE MINIMIZATION

3.3.1 Use in Ceramic Products

Foundry sand sometimes can be used as a bulk silica source in ceramic products and cement. In some cases, the metal impurities may impart desirable qualities such as hardness or color to the ceramic product. Depending on the source of the sand, metals such as iron that are required by the cement-making process also may be present. However, the relatively low cost of raw bulk silica and the rather variable nature of foundry wastes usually makes processing of foundry wastes unattractive to most manufacturers. Furthermore, due to hazardous waste regulations and concerns about a changing regulatory environment, cement kilns currently accept only nonhazardous waste materials as feed (Systech Environmental Corporation, 1993).

The Ceramicbond™ waste conversion system forms an alumina-silicate complex to physically and chemically immobilize metal contaminants. The waste is mixed with a proprietary alumina silicate material and extruded into pellets. The pellets are fired at 1090°C (2,000°F) to form a ceramic solid called Armorite™. This material reportedly is leach resistant and suitable for use as a ceramic-making raw material or as a construction aggregate.

Waste materials amenable to treatment include filter cakes, foundry sand, ash, and sludge. The process treats inorganic wastes containing cadmium, chromium, cobalt, copper, lead, nickel, vanadium, or zinc. Metals that will volatilize under process conditions, such as mercury or arsenic, cannot be treated. Ceramic Bonding staff are reported to be planning to offer processing of F006 waste and some site remediation wastes as an exempt recycler (Ceramic Bonding Ceramic Production, 1992).

* Mention of trade names or products does not constitute endorsement or recommendation for use.

3.3.2 Construction and Bulk Use

Nonhazardous foundry sand waste has seen extensive use in construction applications. The Wisconsin Department of Natural Resources (DNR) is developing a program to encourage responsible beneficial reuse of foundry by-products. In particular, the state is developing fact sheets for beneficial reuse of foundry sand in various applications such as:

- Foundation subgrade fill
- Concrete and asphalt fine aggregate
- Landfill daily cover
- Pavement subbase fill
- Contained embankment fill (Wisconsin DNR, 1993).

As with the case of ceramic and cement manufacturers, the potential uses of leaded-brass foundry sand wastes for these applications are limited by long-range concerns about lead leachability and environmental liability issues.

3.4 PROCESS MODIFICATIONS TO REDUCE LEAD LEVELS

The brass and bronze casting industry has been investigating process changes to prevent lead from entering the casting sand. The two main areas of research are to reduce the lead levels in the alloy being cast and/or applying a face coating to the mold that reduces alloy penetration into the casting sand (Bralower, 1987). Alloy development work has focused recently on the use of bismuth as a partial or total replacement for lead in the alloy. However, the long-range health effects of bismuth have not been established fully, and concerns remain about the cost and availability of bismuth. Further work is needed to identify alloys with low-lead or lead-free compositions that meet all of the cost and performance criteria for leaded brass and bronze castings. Key performance criteria include low-lead leachability, good machinability, adequate mechanical properties, good pressure tightness, and the capability of being cast and finished using near-conventional foundry techniques.

3.5 TREATMENT OF FOUNDRY WASTES

3.5.1 Conventional Cement and Lime Treatment

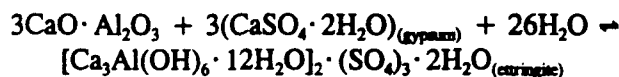
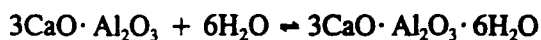
Solidification/stabilization with inorganic binders is a widely accepted and used treatment for wastes containing inorganic forms of lead contamination. Stabilization is identified as the Best Demonstrated Available Technology (BDAT) for treatment of a number of lead-bearing RCRA non-wastewater wastes. For example, solidification/stabilization is a component in the BDAT for D008, lead characteristic; F006, wastewater treatment sludge from electroplating operations; and U144, U145, and U146, various lead chemicals.

Solidification/stabilization waste treatment typically uses cement-based binders. Common binder materials, used alone or in combination, include Portland cement, pozzolans (fly ash or blast furnace slag), cement kiln dust, soluble silicates, or lime. A typical approximate composition for cement is CaO, 65%; SiO₂, 20%; Al₂O₃, 5%; Fe₂O₃, 3%; SO₃, 3%; and MgO, 2% (plus minor

impurities). A typical waste treatment process involves mixing a binder and water with waste solids or sludges. After mixing, the binder hydrates to form a treated waste solid.

The ratio of components varies widely but for most applications falls in the range of 20 to 100 pounds of binder per 100 pounds of waste treated. Theoretically, the greatest strength is obtained with a water-to-cement (W/C) weight ratio of about 0.25 to 0.30. Practical considerations lead to a typical "ideal" W/C ratio of 0.4 to 0.5. If high compressive strength is not needed, the W/C ratio may be 1.0 or higher.

The exact stoichiometry of the cement hydration reactions is complex. The main products are calcium-silicate-hydrate (C-S-H in cement chemistry nomenclature) and calcium hydroxide (Ca(OH)_2 , mineral name portlandite). Cement hydration normally gives about 60 to 70% C-S-H and 20 to 25% calcium hydroxide, with the remainder a mixture of several other compounds. A general indication of the hydration reactions is shown below:



These hydration reactions release calcium hydroxide, which can form as crystals in the solidified matrix. The calcium hydroxide provides considerable reserve alkalinity to precipitate metals as hydroxides. The treatment also can immobilize metals by a combination of other mechanisms including sorption on calcium silicate or other surfaces, precipitation as metal silicates, incorporation into crystal structures, and/or microencapsulation in a leach-resistant silicate matrix.

No specific data were found on cement treatment of foundry sand. However, cement treatment frequently is used to immobilize lead in soils, sludges, abrasive blasting media, and other waste solids. Lead often is found in cement-treated waste as a combination of one or more chemical forms such as Pb(OH)_2 , PbSO_4 , PbCl_2 , carbonates, and silicates (Conner, 1993). Each species has its own solubility equilibrium in the leaching medium (leach test or environmental). Typically, the main immobilization mechanism for transition and heavy metals in cement-treated waste is precipitation as hydroxides. For lead, immobilization appears to be due to a combination of precipitation and incorporation of lead as a silicate (Cocke and Mollah, 1993; Conner, 1991). Lead, particularly when present in the untreated waste as soluble salts, retards the setting of cement. The retardation appears to be caused by rapid precipitation of lead hydroxide which coats the cement particles and slows the hydration reactions (Thomas et al., 1981).

3.5.2 Addition of Metallic Iron Filings or Iron Salts

It is well known within the foundry industry that addition of metallic iron or ferric salts lowers leachable lead to concentrations below hazardous limits, as determined by the TCLP, California WET, and the former EP Toxicity tests. Experiments have demonstrated the effectiveness of metallic iron filings, ferric sulfate, and ferric hydroxide to dramatically limit Pb leachability in contaminated mold sands (Ostrom and Trojan, 1988; Stephens et al., 1984; Trojan and Ostrom, 1987). The chemical mechanisms proposed to explain this effect are

- formation of a redox couple between metallic iron and divalent lead in aqueous solution, which causes lead to be reduced to its elemental oxidation state
- specific adsorption of lead ions by surface sites on colloidal ferric hydroxide
- coprecipitation or substitution of lead ions for other ions in insoluble solids.

Experiments using TCLP and EP Toxicity tests of synthetic and actual hazardous foundry wastes show that lead leachabilities are lowered below 5 ppm when 1 to 10% by weight iron filings are present in the mixtures (Trojan and Ostrom, 1987). Stephens et al. (1984) report similar lowering of lead leachability in EP Toxicity tests when 5 to 7.5% iron filings are added by weight. In the absence of iron, lead leachability was higher when the TCLP test method was used, compared to when the EP Toxicity test method was used (Trojan and Ostrom, 1987). The difference was attributed to the higher amount of acetate ion present. In the TCLP test the acetate ion concentration is 0.1 *N*, whereas in the EP Toxicity test it may be less than 0.1 *N*, depending on how much acetic acid is needed to achieve a solution pH of 5.0 ± 0.2 .

Surfaces of freshly precipitated ferric hydroxide are well known to be highly active for immobilizing many types of metallic ions. Immobilization occurs by two surface processes, adsorption and lattice substitution (Hem, 1977). Adsorption is a mechanism whereby charged or neutral atoms (e.g., Pb^{2+} or $PbAc^+$) adhere to the surface of an adsorbent (e.g., ferric hydroxide). The attractive force operating between the adsorbed species on the adsorbent is relatively weak, being on the same order as van der Waals forces. The term *physisorption* also is used to describe this kind of interaction.

Typically, ferric sulfate is added to waste mold sand and hazardous sludge to immobilize lead. When soluble ferric salts, such as ferric sulfate, are added to pH-neutral water, they precipitate amorphous ferric hydroxide. Adsorption of Pb^{+2} onto ferric hydroxide is largely independent of solution ionic strength and its properties do not change with aging for several months (Swallow et al., 1980). However, the long-term stability of this situation is unknown. Presumably, amorphous ferric hydroxide will eventually crystallize to a stable, low-temperature solid such as goethite. Whether this kind of phase transformation affects lead stabilization also is unknown.

Swallow et al. (1980) showed that Pb^{+2} ions readily adsorb onto amorphous ferric hydroxide. At pH ~ 5, the ionic ratio $Pb^{+2}_{adsorbed}/Pb^{+2}_{free}$ is approximately 0.1, when the concentration of total iron is 5×10^{-5} *M* and total Pb is about 10^{-4} *M*. However, free lead (and iron) concentrations are somewhat affected by the presence of complexing ions, such as acetate. Figures 2, 3, and 4 show the effect of 0.1 *N* acetate on the solubilities of $Fe(OH)_2$, $Fe(OH)_3$, and $Pb(OH)_2$, respectively. It is possible that acetate can lower the ability of ferric hydroxide to adsorb $Pb(II)$, due to higher solubility of ferric hydroxide in the presence of acetate ion.

Coprecipitation of divalent lead in phosphates is discussed in Section 3.5.3.

3.5.3 Addition of Phosphate

Phosphate addition has potential to immobilize metal contaminants by precipitation. Many metals form low-solubility phosphate salts and/or apatite species. Phosphate chemistry is used in low- and medium-pressure boilers to control pH and to precipitate hardness elements and metal impurities. Calcium hardness and metal corrosion products form a flocculent precipitate (mainly hydroxyapatite and brucite) that is removed in the boiler blowdown (Babcock & Wilcox, 1978). Phosphate is added occasionally for specialized waste treatment. There is some experience with treatment of utility boiler cleaning wastes by phosphate addition to immobilize calcium, iron, and copper as various hydroxide, phosphate, and apatite solids. A few treatability studies have used

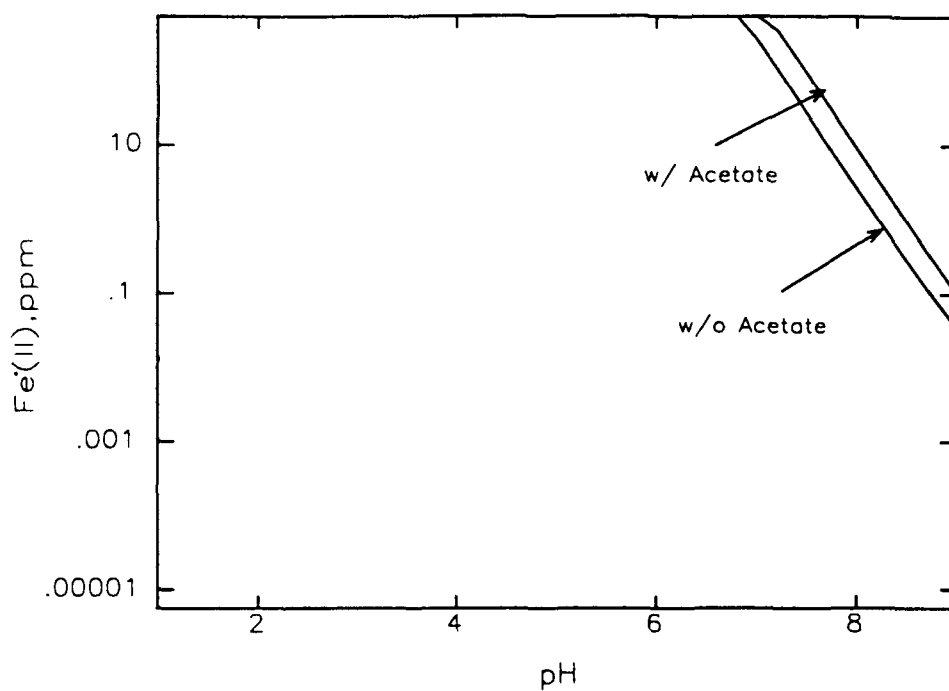


Figure 2. Solubilities of Fe(II) hydroxide.

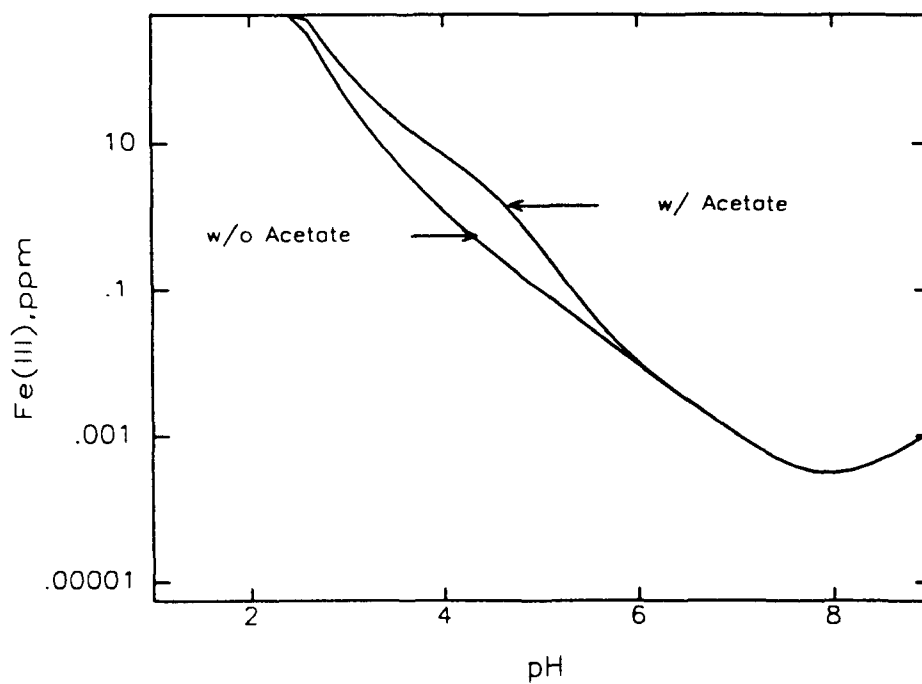


Figure 3. Solubilities of Fe(III) hydroxide.

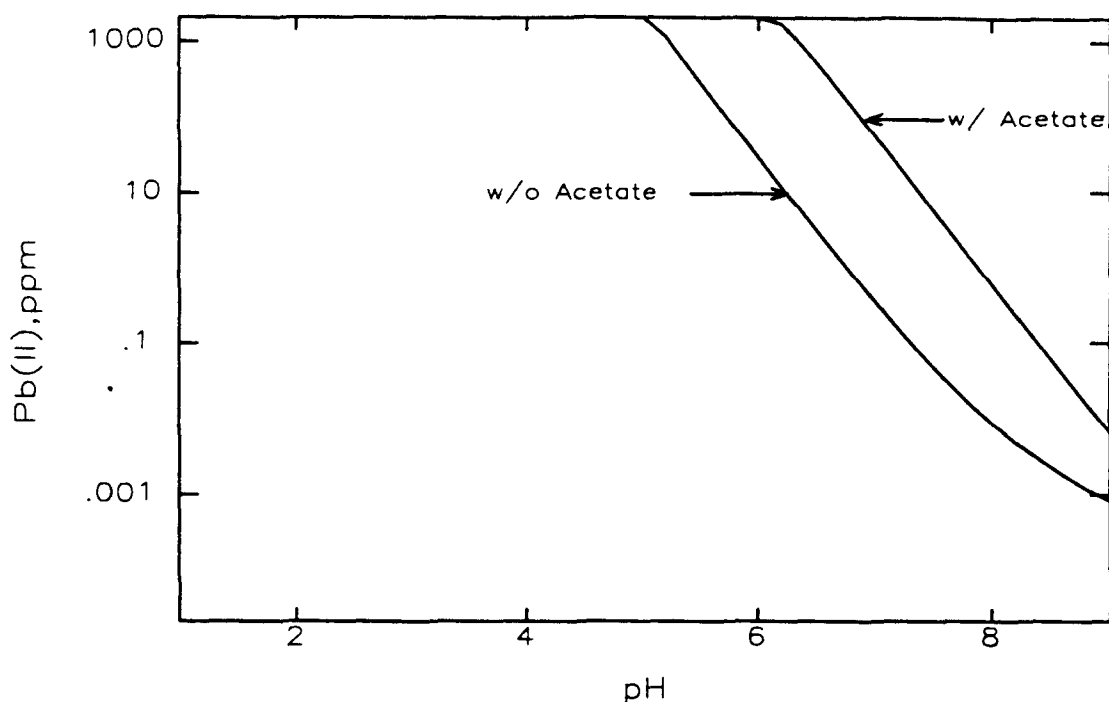


Figure 4. Solubilities of Pb(II) hydroxide.

phosphate additives in cement-based solidification/stabilization binder formulations to improve immobilization of lead. However, phosphate addition is not currently in general use for treatment of metal-bearing wastewater, solids, or sludges (Conner, 1991).

Phosphate addition has been tested for treatment of foundry wastes. A treatability study indicated that phosphoric acid can immobilize lead in cupola emission dust. A treatment level of 3 grams phosphate to 100 grams of waste reduced the EP-toxicity test leachate lead to 0.06 mg/L. Untreated dust showed a leachable lead level of 180 mg/L (Turpin et al., 1990). Low dosages of phosphate (typically 1 to 10% addition as PO_4 by weight) are effective for immobilization of metals in solids and sludges. Triple superphosphate (TSP) is another effective, and less expensive source of phosphate. TSP is monobasic calcium phosphate [$\text{Ca}(\text{H}_2\text{PO}_4)$] that has been treated with phosphoric acid (H_3PO_4) (Farrell-Poe and Etzel, 1991 and 1992).

Research is ongoing to develop a phosphate-based treatment method for in situ immobilization of metals in soil. Tests of hydroxyapatite reaction with aqueous lead, ion-exchangeable lead, and lead-contaminated soil materials have indicated effective lead immobilization. Hydroxyapatite reduced initial lead concentrations from the range of 5 to 500 mg/L to 0.18 to 19.7 mg/L. The concentration of lead in water in contact with lead-contaminated soil was reduced from 2,273 $\mu\text{g/L}$ to 36 $\mu\text{g/L}$ after reaction with hydroxyapatite (Ma et al., 1993).

3.5.4 Treatment of Lead-Based Paint Removal Debris

Lead-based paints were a common protective coating for structural steel in buildings and bridges for many years. The lead-based paints provided good corrosion resistance and could be applied with minimal surface preparation. However, with time the protective coating deteriorates and must be removed and replaced. Most paint removal is done by abrasive blasting. The spent abrasive

blast media contain paint debris with lead- and chromate-bearing pigments. The pigments can cause the spent media to be a RCRA waste due to a lead or chromium leachability toxicity characteristic.

Waste generated by removal of lead paint from structures has some similarities to spent casting sand. Both the casting sand and abrasive blasting media waste are a silicate matrix containing leachable lead contamination. However, the lead species present and the type and condition of the sand are different.

The bridge paint removal industry has examined a similar range of waste management options as that explored by the foundry industry. Techniques are being developed to reduce, to the extent possible, the waste volume produced by cleaning and reusing the abrasive media and to allow beneficial reuse of any remaining waste. A variety of treatment options also are being studied for the spent abrasive media.

Alternatives to abrasive blasting that produce less waste volume are being explored. Alternative paint removal methods include hand scabbling, plastic media bead blasting, CO₂ pellet blasting, bicarbonate blasting, high-pressure water blasting (Randall, 1993), and flame spray vitrification (Petreanu and Kumar, 1993).

Conventional abrasive blasting is still the most common method for lead-based paint removal. For these systems, the volume of waste can be reduced by cleaning and reusing the spent abrasive blast media. Blast media cleaning systems are available using dry separation (Pittsburgh Mineral and Environmental Technology, Pittsburgh, Pennsylvania) or soil washing methods (Westinghouse, Pittsburgh, Pennsylvania). The systems are intended to separate the abrasive blasting media waste into:

- Clean abrasive (for reuse)
- Clean fines (for disposal as industrial waste or reuse in ceramics)
- Paint residue (for disposal as a hazardous waste).

Beneficial reuse of spent blasting media as asphalt aggregate is technically possible, and some pilot projects have indicated both good asphalt performance and good metal immobilization (Means et al., 1993). However, the EPA regulatory mechanism seems to be leaning toward classifying the use of spent abrasive blasting media in asphalt as "use constituting disposal" rather than recycling. In any case, pavers are reluctant to use a material in general commerce if there is any chance of later liability. Reuse of lead-bearing sand as asphalt aggregate generally is feasible only in special circumstances where continued monitoring is possible, for example, when the asphalt can be used for on-site paving.

As with the foundry industry, abrasive blasting operators have explored pretreatment to avoid creating a hazardous waste. Additives are included in the fresh abrasive blasting media. The additive is used along with the abrasive blasting media and arrives in the spent media where it prevents a lead leachability toxicity characteristic. Two basic types of additives have been applied. One is a proprietary silicate material that immobilizes lead, presumably by precipitation of lead as an insoluble silicate. The second method is to include fine iron metal particles in the abrasive. The iron metal shows the same reduction of lead solubility in the TCLP test as indicated from the foundry industry experience.

Posttreatment methods considered for paint debris include conventional lime or cement stabilization and phosphate addition. Portland cement treatment is the most commonly used and generally accepted method (Carrasquillo, 1993). As discussed above, iron metal particulate may be added prior to use of the blast media to prevent the debris from failing the TCLP. The U.S. Department of Transportation (DOT) recommends cement addition to give more permanence, even if iron metal particulate addition to the fresh blasting media reduces the initial lead leachability in the spent media (Smith, 1993; Peart, 1993).

4.0 ANALYSIS OF DATA AND RESULTS OF MODELING

Tables 5 and 6 contain electrochemical information abstracted from Appendix B. The electrochemical data in the appendix were used to model stability of various iron and lead species to study the effectiveness of the Fe-Pb redox couple in reducing Pb(II) aqueous species. Acetate ion was included in subsequent calculations because both Fe(II) and Pb(II) form aqueous complexes with acetate. The tendency of metal ions to form complexes will shift equilibrium calculations based on hydrolysis species. However, in the pH region 4.9 to 5.0, where the TCLP and EP Toxicity tests are performed, neither Fe^{+2} nor Pb^{+2} hydrolyzes significantly, particularly when their concentrations are relatively low. Based on the chemical conditions of the TCLP and EP Toxicity tests, a set of redox reactions that describe equilibria were constructed from the data in Tables 5 and 6.

Table 7 shows the standard state electrical and Gibbs free energy changes for the reactions which describe the reduction of Pb(II) to Pb(0) in pure water and when acetate is present. In the absence of acetate, reduction of Pb(II) by iron metal is strongly favored ($\Delta \mathcal{E}^0 = +0.283\text{V}$, $\Delta G^0 = -54.6 \text{ kJ/mole}$). In general, reduction of Pb(II) is less strongly favored when acetate is present, but the reactions still proceed in the direction of lead reduction. The tendency of Pb(II) to become reduced under actual conditions of the TCLP and EP Toxicity tests can be found from a calculation of solution Eh, which is defined as follows:

$$Eh = \Delta \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \ln Q$$

where \mathcal{F} is Faraday's constant and Q is the reaction quotient. For example, $Q = [\text{Fe}^{+2}]/[\text{Pb}^{+2}]$, in the absence of acetate. Diagrams of Eh vs. pH for relevant systems are shown in Figures 5 through 8.

The equilibrium phases shown in Figures 5 through 8 are consistent with lead solubility reduction by either a redox couple mechanism or sorption on $\text{Fe}(\text{OH})_3$. These figures indicate the predominant chemical species present at equilibrium under various conditions of Eh (oxidation/reduction potential) and pH (acidity). The stability regions for aqueous systems of iron (Figures 5 and 6)

TABLE 5. STANDARD REDUCTION POTENTIALS FOR IRON AND LEAD IN AQUEOUS MEDIA

Reaction	$\mathcal{E}^0\text{V}$	n	$\Delta G^0/\text{kJ}$
$\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}^0$	-0.41	2	78.9
$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.770	1	74.3
$\text{Pb}^{+2} + 2\text{e}^- \rightarrow \text{Pb}^0$	-0.13	2	24.3

TABLE 6. EQUILIBRIUM CONSTANTS AND FREE ENERGIES FOR IRON, LEAD, AND ACETATE REACTIONS IN AQUEOUS MEDIA

Reaction	Log <i>K</i>	$\Delta G^\circ/\text{kJ}$
$\text{Fe(OH)}_{2(\text{s})} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{+2} + 2\text{H}_2\text{O}$	12.5	-71.32
$\text{Fe(OH)}_{3(\text{s})} + 3\text{H}^+ \rightleftharpoons \text{Fe}^{+3} + 3\text{H}_2\text{O}$	3.2	-18.26
$\text{Fe}^{+2} + \text{Ac}^- \rightleftharpoons \text{FeAc}^+$	1.4	0.00
$\text{Pb}^{+2} + \text{Ac}^- \rightleftharpoons \text{PbAc}^+$	2.5	0.00
$\text{Pb}^{+2} + 2\text{Ac}^- \rightleftharpoons \text{PbAc}_2^0$	4.1	0.00
$\text{Pb}^{+2} + 3\text{Ac}^- \rightleftharpoons \text{PbAc}_3^-$	3.6	0.00
$\text{Pb}^{+2} + 4\text{Ac}^- \rightleftharpoons \text{PbAc}_4^{-2}$	2.9	0.00
$\text{Pb(OH)}_{2(\text{s})} + 2\text{H}^+ \rightleftharpoons \text{Pb}^{+2} + 2\text{H}_2\text{O}$	8.1	0.00

or lead (Figures 7 and 8) with and without acetate are shown. In Figures 6 and 8, the total acetate concentrations is 0.1 *N*.

In all of the Eh-pH diagrams the stability line for lead metal is located at higher Eh voltage than the line for iron metal in the pH range of interest. These diagrams are a graphic representation of the reduction potentials shown in Tables 5 and 6. The reduction potential and the diagrams show that the Pb(II) → Pb(0) couple is favored over the Fe(II) → Fe(0) couple. As a result, the presence of an available surface of iron metal will tend to reduce lead ions in solution to lead metal.

When iron metal contacts an acetate solution, the stable species under oxidizing conditions with a pH higher than about 3.8, the stable species is Fe(OH)₃ solid. Iron is somewhat unusual in that it has a stable hydroxide precipitate with such a low pH (high acidity). For lead metal, dissolved species (ionic lead or a lead acetate complex) predominate at pH below about 6. The Fe(OH)₃ precipitate is a strong sorbent for dissolved species. The diagrams indicate that addition of iron metal can result in formation of Fe(OH)₃ which has the capacity to sorb the dissolved lead species.

TABLE 7. ELECTRICAL POTENTIALS AND FREE ENERGIES FOR IRON, LEAD, AND ACETATE REDOX REACTIONS IN AQUEOUS MEDIA

Reaction	$\Delta E^\circ/\text{V}$	<i>n</i>	$\Delta G^\circ/\text{kJ}$
$\text{Pb}^{+2} + \text{Fe}^0 \rightleftharpoons \text{Pb}^0 + \text{Fe}^{+2}$	0.283	2	-54.60
$\text{PbAc}^+ + \text{Fe}^0 \rightleftharpoons \text{Pb}^0 + \text{Fe}^{+2} + \text{Ac}^-$	0.209	2	-40.30
$\text{Pb(Ac)}_2^0 + \text{Fe}^0 \rightleftharpoons \text{Pb}^0 + \text{Fe}^{+2} + 2\text{Ac}^-$	0.162	2	-31.20
$\text{Pb(Ac)}_2^0 + \text{Fe}^0 \rightleftharpoons \text{Pb}^0 + \text{FeAc}^+ + \text{Ac}^-$	0.203	2	-39.20

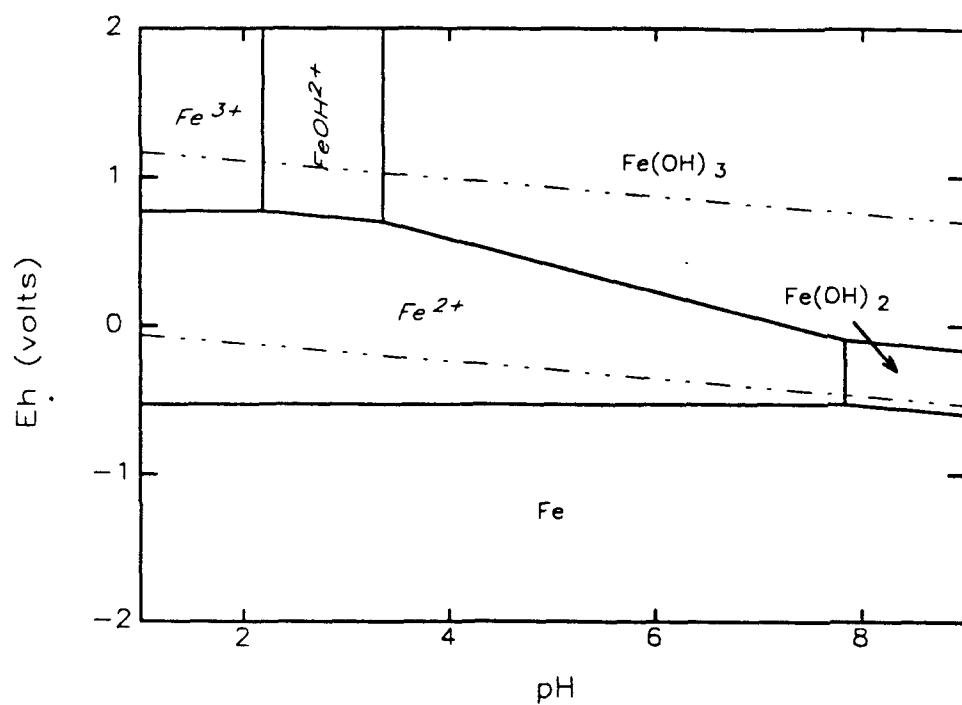


Figure 5. Eh-pH diagram of the Fe-H₂O system.

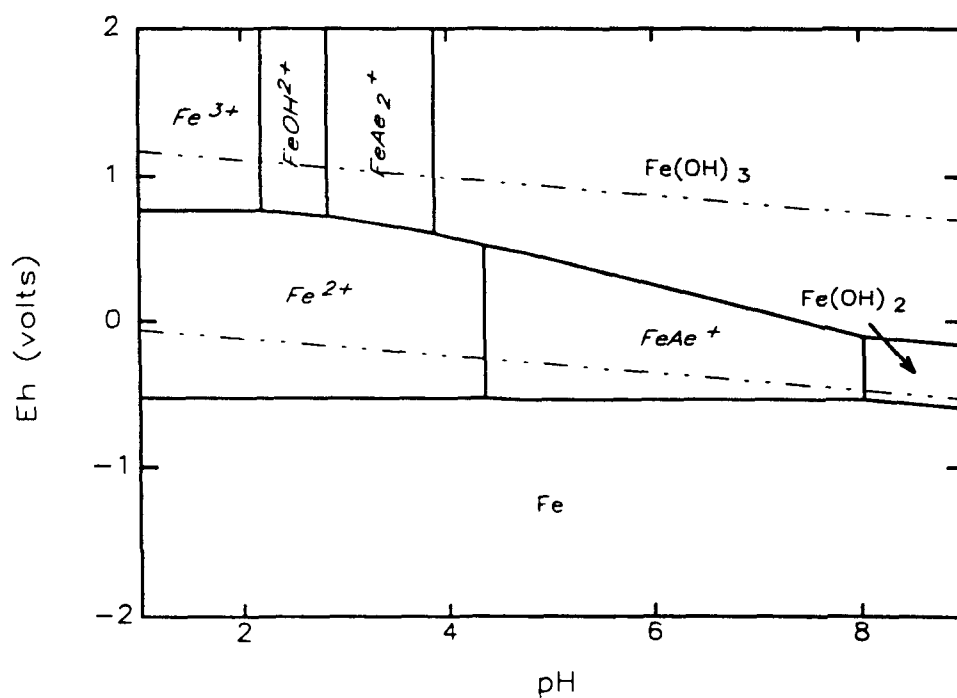


Figure 6. Eh-pH diagram of the Fe-H₂O-acetate system.

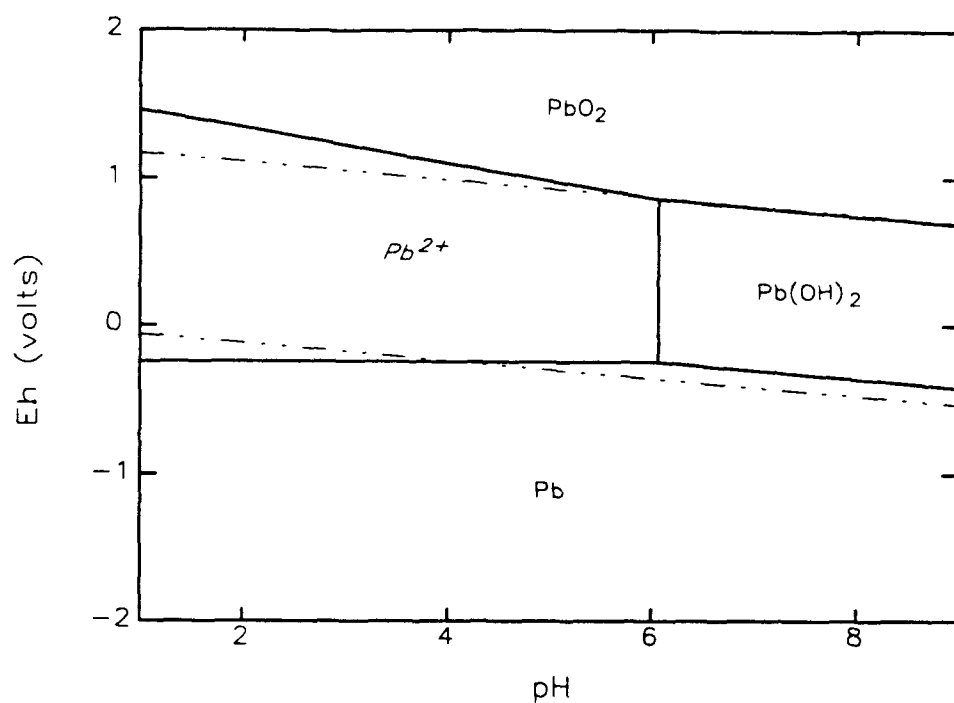


Figure 7. Eh-pH diagram of the Pb-H₂O system.

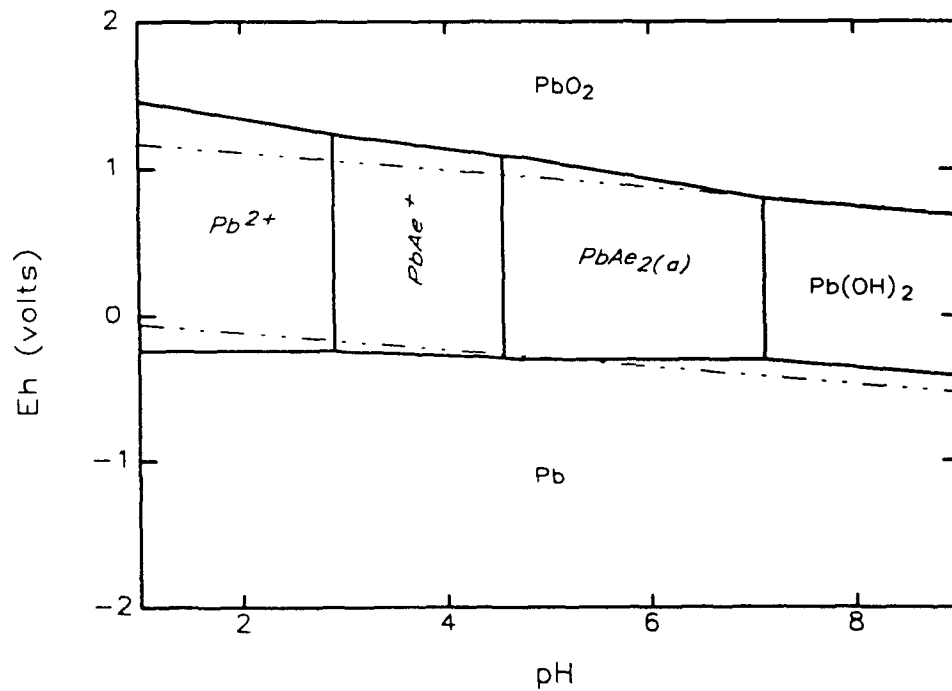


Figure 8. Eh-pH diagram of the Pb-H₂O-acetate system.

5.0 PROPOSED EXPERIMENTAL APPROACH

5.1 DATA GAPS AND ISSUES

As a result of this preliminary analysis, the following questions with regard to data gaps and issues remain to be addressed.

1. Is the metallic iron addition susceptible (because of its higher density) to segregation during waste handling and transport to the landfill? If so, does this impair its ability to tie up lead? How is segregation affected by the characteristics of the waste and the iron addition?
2. What is the economic feasibility of using the iron addition in the 5 to 10% levels described? How does this feasibility change with variations in iron prices? How does the cost compare with other treatment methods?
3. What are the safety and health issues associated with handling fine iron filings? What respiratory requirements and fire prevention measures exist?
4. What are the optimal properties of the iron filings in terms of tying up lead. What are the useful size ranges and particle shapes? Are their economical sources of suitable filings exist as a wastestream from other manufacturing processes?
5. How stable is the iron effect over time? Does it lose effectiveness if the iron gets wet from the waste and oxidizes to iron oxide? Is it just as effective in a foundry monofill as it would be in a municipal landfill. How does the iron effect change with acid species (acetic vs. acid rain)?
6. What is the effect of iron on the leachability of other species in the surrounding waste? Does iron have the potential to increase the mobility of other objectionable species (TCLP toxics)?
7. Even if effective in the short term, are foundries exposed to risk for cleanup costs if the disposed iron-treated waste begins to leach out lead at a later time?
8. How is the regulatory environment likely to change to enable foundries to obtain permits to treat wastes in this manner?
9. How would costs and the long-range effectiveness compare with those for waste vitrification techniques? Could a low-grade, environmentally acceptable waste glass product be made for some application that would provide a recycle stream? What are some possible applications?

10. What is the nature of the lead (metallic, lead oxide, lead-aluminosilicates, etc.) from actual brass foundry wastes? Samples in literature seem to be mostly from casting experiments done under simulated conditions at a university laboratory. Using actual wastes, how does the iron effect depend on the form of the lead contamination?

5.2 DESCRIPTION OF PROPOSED EXPERIMENTS

The following experiments are proposed as a result of the preliminary analysis.

1. Obtain actual samples of wastes from leaded brass foundry operation from every wastestream (shakeout, blast baghouse, blast discharge, mold after casting, etc.). Characterize the form and distribution of the lead carefully. Sand samples were obtained from two foundries in order to make a preliminary assessment of lead contamination. Results of several types of analyses are described in Appendix C.
2. Select wastes to be exposed to long-term leachability testing. Perform a statistically designed matrix of experiments for long-term TCLP tests. Include variables of iron particle size, shape, composition (steel vs. irons), temperature, iron concentration, and acid species.
3. Select or simulate wastes with other species and perform long-range TCLP tests to determine if leachability of other heavy metals will be accelerated. Perhaps some of this could be precluded with a study of the relevant chemistry for iron and other compounds.
4. Investigate iron powder segregation problems. Subject the iron-treated waste to a variety of handling processes to determine conditions with the potential of causing segregation of the iron metal particulate and the waste.
5. Perform a literature study to compile information on the health and safety aspects of fine iron powders. Perform a cost/benefit evaluation to compare the iron filing approach to other potential treatment methods.
6. Conceptualize a prototype foundry waste vitrification system. Measure waste leachability and perform a technical/economic feasibility study. Conceptualize potential markets for low-grade ceramic/vitrified products.

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40 CFR Part 261, Appendix II (p. 1)

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Conner, J. R. 1993. "Chemistry of Cementitious Solidified/Stabilized Waste Forms." In *Chemistry and Microstructure of Solidified Waste Forms*. Lewis Publishers, Ann Arbor, Michigan. pp. 41-82.

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- * Douglas, J., and P. McDonough. 1991. "Foundry Waste Reduction." *EPRI Journal*, 16(7):17-23.
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* See the annotated bibliography in Appendix A for more information on this title.

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Hem, J. D. 1977. "Reactions of Metal Ions at Surfaces of Hydrous Iron Oxide." *Geochim. Cosmochim. Acta*. 41:527-538.

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Means, J. L., K. W. Nehring, and J. C. Heath. 1993. "Abrasive Blast Material Utilization in Asphalt Roadbed Material." In: T. M. Gilliam (Ed.), *Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Wastes*. ASTM STP 1240, American Society for Testing and Materials.

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Petreanu, J. P., and A. Kumar. 1993. "Vitrification of Lead Contained in Lead Based Organic Coatings Using Thermal Spray Technologies." *Third International Symposium on Stabilization/Solidification of Hazardous, Radioactive, and Mixed Wastes*, Williamsburg, Virginia. American Society for Testing and Materials. November 1-5.

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- * Smith, V. D. 1992. "The Greening of the Foundry Industry." *Foundry Management and Technology*, 120(9):158-160.
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 - * Wisconsin Department of Natural Resources. 1993. *Foundry Waste Beneficial Reuse Study*. PUBL-SW-181-93, Bureau of Solid and Hazardous Waste Management, Madison, Wisconsin.

APPENDIX A

ANNOTATED BIBLIOGRAPHY

Baillod, C. R., L. Coduti, S. L. Murto, K. B. Rundman, and D. A. Talford. 1991. "Foundry Wastes in Michigan: Inventory and Minimization Potential." *American Foundrymen's Society Transactions*, 99:673-680.

The paper describes the results of a survey sent to 128 foundries in Michigan and outlines methods to reduce foundry waste disposal. Of the 128 survey forms sent out, 48 responses were received. Fourteen respondents used chemically bonded molds for nonferrous casting and reported 73,283 tons per year of sand and 9,292 tons per year of slag waste with a casting production of 188,120 tons per year. Thirteen respondents using other mold systems for nonferrous casting reported 11,380 tons per year of sand and 416 tons per year of slag waste with a casting production of 13,249 tons per year. Most of the foundries did not clean and reclaim the sand. The only sand reclamation approach in use was mechanical cleaning of resin-bonded sand. The paper describes and evaluates various on-site and off-site options for sand reclamation and disposal.

Bralower, Paul M. 1987. "Now is the Time to Treat Lead in Brass Sands." *Modern Casting*, 77(4):62-63.

This is short review article describing the regulation of brass and bronze foundry sand disposal and the progress of research into methods for either reducing lead levels in the spent sand or treating the sand to reduce lead leachability. Although the article was written before the Pollution Prevention Act of 1990, it follows the recommended approach to (1) attempt to modify the process to eliminate the pollution, (2) reclaim on-site as much waste as possible for return to the process, and (3) treat any residuals.

Ceramic Bonding Ceramic Production. 1992. 939 San Rafael Avenue, Suite C, Mountain View, California 94043. Personal communication, Mr. Barrett A. Johnson, (415) 940-1146; fax (415) 940-1634.

Telephone discussions with personnel indicate that Ceramic Bonding provides processing for a variety of metal-bearing solid wastes.

Davis, C. M., and W. A. Baker. 1990. "Waste Minimization Contributes to Profits Through Solid Waste Recycling." *American Foundrymen's Society Transactions*, 98:953-955.

This article summarizes the development and implementation of an action plan to minimize waste at a foundry that produces plumbing products. The article tabulates

the metal content of shotblast baghouse dust, shotblast discharge, dust collector wastes, furnace baghouse dust, and molding sand. The metal content of shotblast baghouse dust and discharge was found to be high enough to allow the material to be sold as feed to secondary smelting. The molding sand is reused without processing for reclamation (binder removal). Wastes from shakeout, sand screening, melting, and pour off are crushed and screened to produce a metal stream suitable for sale as feed to secondary smelting.

Douglas, John, and Patrick McDonough. 1991. "Foundry Waste Reduction." *EPRI Journal*, 16(7):17-23.

This article outlines the technologies currently used in the U.S. metal casting industry and describes EPRI-funded research to determine ways to increase efficiency throughout the casting process.

Farrell-Poe, Kathryn L., and James E. Etzel. 1992. "Comparison of Phosphate Complexing of Heavy Metals Through Qualitative Analysis." *Proceedings of the 47th Industrial Waste Conference*. Purdue University, West Lafayette, Indiana, May 11-13. pp. 691-698.

Farrell-Poe and Etzel have measured the soluble concentrations of copper, nickel, and zinc in solution as a function of pH for hydroxide and phosphate additions. Six types of phosphate materials were compared as potential phosphate sources. The study concluded that phosphate complexation is an alternative to hydroxide precipitation for metal removal from wastewater.

Farrell-Poe, Kathryn L., and James E. Etzel. 1991. "Complexing of Heavy Metals with Phosphates." *Proceedings of the 46th Industrial Waste Conference*. Purdue University, West Lafayette, Indiana, May 14-16. pp. 329-337.

This paper discusses treatment of wastewater with phosphate addition to remove copper, nickel, and zinc. The paper also mentions the use of phosphate addition to immobilize copper, lead, nickel, and cadmium in waste sludges. This study concluded that triple superphosphate (TSP) [$\text{Ca}(\text{H}_2\text{PO}_4)_2$] addition will remove metals from wastewater and form a sludge that is not leachable by the EP Toxicity test. The removal and immobilization of the metal ions is attributed to a surface reaction phenomenon between the metal ion and the TSP.

Hoyt, Daryl F. 1988. "A Foundryman's Perspective on Sand Reclamation." *American Foundrymen's Society Transactions*, 96:555-566.

This paper discusses washing, thermal, and mechanical methods for sand reclamation and describes selection criteria for reclamation systems and quality control tests for the reclaimed sand.

Hwang, J. Y., G. D. Mendenhall, X. Liu, T. J. Hozeska, A. M. Hein, R. I. Kramer, J. W. Keck, Y. Wu, Uma S. Ghose, Gerhard Heimowski, Scott L. Holman, and John Holman. 1992. *Development of a Steel-Foundry Waste Sand Reclamation Process*. Solid Waste Alternatives Program Project, WRRD-1-31-00054. Michigan Technological University, 1400 Townsend Drive, Houghton,

Michigan 49931-1295. Director of the Institute of Minerals Processing, (906) 487-2600; fax (906) 487-2921.

This report gives the details of a program to optimize recycling methods for mixed silica and chromite mold sands. The program examined a number of mechanical and thermal methods for cleaning spent mold sand.

Jacobs, 1989. *Reducing California's Metal-Bearing Waste Streams*. Technical report prepared by the Jacobs Engineering Group, Inc, Pasadena, California, for the California Department of Health Services, Toxic Substances Control Division, Alternative Technology Section.

This report describes a variety of metal-bearing wastestreams produced by California industries and describes and assesses methods to reduce the volume or toxicity of the wastes.

LaChapelle, Gary W., and Jeffery S. Dyas. 1993. "Cyprus Miami Property Overview and Mine Modernization." *Mining Engineering*, 45(4):344-346.

This article describes the ore deposit, mining operations, and smelting operations at Cyprus Miami Mining, Highway 60, P.O. Box 4444, Claypool, AZ 85532, (602) 473-7135. Additional discussions by telephone were conducted with company personnel to clarify the use of recycled materials for metals recovery and as a source of silicate flux.

Lawson, D., and D. S. Leidel. 1984. "Reclaimed Shakeout Sand as New Sand Substitute in Green Sand Molding Lines." *American Foundrymen's Society Transactions*, 92:1-6.

This article discusses a mechanical method for cleaning and reclaiming bentonite-bonded mold sand. Various parameters to characterize the quality of reclaimed sand and molds made from reclaimed sand are discussed. The article concludes that bentonite-bonded sand can be reclaimed successfully by mechanical processing.

Lead Industries Association, Inc., 295 Madison Avenue, New York, New York 10017. Tel. (212) 578-4750, fax (212) 684-7714.

A 14-minute video program entitled "Control of Exposure to Lead in the Brass and Bronze Industry" is available from the Lead Industries Association. The program is designed for owners and workers in industries that produce brass or bronze ingots, or castings made of brass or bronze. The cost of the video is \$27.99.

Ma, Qi Ying, Samuel J. Traina, Terry J. Logan, and James Ryan. 1993. "In Situ Lead Immobilization by Apatite." *Environmental Science and Technology*, 27(9):1803-1810.

The program tested addition of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] or natural apatite as a potential in situ treatment to immobilize lead. Apatite immobilization of various forms of lead was tested. Lead forms treated include aqueous solution, on ion-exchange resin, and in soil; these all were tested. In all cases, the aqueous solubility of lead was greatly reduced by apatite addition. Chemical analysis, x-ray diffraction,

and electron microscope analysis indicate that lead immobilization occurs by dissolution of hydroxyapatite followed by reprecipitation of hydroxypyromorphite $[\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2]$.

Miske, Jack C. 1992. "100 Years of Sand Preparation and Reclamation." *Foundry Management and Technology*, 120(9):174-181.

This article summarized the history of sand mold preparation and the technologies used for sand reclamation over the last 100 years.

Mondloch, P. A., D. W. Becker, and L. Euvrard. 1987. "Effects of Process Parameters on Leachable Lead in Brass Foundry Sands." *American Foundrymen's Society Transactions*, 95:385-392.

This paper describes the results of testing of four methods to reduce leachable lead content of foundry sand. The methods tested were sieve separation to reduce lead content, adjustment of pouring temperature, adjustment of zinc content, and adjustment of the mold atmosphere. Physical separation of lead from the sand was found to be ineffective. The study concluded that reduced pouring temperatures reduced the lead content of the sand but not sufficiently to render it nonhazardous. Most lead in the sand is in the form of lead nodules. This result conflicts with the results of other studies and is attributed to the shorter exposure times used in this study. The lead deposits preferentially on zinc oxide-coated sand particles. Variations of zinc in the poured alloy do not affect the leachability of the lead. Coating the mold with organic or inorganic carbon sources to cause a reducing atmosphere at the mold surface decreased leachable and total lead at the interface but increased it deeper in the mold resulting in no reduction of leachable or total lead. The study indicates that process changes are unlikely to sufficiently reduce lead leachability. Options described for management of spent sand containing leachable lead include disposal at a permitted RCRA landfill, sand reclamation, use of a permanent mold, and development of low-lead or lead-free brass.

Nagel, D. L., R. R. Stanforth, P. E. Duranceau, and T. P. Kunes. 1983. "Treatment of Hazardous Foundry Melting Furnace Dust and Sludges." *American Foundrymen's Society Transactions*, 91:715-720.

This paper describes a variety of options for on-site treatment of foundry wastes. Options discussed include mixing with a nonhazardous waste; chemical treatment with phosphate, clay, or metallic iron; solidification/stabilization; or removal of the toxic metals from the waste. The article advises systematic evaluation of the options to identify the best approach for site-specific needs.

Ostrom, T. R., J. Biel, W. Wagner, R. A. Flinn, and P. K. Trojan. 1982. "Interface Reactions Between Molding Sand and Leaded Copper Alloys." *American Foundrymen's Society Transactions*, 90:701-709.

This paper reports the results of a study to determine the forms of lead present in molding sand used with leaded copper alloys, the mechanisms of lead intrusion into

the sand, and methods to reduce lead levels in the sand. The study examined the alloy sand interface for portions of full-scale castings and from specimens prepared in the laboratory. Lead was found as metal due to mechanical entrapment in the sand, and as oxides and silicate, mainly due to reaction of the lead with the bentonite binder.

Ostrom, T. R., and P. K. Trojan. 1986. "Lead Compound Formation in Alloy CDA 84400 and the Effect of Iron on Leachable Lead." *American Foundrymen's Society Transactions*, 94:725-734.

This paper reports results on the transfer and leaching of lead in foundry sand when casting a higher zinc content copper-based alloy (CDA 84400). The results are compared to results of an earlier study with a medium lead alloy (CDA 83600) and a high lead (CDA 94300). The report describes the formation of lead containing compounds in and penetration into foundry sand while casting CDA 84400 and the effects of iron addition on the leachability of lead. The mold system tested was bentonite bonded olivine sand. Lead in the sand was characterized as being present mainly as oxides or silicates. Phosphorus in the alloy increased lead penetration into the sand. All tests with addition of 100 ppm lead equivalent added to the sand as PbO, PbSiO₃, or alloy showed high EP Toxicity leachable lead (over 40 ppm). Addition of 1 wt % iron reduced lead leachability dramatically for the PbO and PbSiO₃. Leachability of the alloy also decreased due to iron addition, but the reduction of solution concentration was only about 50%.

Ostrom, T. R., and P. K. Trojan. 1988. "The Leachability of Lead From Brass and Bronze Foundry Waste Sand Streams." *American Foundrymen's Society Transactions*, 96:435-442.

This paper describes the effects of a variety of leaching conditions on lead solubility and outlines possible methods to reduce lead penetration into the mold sand. Iron metal was shown to effectively reduce leachate concentrations of lead in the EP toxicity and TCLP tests. Iron salts had varying effects with both the ferric and ferrous compounds generally being effective but ferrous acetate being ineffective. Lead leachability by the acid rain test (nitric and sulfuric acid at pH 5) also was studied. The leachate concentration of lead was lower for all forms of lead in the acid rain tests.

In the mold penetration portion of the testing, zircon mold coating was found to be effective in preventing lead penetration into the sand. Silicate bonding with CO₂ activation reduced lead penetration but still allowed formation of lead silicates at the mold interface. Organic additions such as sea coal or dextrin to Southern bentonite-bonded dry sand suppressed the lead reaction with the sand and decreased the lead penetration into the mold, apparently due to the carbon source causing reducing conditions at the mold interface.

Ostrom, T. R., B. P. Winter, and P. K. Trojan. 1985. "Lead Transfer from Copper-Base Alloys into Molding Sand." *American Foundrymen's Society Transactions*, 93:757-762.

The study found that lead in spent foundry sand is present as metal in the alloy, oxide, and silicates. A 1% iron metal addition reduced lead leachability by 5 ppm. The form of the iron was important, with iron present as rust (ferric hydroxide)

showing little reduction in lead leachability. Zinc, present as ZnO, greatly reduced the effectiveness of the iron addition. Bentonite at a concentration of 4% reduced the lead leachability when no iron was added. When iron is added to the combination of lead metal and bentonite, the lead leachability increases.

Peters, D. M. (Ed). 1993. Section D: Sand/Binders/Sand Preparation/Coremaking. *Foundry Management & Technology, 1993 Databook for Metalcasters*, 121(1).

This article summarizes information on types of sand and binders, techniques for sand preparation, sand conditioning, sand heating and temperature control, sand reclamation, various types of coremaking, and nonhazardous binders.

Smith, Virginia D. 1992. "The Greening of the Foundry Industry." *Foundry Management and Technology*, 120(9):158-160.

This article reviews environmental problems in the foundry industry and discusses approaches to reduce adverse environmental effects from foundry activities.

Smith, Lloyd, Gary L. Tinkleberg, and Barbara A. Doeza. 1991. *Stabilization of Lead-Containing Abrasive Blasting Debris*. Prepared for the Federal Highway Administration. April.

This report reviews the regulatory effects of the June 1, 1990 (55 FR 22520-22720) final rule on land disposal restriction on management of debris from lead-based paint removal and details the results of evaluations of four candidate solidification/stabilization reagents. The reagents tested were Type I Portland cement, lime, elemental iron, and sodium bicarbonate. Of the four stabilizing methods tested, Portland cement, iron, and sodium bicarbonate reliably reduced the TCLP leachable lead concentration to less than 5 mg/L. Lime was effective over a limited range of added amounts, but increased amounts of lime raised the pH above the minimum solubility point for lead. Portland cement addition of 10% was sufficient to meet TCLP limits. Sodium bicarbonate was effective at relatively high levels of addition. With fine iron filings, only a 1% addition is required to reduce the leachable lead to below the TCLP limit. Steel blasting grit required additions of about 6% to reduce leachable lead to below the TCLP limit. The report mentions work in the foundry industry as indicating that the iron stabilizes lead by a redox reaction and mentions the concern that the stabilizing effect would be lost once the elemental iron surface is occluded by rust. One approach mentioned is adding iron to the blasting grit to ensure that the paint removal debris is nonhazardous and then treating the debris with Portland cement to provide some longer term stabilization.

Stanforth, R., D. Nichols, T. Kunes, D. Oman, D. Trainor, R. Ham, W. Boyle, and F. Blaha. 1988. "Foundry Waste Landfills and Ground Water Quality." *American Foundrymen's Society Transactions*, 96:873-880.

This paper summarizes a study of leaching of metals from ferrous foundry wastes in monofilled waste industrial landfills. Groundwater samples from upgradient and downgradient wells around 7 foundry landfills were collected. The samples were analyzed to determine levels of As, Ba, Cd, Cr, Pb, Hg, Se, Ag, TDS, COD, Cl⁻, F⁻,

Fe, Mn, SO₄, and phenols. Leach testing was performed on samples using the EP toxicity test, the EP toxicity test with water rather than an acetate buffer, and a water leach test using three elutions. Comparison of the laboratory leaching tests results and field analyses indicated that attempting to establish a quantitative relationship between leach tests and landfill leaching is a complex process.

Stephens, William A., Thomas R. Stolzenburg, Robert R. Stanforth, and James Etzel. 1984. "Iron Conditioning of Sludge from Foundry Furnace Emission Control Systems for Elimination of EP Toxicity." *Proceedings of the 39th Industrial Waste Conference*. Purdue University, West Lafayette, Indiana, May 8-10. pp. 511-514.

This paper reports results of tests of methods to reduce lead leachability in sludges originating from emission control systems for metal-melting cupolas. Aluminum sulfate additions were not effective for immobilizing lead, but ferric sulfate additions were successful. Data are presented on the sorption of a variety of metals to gels of ferric hydroxide or aluminum hydroxide as a function of pH. The graphs show >95% sorption of lead to ferric hydroxide at pH 4 or higher. For similar partitioning of lead sorption to aluminum hydroxide, the pH must be above pH 6. The authors also note that iron added as ferric hydroxide, ferric sulfate, or metallic iron is effective in all forms for immobilization of lead. Lead immobilization is believed to be the result of a combination of adsorption to ferric hydroxide, reduction of divalent lead to lead metal, and pH neutralization.

Systech Environmental Corporation. 1993. 245 North Valley Road, Xenia, Ohio 45385-9354. Personal communication, Rick Haverland, 1-800-888-8011.

Systech Resource Recovery Services accepts nonhazardous wastestreams containing low levels of transition metals as feedstock for cement kilns. Systech has a network of 16 cement kilns to process by-product materials. Examples of acceptable feed materials include:

- silica sources, abrasives, ceramics, clay filters and sludges, foundry sand, sand blast media, and water filtration media
- alumina sources such as catalysts, ceramics and refractories, coal ash, and adsorbents for gases and vapors
- calcium sources such as lime sludges
- iron sources such as foundry baghouse residuals and iron mill scale.

Trojan, P. K., and T. R. Ostrom. 1987. "Possible Controls for Lead as Found in Brass and Bronze Molding Sands." *American Foundrymen's Society Transactions*, 95:711-722.

This paper studies the role of iron in reducing lead leachability from molding sands and possible methods to reduce the penetration of lead into the mold. Addition of iron metal was able to reduce lead leaching with the EP Toxicity test, the TCLP test, and a simulated acid rain test. In most cases, 2 wt % iron was effective, but in one

case an addition of 10 wt % iron was needed. Testing also showed that addition of metallic iron will remove lead from solution, iron in solution prevents lead from going into solution if acetate is not present, and lead is not removed from solution by addition of dissolved iron ions.

The portion of the research studying ways to reduce lead penetration into the mold looked at three mold surface coatings: graphite in isopropyl alcohol, zircon in water, and zircon and graphite in water. The zircon mold coating was found to reduce lead penetration.

In a comment, P.J. Vasquez of Lee Brass Company expressed concern that iron addition has not been shown to be permanent and should not be proposed as a treatment. The author responded that the study was aimed at determining the nature of the iron/lead interaction not to propose it as a treatment method.

Trojan, P. K., T. R. Ostrom, J. Biel, and R. A. Flinn. 1984. "Leaded Copper Alloy Reactions With Molding Sands and Sand Response to Acid Leaching." *American Foundrymen's Society Transactions*, 92:793-802.

This paper reports analysis of the interaction of medium-lead (CDA 83600) and high-lead (CDA 94300) alloy with casting sand and the leachability of the lead compounds potentially present in spent foundry sand. The study concluded that higher lead content in the alloy results in more lead penetration into the sand; lead can be present as metal, oxides, and silicates; phosphorous in the alloy causes a thicker scale on the metal surface; and zinc not in solution appears as complex oxides and silicates and is not always associated with the presence of lead. Testing by the EP Toxicity method indicated lead leachability over regulatory limits for both actual foundry sands and clean sand spiked with known amounts of alloy, lead oxide, and lead silicate. Treatment methods considered for reduction of leachable lead levels include chemical conversion to silicate by heating, mechanical separation, and thermal treatment during cleaning of the sand for reuse.

Turpin, P. D., and B. E. Dudzik. 1987. "Case Studies in Successful Foundry Waste Treatment." *American Foundrymen's Society Transactions*, 95:695-698.

This paper presents two case studies of methods to reduce the cost of foundry waste management. The methods discussed include sludge dewatering and treatment of dry hazardous wastes by using other foundry wastes as the treatment additive. The treatment approach discussed is the addition of a foundry wastestream containing iron metal to other foundry wastes showing lead leachability. The treated wastes included excess system sand, casting cleaning sand, and casting cleaning and finishing dust. The lead leaching from the waste was controlled over nine acidic leaching steps in the EPA Multiple Extraction Procedure.

Turpin, Paul D., Robert R. Stanforth, and Thomas P. Kunes. 1990. "Treatment of EP-Toxic Foundry Waste: Regulatory and Technical Overview." Presented at Cast-Expo 1990, Detroit, Michigan, April 21-24. American Foundrymen's Society.

This paper reviews alternatives to manage metal-bearing foundry wastes. The waste types considered include foundry melting furnace emission control wastes and waste sands and dusts from brass and bronze casting. The paper outlines a systematic approach to minimization of waste and treatment of residuals. The treatment options discussed are proprietary processes, solidification/stabilization with cements and pozzolans, precipitation, pH adjustment, and chemical reduction of lead by metallic iron. The paper reports consistent reduction of leachable lead levels in the range of 10 to 120 mg/L for untreated waste to nondetectable to 3 mg/L for waste containing iron metal particulate. The paper describes electrochemical reduction of lead ions to lead metal by the iron as the likely mechanism for control of lead leachability. The paper describes the results of 3 years of experience with iron addition. It appears that the results represent a sequence of separate samples taken over a 3-year period, not a long-term test on one set of samples for 3 years.

Turpin, Paul D., Thomas R. Stolzenburg, William A. Stephens, and Thomas P. Kunes. 1985. "Methods to Treat EP Toxic Foundry Wastes and Wastewaters." *American Foundrymen's Society Transactions*, 93:737-740.

This article reviews foundry wastes that can exhibit EP toxicity and outlines options for treatment to eliminate the toxicity characteristic. The discussion applies generally to melt emission control dusts or sludges from ferrous foundries and a variety of emission control dusts or sludges and spent casting sand from nonferrous foundries. Chemical treatment by addition of ferric hydroxide, aluminum hydroxide, magnesium hydroxide, metallic iron, lime, and phosphate are discussed. Treatment mechanisms described include precipitation, adsorption, chemical reduction, and pH control of solubility. The article describes some of the major applications of each of the stabilization mechanisms. Phosphate addition is noted as precipitating a stable, low-solubility salt of lead. Ferric hydroxide is described as being far more effective than alum in reducing EP lead leachability. Metallic iron was found to effectively reduce lead leachability. The proposed mechanism is a redox reaction that reduces divalent lead to metallic lead. The article also notes that the solubility of lead and many other metals is low in moderately alkaline media and discusses slaked lime as a simple and cost-effective additive to raise pH. The article also mentions that magnesium hydroxide is more desirable for pH adjustment because the pH cannot be raised too high by magnesium hydroxide additions. However, $Mg(OH)_2$ is more expensive than lime.

Turpin, Paul D., Thomas R. Stolzenburg, William A. Stephens, and Thomas P. Kunes. 1985. "Treatment of EP-Toxic Foundry Waste: Regulatory and Technical Overview." *American Foundrymen's Society Transactions*, 93:737-740.

This article updates the review of waste management options for various foundry wastes with a leachability toxicity characteristic. The article outlines an approach to evaluating the effects of technical factors, materials-handling factors, regulatory factors, and economic factors on selection of waste management options. The article mentions the importance of considering waste minimization before treatment. The article also points out that meeting the minimum requirements of a regulatory test such as the EP Toxicity Test may not be sufficient and suggests consideration of

additional long-term leaching tests or neutral pH water tests. Treatment options outlined by the article include solidification/stabilization (e.g., cement, pozzolan, or silicate), chemical precipitation (e.g., phosphate addition), pH solubility control (eg lime addition), and chemical reduction (e.g., iron metal dust addition). The article mentions the potential effects of treatment, storage, and disposal (TSD) permitting and Land Disposal Restriction (LDR) treatment standards (i.e., the BDATs) on selection of waste management alternatives.

Van Note, K., C. C. Miller, and J. C. Lichter. 1985. "Foundry Waste Stabilization Laboratory Testing and Conceptual Design." *American Foundrymen's Society Transactions*, 93:395-404.

This paper describes laboratory testing and conceptual designs and cost estimates for solidification/stabilization treatment of foundry wastes. The binders tested were Type I Portland cement, Type I Portland cement with calcium carbide, and Type I Portland cement with lime. The Portland cement and lime combination gave the greatest reduction in lead and cadmium leachability. Portland cement alone also was effective and could be implemented at lower cost because the lime hopper and feeder were not required.

Wisconsin Department of Natural Resources. 1993. *Foundry Waste Beneficial Reuse Study*. PUBL-SW-181-93, Bureau of Solid and Hazardous Waste Management, Madison, Wisconsin.

This report was prepared to fulfill the requirements of 1991 Wisconsin Act 269, Section 9142(3dp), requiring the Wisconsin Department of Natural Resources to identify ways to reuse foundry sand. The report describes current industry practices, potential reuse options, results of the characterization of foundry sand, potential environmental risks, and impediments to the reuse of foundry sand. The report presents conclusions on likely beneficial reuse options and recommends changes to increase foundry sand reuse in a responsible manner.

APPENDIX B
SOLUBILITY EQUILIBRIUM DATA

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References [*]
Acetates			
H(CH ₃ CO ₂) (acetic acid)	H(CH ₃ CO ₂) ⇌ H ⁺ + CH ₃ CO ₂ ⁻	-4.757 ± 0.002	D, p. 3 ⁽³⁾
Fe(CH ₃ CO ₂) ⁺	Fe(CH ₃ CO ₂) ⁺ ⇌ Fe ²⁺ + CH ₃ CO ₂ ⁻	-1.4	D, p. 5
Fe(CH ₃ CO ₂) ⁺	Fe(CH ₃ CO ₂) ²⁺ ⇌ Fe ³⁺ + CH ₃ CO ₂ ⁻	-3.38 (20.1 = 0.1)	D, p. 5 ⁽³⁾
Fe(CH ₃ CO ₂) ⁺	Fe(CH ₃ CO ₂) ₂ ⁺ ⇌ Fe ³⁺ + 2CH ₃ CO ₂ ⁻	-6.5 (20.1 = 0.1)	D, p. 5 ⁽³⁾
Fe(CH ₃ CO ₂) ₃ ⁰	Fe(CH ₃ CO ₂) ₃ ⁰ ⇌ Fe ³⁺ + 3CH ₃ CO ₂ ⁻	-8.3 (20.1 = 0.1)	D, p. 5 ⁽³⁾
Pb(CH ₃ CO ₂) ⁺	Pb(CH ₃ CO ₂) ⁺ ⇌ Pb ²⁺ + CH ₃ CO ₂ ⁻	-2.4	Geochem, 1990 ⁽⁴⁾
		-2.68	D, p. 6 ⁽³⁾
Pb(CH ₃ CO ₂) ₂	Pb(CH ₃ CO ₂) ₂ ⇌ Pb ²⁺ + 2CH ₃ CO ₂ ⁻	-4.1	Geochem, 1990 ⁽⁴⁾
		-4.08	D, p. 6 ⁽³⁾
Pb(CH ₃ CO ₂) ₃ ⁻	Pb(CH ₃ CO ₂) ₃ ⁻ ⇌ Pb ²⁺ + 3CH ₃ CO ₂ ⁻	-3.60 (I = 3.0)	D, p. 6 ⁽³⁾
Pb(CH ₃ CO ₂) ₄ ²⁻	Pb(CH ₃ CO ₂) ₄ ²⁻ ⇌ Pb ²⁺ + 4CH ₃ CO ₂ ⁻	-2.9 (I = 3.0)	D, p. 6 ⁽³⁾
Hydroxides			
H ₂ O	H ⁺ + OH ⁻ ⇌ H ₂ O	13.993 ± 0.003	C, p. 1 ⁽³⁾
Al(OH) ₃ (gibbsite)	Al(OH) ₃ + 3H ⁺ ⇌ Al ³⁺ + 3H ₂ O	8.5 ± 0.1	E, p. 121 ⁽³⁾
AlOH ²⁺	Al ³⁺ + H ₂ O ⇌ AlOH ²⁺ + H ⁺	-4.97 ± 0.02	E, p. 113 ⁽³⁾
Al(OH) ₂ ⁺	Al ³⁺ + 2H ₂ O ⇌ Al(OH) ₂ ⁺ + 2H ⁺	-9.9 (I + 0.1)	E, p. 114 ⁽³⁾
Al(OH) ₃ ⁰	Al ³⁺ + 3H ₂ O ⇌ Al(OH) ₃ ⁰ + 3H ⁺	-15.6 (I + 0.1)	E, p. 114 ⁽³⁾
Al(OH) ₄ ⁻	Al ³⁺ + 4H ₂ O ⇌ Al(OH) ₄ ⁻ + 4H ⁺	-23.0 ± 0.3	E, p. 115 ⁽³⁾
CaOH ⁺	CaOH ⁺ ⇌ Ca ²⁺ + OH ⁻	-1.510	A, p. 146
Fe(OH) ₂ (s)	Fe(OH) ₂ ⇌ Fe ²⁺ + 2OH ⁻	-14.5 ± 0.6	A, p. 391
		-15.1	C, p. 5
FeOH ⁺	FeOH ⁺ ⇌ Fe ²⁺ + OH ⁻	-4.5	C, p. 5 ⁽³⁾
FeOH ⁺	FeOH ⁺ + H ⁺ ⇌ Fe ²⁺ + H ₂ O	+9.5 ± 0.1	E, p. 228

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References [*]
Fe(OH) ₂ (act)	Fe(OH) ₂ ⇌ Fe ²⁺ + 2OH ⁻	+12.85 ± 0.2	E, p. 228
Fe(OH) ₂	Fe(OH) ₂ ⇌ Fe ²⁺ + 2OH ⁻	-7.4	C, p. 5
Fe(OH) ₃ ⁻	Fe(OH) ₃ ⁻ ⇌ Fe ²⁺ + 3OH ⁻	-10.0	C, p. 5
Fe(OH) ₄ ²⁻	Fe(OH) ₄ ²⁻ ⇌ Fe ²⁺ + 4OH ⁻	-9.6	C, p. 5
Fe(OH) ₃ (s)	Fe(OH) ₃ ⇌ Fe ³⁺ + 3OH ⁻	-38.8 ± 0.2	C, p. 7 ⁽³⁾
α-FeOOH	α-FeOOH + H ₂ O ⇌ Fe ³⁺ + 3OH ⁻	41.5 (* * 7 - 41.1 at I=3)	C, p. 7 ⁽³⁾
α-Fe ₂ O ₃	0.5(α-Fe ₂ O ₃) + 1.5(H ₂ O) ⇌ Fe ³⁺ + 3OH ⁻	-42.7	C, p. 7
FeOH ²⁺	FeOH ²⁺ ⇌ Fe ³⁺ + OH ⁻	-11.81 ± 0.03	C, p. 7 ⁽³⁾
Fe(OH) ₂ ⁺	Fe(OH) ₂ ⁺ ⇌ Fe ³⁺ + 2OH ⁻	-22.3	C, p. 7 ⁽³⁾
Fe(OH) ₄ ⁺	Fe(OH) ₄ ⁺ ⇌ Fe ³⁺ + 4OH ⁻	-34.4	C, p. 7
Fe ₂ (OH) ₂ ⁺	Fe ₂ (OH) ₂ ⁺ ⇌ 2Fe ³⁺ + 2OH ⁻	-25.1	C, p. 7 ⁽³⁾
Fe ₃ (OH) ₄ ⁺	Fe ₃ (OH) ₄ ⁺ ⇌ 3Fe ³⁺ + 4OH ⁻	-49.7	C, p. 7 ⁽³⁾
PbOH ⁺	Pb ²⁺ + H ₂ O ⇌ PbOH ⁺ + H ⁺	-7.7 -7.23	Geochem, 1990 ⁽⁴⁾ G, p. 91
PbOH ⁺	Pb ²⁺ + OH ⁻ ⇌ PbOH ⁺	6.3 6.77	C, p. 10 ⁽³⁾ F, p. 36
Pb(OH) ₂ (freshly precipitated)	Pb(OH) ₂ ⇌ Pb ²⁺ + 2OH ⁻	-14.94	F, p. 697
Pb(OH) ₂ (aged solid)	Pb(OH) ₂ ⇌ Pb ²⁺ + 2OH ⁻	-19.85	F, p. 697
Pb(OH) ₂ ⁰	Pb ²⁺ + 2H ₂ O ⇌ Pb(OH) ₂ ⁰ + 2H ⁺	-17.8 -17.12 -16.9 -16.93	Geochem, 1990 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾ G, p. 91 H, p. 77
Pb(OH) ₂ ⁰	Pb ²⁺ + 2OH ⁻ ⇌ Pb(OH) ₂ ⁰	10.9 11.07	C, p. 10 (c) F, p. 36

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References [*]
$\text{Pb}(\text{OH})_3^-$	$\text{Pb}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_3^- + 3\text{H}^+$	-28.1 -28.06 -28.1	Geochem, 1990 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾ G, p. 91
$\text{Pb}(\text{OH})_3^-$	$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_3^-$	13.9 13.9	C, p. 10 (c) F, p. 36
$\text{Pb}(\text{OH})_4^{2-}$	$\text{Pb}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pb}(\text{OH})_4^{2-} + 4\text{H}^+$	-39.5 -39.699 -39.7	Geochem, 1990 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾ G, p. 91
$\text{Pb}_2\text{OH}^{3+}$	$2\text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Pb}_2\text{OH}^{3+} + \text{H}^+$	-6.4 -6.36	Geochem, 1990 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾
$\text{Pb}_3\text{OH}^{3+}$	$2\text{Pb}^{2+} + \text{OH}^- \rightleftharpoons \text{Pb}_3\text{OH}^{3+}$	7.6 7.63	C, p. 10 ⁽³⁾ F, p. 36
$\text{Pb}_3(\text{OH})_4^{2+}$	$3\text{Pb}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pb}_3(\text{OH})_4^{2+} + 4\text{H}^+$	-23.9 -23.88	Geochem, 1990 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾
$\text{Pb}_3(\text{OH})_4^{2+}$	$3\text{Pb}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Pb}_3(\text{OH})_4^{2+}$	32.1 32.1	C, p. 10 ⁽³⁾ F, p. 36
$\text{Pb}_4(\text{OH})_4^{4+}$	$4\text{Pb}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Pb}_4(\text{OH})_4^{4+} + 4\text{H}^+$	-20.89	Lindsay, 1979 ⁽⁴⁾
$\text{Pb}_4(\text{OH})_4^{4+}$	$4\text{Pb}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Pb}_4(\text{OH})_4^{4+}$	35 35.09	C, p. 10 ⁽³⁾ F, p. 36
$\text{Pb}_6(\text{OH})_8^{4+}$	$6\text{Pb}^{2+} + 8\text{H}_2\text{O} \rightleftharpoons \text{Pb}_6(\text{OH})_8^{4+} + 8\text{H}^+$	-43.58	Lindsay, 1979 ⁽⁴⁾
$\text{Pb}_6(\text{OH})_8^{4+}$	$6\text{Pb}^{2+} + 8\text{OH}^- \rightleftharpoons \text{Pb}_6(\text{OH})_8^{4+}$	68.4 68.31	C, p. 10 ⁽³⁾ F, p. 36
Carbonates			
H_2CO_3 (carbonic acid)	$\text{H}_2\text{O} + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{CO}_3$	-1.46	F, p. 697
H_2CO_3 (carbonic acid)	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	-6.35	F, p. 697
HCO_3^-	$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	-10.33 -10.33	F, p. 697 H, p. 77

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References [*]
PbCO ₃ (cerussite)	PbCO ₃ (cerussite) \rightleftharpoons Pb ²⁺ + CO ₃ ²⁻	-13.2 -13.13 -13.11	Geochem, 1909 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾ F, p. 697 (s)
PbCO ₃	Pb ²⁺ + CO ₃ ²⁻ \rightleftharpoons PbCO ₃ ⁰ (aq)	7.1 7.1 7.1	F, p. 36 G, p. 91 H, p. 77
Pb ₃ (CO ₃) ₂ ²⁻	Pb ²⁺ + 2CO ₃ ²⁻ \rightleftharpoons Pb ₃ (CO ₃) ₂ ²⁻	10.33 10.3 10.4	F, p. 36 G, p. 91 H, p. 77
Pb ₂ CO ₃ Cl ₂ (phosgenite)	Pb ₂ CO ₃ Cl ₂ (phosgenite) + 2H ⁺ \rightleftharpoons 2Pb ²⁺ + CO ₂ (g) + H ₂ O + 2Cl ⁻	-1.80	Lindsay, 1979 ⁽⁴⁾
Pb ₂ CO ₃ Cl ₂ (phosgenite)	Pb ₂ CO ₃ Cl ₂ (phosgenite) \rightleftharpoons 2Pb ²⁺ + 2Cl ⁻ + CO ₃ ²⁻	-19.81	Minteqa2, 1990 ⁽⁴⁾
Pb ₃ (CO ₃) ₂ (OH) ₂ (hydrocerussite)	Pb ₃ (CO ₃) ₂ (OH) ₂ (hydrocerussite) + 6H ⁺ \rightleftharpoons 3Pb ²⁺ + 2CO ₂ (g) + 4H ₂ O	17.51	Lindsay, 1979 ⁽⁴⁾
Pb ₃ (CO ₃) ₂ (OH) ₂ (c)	Pb ₃ (CO ₃) ₂ (OH) ₂ (c) + 2H ⁺ \rightleftharpoons 3 Pb ²⁺ + 2CO ₃ ²⁻ + 2H ₂ O	-17.46 -18.9 -18.8	Minteqa2, 1990 ⁽⁴⁾ Geochem, 1990 ⁽⁴⁾ H, p. 77
Pb ₃ (CO ₃) ₂ (OH) ₂ (s)	Pb ₃ (CO ₃) ₂ (OH) ₂ (s) \rightleftharpoons 3 Pb ²⁺ + 2CO ₃ ²⁻ + 2OH ⁻	-46.78	F, p. 697
PbCO ₃ · PbO (c)	PbCO ₃ · PbO (c) + 4H ⁺ \rightleftharpoons 2Pb ²⁺ + CO ₂ (g) + 2H ₂ O	17.39	Lindsay, 1979 ⁽⁴⁾
Pb ₂ OCO ₃ (c)	Pb ₂ OCO ₃ (c) + 2H ⁺ \rightleftharpoons 2Pb ²⁺ + H ₂ O + CO ₃ ²⁻	-0.5	Minteqa2, 1990 ⁽⁴⁾
Pb ₃ O ₂ CO ₃ (c)	Pb ₃ O ₂ CO ₃ (c) + 4H ⁺ \rightleftharpoons 3Pb ²⁺ + 2H ₂ O + CO ₃ ²⁻	11.02	Minteqa2, 1990 ⁽⁴⁾
Oxides			
Fe ₃ O ₄ (c)	1/3(Fe ₃ O ₄) + 2H ⁺ + 1/3(H ₂) \rightleftharpoons Fe ²⁺ + 4/3(H ₂ O)	+12.02	E, p. 229
PbO (yellow)	PbO + 2H ⁺ \rightleftharpoons Pb ²⁺ + H ₂ O	12.89 12.9 12.9	Lindsay, 1979 ⁽⁴⁾ Geochem, 1984 ⁽⁴⁾ Geochem, 1990 ⁽⁴⁾
PbO (yellow)	PbO + H ₂ O \rightleftharpoons Pb ²⁺ + 2OH ⁻	-15.1	C, p. 10
PbO · 0.33H ₂ O	PbO · 0.33H ₂ O + 2H ⁺ \rightleftharpoons Pb ²⁺ + 1.33H ₂ O	12.98	Minteqa2, 1990 ⁽⁴⁾

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References ³
PbO (red)	$\text{PbO} + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{O}$	12.72 12.7	Lindsay, 1979 ⁽⁴⁾ Geochem, 1990 ⁽⁴⁾
PbO (red)	$\text{PbO} + \text{H}_2\text{O} \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^-$	-15.3	C, p. 10
PbO (c)	$\text{PbO} + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{O}$	8.2 12.72	Geochem, 1990 ⁽⁴⁾ E, p. 358
PbO (c)	$\text{PbO} + \text{H}_2\text{O} \rightleftharpoons \text{Pb(OH)}_2 \text{ (aq)}$	-4.4	E, p. 358
Pb(OH) ₂ (c)	$\text{Pb(OH)}_2 + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	8.16 8.15	Lindsay, 1979 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾
Pb(OH) ₂ (litharge)	$\text{Pb(OH)}_2 + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	12.72	Minteqa2, 1990 ⁽⁴⁾
Pb(OH) ₂ (massicot)	$\text{Pb(OH)}_2 + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	12.91	Minteqa2, 1990 ⁽⁴⁾
Pb ₃ O ₄ (minium)	$\text{Pb}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \rightleftharpoons 3\text{Pb}^{2+} + 4\text{H}_2\text{O}$	73.79 73.69	Lindsay, 1979 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾
PbO ₂ (c)	$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	49.68 49.3	Lindsay, 1979 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾
Pb ₂ O ₃ (c)	$\text{Pb}_2\text{O}_3 + 2\text{e}^- + 6\text{H}^+ \rightleftharpoons 2\text{Pb}^{2+} + 3\text{H}_2\text{O}$	61.04	Minteqa2, 1990 ⁽⁴⁾
Pb(OH)Cl (laurionite)	$\text{Pb(OH)Cl} + \text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{O} + \text{Cl}^-$	0.623	Minteqa2, 1990 ⁽⁴⁾
Pb ₂ (OH) ₂ Cl (c)	$\text{Pb}_2(\text{OH})_2\text{Cl} + 3\text{H}^+ \rightleftharpoons 2\text{Pb}^{2+} + 3\text{H}_2\text{O} + \text{Cl}^-$	8.793	Minteqa2, 1990 ⁽⁴⁾
Pb ₂ O(OH) ₂ (c)	$\text{Pb}_2\text{O(OH)}_2 + 4\text{H}^+ \rightleftharpoons 2\text{Pb}^{2+} + 3\text{H}_2\text{O}$	-26.2	Minteqa2, 1990 ⁽⁴⁾
PbO ₂ (s)	$\text{PbO}_2 - K_{\text{sp}} \text{ *** Rx not given}$	-65.5	B, p. 137
Phosphates			
AlPO ₄ (s)	$\text{AlPO}_4 \rightleftharpoons K_{\text{sp}} \text{ *** Rx not given}$	-19.6±2.0	A, p. 391
AlPO ₄ ·2H ₂ O (variscite)	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O}$	-2.52	A, p. 177
PO ₄ ³⁻	$\text{PO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{PO}_4^-$	+19.55	A, p. 174
HPO ₄ ²⁻	$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$	-12.367 -12.35±0.02	A, p. 146 C, p. 56 ⁽⁵⁾

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ^m	References [*]
HPO ₄ ²⁻	HPO ₄ ²⁻ + H ⁺ ⇌ H ₂ PO ₄ ⁻	+7.205 [*] +7.199 ± 0.002	A, p. 174 C, p. 56 ⁽³⁾
H ₂ PO ₄ ⁻	H ₂ PO ₄ ⁻ ⇌ H ⁺ + HPO ₄ ²⁻	7.2	H, p. 77
H ₃ PO ₄ ⁰	H ₃ PO ₄ ⇌ H ⁺ + H ₂ PO ₄ ⁻	-2.148 -2.148 ± 0.001	A, p. 174 C, p. 56 ⁽³⁾
CaPO ₄ ⁻	CaPO ₄ ⁻ ⇌ Ca ²⁺ + PO ₄ ³⁻	-6.46 -6.46	A, p. 146 C, p. 56
CaPO ₄ ⁻	CaPO ₄ ⁻ + 2H ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻	+13.09	A, p. 174
CaHPO ₄ (s)	CaHPO ₄ ⇌ K _{sp} *** Rx not given	-6.73 ± 0.15	A, p. 391
CaHPO ₄ (monetite)	CaHPO ₄ + H ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻	-0.43 ± 0.17	A, p. 176
CaHPO ₄ · 2H ₂ O (s)	CaHPO ₄ · 2H ₂ O ⇌ K _{sp} *** Rx not given	-6.59	A, p. 391
CaHPO ₄ · 2H ₂ O (s)	CaHPO ₄ · 2H ₂ O ⇌ Ca ²⁺ + HPO ₄ ²⁻ + 2H ₂ O (l)	-6.58 ± 0.03	C, p. 56
CaHPO ₄ · 2H ₂ O (brushite)	CaHPO ₄ · 2H ₂ O + H ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻ + 2H ₂ O (l)	+0.63 ± 0.03	A, p. 176
CaHPO ₄ ⁰	CaHPO ₄ ⁰ + H ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻	+4.494	A, p. 174
CaHPO ₄ ⁰	CaHPO ₄ ⁰ ⇌ Ca ²⁺ + HPO ₄ ²⁻	-2.74 ± 0.06	C, p. 56 ⁽³⁾
CaH ₂ PO ₄ ⁺	CaH ₂ PO ₄ ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻	-1.407	A, p. 174
CaH ₂ PO ₄ ⁺	CaH ₂ PO ₄ ⁺ ⇌ Ca ²⁺ + H ₂ PO ₄ ⁻	-1.4 ± 0.6	C, p. 56 ⁽³⁾
Ca ₃ (PO ₄) ₂ (s)	Ca ₃ (PO ₄) ₂ ⇌ K _{sp} *** Rx not given	-26.6 ± 2.1	A, p. 391
Ca ₃ (PO ₄) ₂ (beta whitlockite)	Ca ₃ (PO ₄) ₂ + 4H ⁺ ⇌ 3Ca ²⁺ + 2H ₂ PO ₄ ⁻	+10.18	A, p. 176
Ca ₃ (PO ₄) ₂ OH (s)	Ca ₃ (PO ₄) ₂ OH ⇌ K _{sp} *** Rx not given	-57 ± 1	A, p. 391
Ca ₁₀ (PO ₄) ₆ (OH) ₂ (synthetic hydroxyapatite)	Ca ₁₀ (PO ₄) ₆ (OH) ₂ + 12H ⁺ ⇌ 10Ca ²⁺ + 6H ₂ PO ₄ ⁻ + 2OH ⁻	+3.7 ± 3.4	A, p. 178
Ca ₁₀ (PO ₄) ₆ Cl ₂ (synthetic chlorapatite)	Ca ₁₀ (PO ₄) ₆ Cl ₂ + 12H ⁺ ⇌ 10Ca ²⁺ + 6H ₂ PO ₄ ⁻ + 2Cl ⁻	+11.14	A, p. 178

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References ⁽³⁾
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (synthetic fluorapatite)	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 12\text{H}^+ \rightleftharpoons 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{F}^-$	-2.2 ± 1.3	A, p. 178
$\text{CaAlH}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$	$\text{CaAlH}(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O} + 4\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{Al}^{3+} + 2\text{H}_2\text{PO}_4^- + 6\text{H}_2\text{O}$	0.10	A, p. 178
FePO_4 (s)	$\text{FePO}_4 - K_{sp} \quad \text{*** Rx not given}$	-20.9 ± 2.7	A, p. 391
FePO_4 (s)	$\text{FePO}_4 - K_{sp} \quad \text{*** Rx not given}$	-21.89 (18-20)	B, p. 137
FePO_4 (c)	$\text{FePO}_4 + 2\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-2.34	A, p. 177
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (strengite)	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^- + 2\text{H}_2\text{O}$	-6.78 ± 0.85 -26.4 (crystal)	A, p. 177 C, p. 57
FeHPO_4^0	$\text{FeHPO}_4^0 + \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{H}_2\text{PO}_4^-$	-3.601	A, p. 174
FeHPO_4^0	$\text{FeHPO}_4^0 \rightleftharpoons \text{Fe}^{2+} + \text{HPO}_4^{2-}$	-3.6	B, p. 57
FeHPO_4^+	$\text{FeHPO}_4^+ + \text{H}^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-3.681	A, p. 174
FeHPO_4^+	$\text{FeHPO}_4^+ \rightleftharpoons \text{Fe}^{3+} + \text{HPO}_4^{2-}$	-8.3 (I=0.5)	C, p. 57
$\text{FeH}_2\text{PO}_4^{2+}$	$\text{FeH}_2\text{PO}_4^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-3.47 (I=0.5)	C, p. 57
$\text{FeH}_2\text{PO}_4^+$	$\text{FeH}_2\text{PO}_4^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-2.7	A, p. 174
$\text{FeH}_2\text{PO}_4^+$	$\text{FeH}_2\text{PO}_4^+ \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-2.7	C, p. 57
$\text{FeH}_2\text{PO}_4^{2+}$	$\text{FeH}_2\text{PO}_4^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{H}_2\text{PO}_4^-$	-5.43	A, p. 174
$\text{Fe}_3(\text{PO}_4)_2$ (s)	$\text{Fe}_3(\text{PO}_4)_2 - K_{sp} \quad \text{*** Rx not given}$	-34.5 ± 2.1	A, p. 391
$\text{Fe}_3(\text{PO}_4)_2$ (c)	$\text{Fe}_3(\text{PO}_4)_2 + 4\text{H}^+ \rightleftharpoons 3\text{Fe}^{2+} + 2\text{H}_2\text{PO}_4^-$	+9.20	A, p. 176
$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (c)	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} + 4\text{H}^+ \rightleftharpoons 3\text{Fe}^{2+} + 2\text{H}_2\text{PO}_4^- + 8\text{H}_2\text{O}$ (l)	$+3.4 \pm 0.42$	A, p. 176
$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (s)	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \rightleftharpoons 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$ (l)	-36.0	C, p. 57
NaHPO_4^-	$\text{NaHPO}_4^- + \text{H}^+ \rightleftharpoons \text{Na}^+ + \text{H}_2\text{PO}_4^-$	+6.005	A, p. 174
PbPO_4^-	$\text{Pb}^{2+} + \text{PO}_4^{3-} \rightleftharpoons \text{PbPO}_4^-$	9.1	Soilchem, 1988 ⁽⁴⁾
$\text{Pb}(\text{PO}_4)_2^{4-}$	$\text{Pb}^{2+} + 2\text{PO}_4^{3-} \rightleftharpoons \text{Pb}(\text{PO}_4)_2^{4-}$	14.5	Soilchem, 1988 ⁽⁴⁾

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References ³
$\text{PbP}_2\text{O}_7^{2-}$	$\text{Pb}^{2+} + \text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{PbP}_2\text{O}_7^{2-}$	11.3	Lindsay, 1979 ⁽⁴⁾
$\text{Pb}(\text{P}_2\text{O}_7)_2^{6-}$	$\text{Pb}^{2+} + 2\text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{Pb}(\text{P}_2\text{O}_7)_2^{6-}$	5.2	Geochem, 1990 ⁽⁴⁾
PbHPO_4^0	$\text{PbHPO}_4^0 + \text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{PO}_4^-$	+4.11 +4.10	A, p. 174 Lindsay, 1979 ⁽⁴⁾
PbHPO_4^0	$\text{PbHPO}_4^0 \rightleftharpoons \text{Pb}^{2+} + \text{HPO}_4^{2-}$	-3.1	C, p. 58
PbHPO_4^0	$\text{PbHPO}_4^0 \rightleftharpoons \text{Pb}^{2+} + \text{PO}_4^{3-} + \text{H}^+$	-15.5 -15.4	Geochem, 1990 ⁽⁴⁾ Soilchem, 1988 ⁽⁴⁾
$\text{PbHPO}_4(\text{c})$	$\text{PbHPO}_4 + \text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{PO}_4^-$	-3.68 ± 0.89 -4.25	A, p. 176 Lindsay, 1979 ⁽⁴⁾
$\text{PbHPO}_4(\text{c})$	$\text{PbHPO}_4 \rightleftharpoons \text{Pb}^{2+} + \text{H}^+ + \text{PO}_4^{3-}$	-12.6 -23.8	Soilchem, 1988 ⁽⁴⁾ Geochem, 1990 ⁽⁴⁾
$\text{PbHPO}_4(\text{s})$	$\text{PbHPO}_4 \rightleftharpoons \text{Pb}^{2+} + \text{HPO}_4^{2-}$	-11.43	C, p. 58
$\text{Pb}(\text{HPO}_4)_2^{2-}$	$\text{Pb}^{2+} + 2\text{PO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{Pb}(\text{HPO}_4)_2^{2-}$	27.2	Soilchem, 1988 ⁽⁴⁾
$\text{Pb}(\text{H}_2\text{PO}_4)^+$	$\text{Pb}(\text{H}_2\text{PO}_4)^+ \rightleftharpoons \text{Pb}^{2+} + \text{H}_2\text{PO}_4^-$	-1.50 -1.5 -1.5	A, p. 174 C, p. 58 Lindsay, 1979 ⁽⁴⁾
$\text{PbH}_2\text{PO}_4^+$	$\text{Pb}^{2+} + \text{PO}_4^{3-} + 2\text{H}^+ \rightleftharpoons \text{PbH}_2\text{PO}_4^+$	21.0 21.1	Soilchem, 1988 ⁽⁴⁾ Geochem, 1990 ⁽⁴⁾
$\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$	$\text{Pb}(\text{H}_2\text{PO}_4)_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{PO}_4^-$	-9.85	Lindsay, 1979 ⁽⁴⁾
$\text{Pb}(\text{H}_2\text{PO}_4)_2(\text{c})$	$\text{Pb}(\text{H}_2\text{PO}_4)_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{PO}_4^{3-} + 4\text{H}^+$	-49.0	Geochem, 1990 ⁽⁴⁾
$\text{Pb}_3(\text{PO}_4)_2(\text{s})$	$\text{Pb}_3(\text{PO}_4)_2 - K_{\text{sp}}$ *** Rx not given	-44.60	B, p. 137
$\text{Pb}_3(\text{PO}_4)_2(\text{s})$	$\text{Pb}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Pb}^{2+} + 2\text{PO}_4^{3-}$	-43.53 (38) -43.0	C, p. 58 Soilchem, 1988 ⁽⁴⁾
$\text{Pb}_3(\text{PO}_4)_2(\text{c})$	$\text{Pb}_3(\text{PO}_4)_2 + 4\text{H}^+ \rightleftharpoons 3\text{Pb}^{2+} + 2\text{H}_2\text{PO}_4^-$	-4.86 ± 0.61 -5.26	B, p. 176 Lindsay, 1979 ⁽⁴⁾
$\text{Pb}_3\text{O}(\text{PO}_4)_2(\text{s})$	$\text{Pb}_3\text{O}(\text{PO}_4)_2 - K_{\text{sp}}$ *** Rx not given	-65.17	B, p. 137

TABLE B-1. SOLUBILITY EQUILIBRIUM DATA (Continued)

Compound ⁽¹⁾	Reaction	Log K ⁽²⁾	References [*]
Pb ₃ O(PO ₄) ₂ (c)	Pb ₃ O(PO ₄) ₂ + 6H ⁺ ⇌ 4Pb ²⁺ + 2(H ₂ PO ₄ ⁻) + H ₂ O	+2.24	Lindsay, 1979 ⁽⁴⁾
Pb ₃ (PO ₄) ₂ OH (s)	Pb ₃ (PO ₄) ₂ OH - K _{sp} *** Rx not given	-76.80	B, p. 137
Pb ₃ (PO ₄) ₂ (OH) (hydroxy-pyromorphite)	Pb ₃ (PO ₄) ₂ (OH) + 6H ⁺ ⇌ 5Pb ²⁺ + 3H ₂ PO ₄ ⁻ + OH ⁻	-18.15	A, p. 178
Pb ₃ (PO ₄) ₂ (OH) (hydroxy-pyromorphite)	Pb ₃ (PO ₄) ₂ (OH) + 7H ⁺ ⇌ 5Pb ²⁺ + 3H ₂ PO ₄ ⁻ + H ₂ O	-4.14	Lindsay, 1979 ⁽⁴⁾
Pb ₃ (PO ₄) ₂ (OH) (hydroxy-pyromorphite)	Pb ₃ (PO ₄) ₂ (OH) + H ⁺ ⇌ 5Pb ²⁺ + 3PO ₄ ³⁻ + H ₂ O	-60.9 -62.79 -62.79	Soilchem, 1979 ⁽⁴⁾ Minteqa2, 1990 ⁽⁴⁾ H, p. 77
Pb ₃ (PO ₄) ₂ Cl (s)	Pb ₃ (PO ₄) ₂ Cl ⇌ 5Pb + 3PO ₄ + Cl	-84.4 -80.4 -84.43	B, p. 137 Geochem, 1990 ⁽⁴⁾ Minteqa, 1990 ⁽⁴⁾
Pb ₃ (PO ₄) ₂ Cl (pyromorphite)	Pb ₃ (PO ₄) ₂ Cl + 6H ⁺ ⇌ 5Pb ²⁺ + 3H ₂ PO ₄ ⁻ + Cl ⁻	-18.9 ± 7.8 -25.05	A, p. 178 Lindsay, 1979 ⁽⁴⁾
PbAl ₃ (PO ₄) ₂ (OH) ₂ ·H ₂ O (plumbogummite)	PbAl ₃ (PO ₄) ₂ (OH) ₂ ·H ₂ O + 5H ⁺ ⇌ Pb ²⁺ + 3Al ³⁺ + 2PO ₄ ⁻ + 6H ₂ O	-32.79 -29.4	Minteqa2, 1990 ⁽⁴⁾ Soilchem, 1988 ⁽⁴⁾

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(1) s = solid, c = crystal, act = active solid

(2) K_{sp} at 25°C and infinite dilution unless other data are indicated.

(3) Ionic strength data available in reference.

(4) Database, not a reference.

APPENDIX C

MICROCHARACTERIZATION OF TWO FOUNDRY SANDS

Battelle collected sand samples from two foundries that perform brass and bronze casting. The casting practices at both foundries are considered typical within the industry. The sand at one foundry (foundry A) had been called an olivine type by the company, but our analysis showed the non-clay content to be primarily quartz. The clay content of the "olivine" sand was reported to be a mixture of Southern and Western bentonites. Foundry A casts a wide variety of industrial parts, such as pump components; many parts are plated after finishing. The foundry currently processes only brass alloys, but in the past had cast many other types of metals, so a fraction of the analyzed material probably was exposed to other metals. Now, approximately 25 different types of brass alloys are cast, ranging in composition from 60-70% copper and 0-10% lead. Foundry A contracts an outside firm to perform TCLP tests on waste sand. The foundry indicated that their waste sand normally passes the TCLP test, although this would not have been the case if the sand sample obtained by Battelle had been tested.

The casting operation at foundry A is a semi-automated process. The molds are fabricated at a compaction station where sand flows from an overhead hopper. An operator uses a sieve to filter and break up large clumps of sand that may be present. Then, sand is placed in a compaction mold with the appropriate core materials. Silica (quartz) sand is used with most core molds and several types of binders are used. Battelle obtained one sample core in which a heat-activated binder was used and another sample in which a phenolic/resin-activated binder was used. No analyses were performed on these cores. After compaction, the finished sand casting is removed from the compaction mold and is conveyed to the melt filling station. After several molds are fabricated, molten brass alloy is conveyed into the casting room and an operator pours each mold individually. The brass casting is removed from the mold after cooling. Then, the sand is thrown onto a large floor grate, beneath which a conveyer transports the sand to a machine that pulverizes it. Pieces of core that do not pass through the grate are removed manually. Small pieces of core that pass through the grate also are blended with the mold sand. The processed sand mixture is passed back into the hopper, where it is used again.

A sample of a green sand was obtained from another foundry (foundry B). The green sand is a system sand consisting primarily of quartz and clay. Foundry B is a red brass foundry that produces leaded, red brass plumbing ware castings. Because the sand sample arrived very late in the study, only a cursory level of characterization was possible.

WET CHEMICAL AND TCLP ANALYSES

Several kinds of analyses were performed on the olivine sand. Table C-1 shows results of wet chemical analyses of the bulk material and Table C-2 shows results of a TCLP test on the same sample. Note that the sample would have failed the TCLP test for lead, had it been a waste material designated for disposal. Wet chemical analysis was not performed on the green sand.

**TABLE C-1. BULK WET CHEMICAL
ANALYSIS OF OLIVINE SAND**

Metal	Concentration
Copper	1510
Iron	2650
Lead	2050
Tin	267
Zinc	706

TABLE C-2. RESULTS OF TCLP TEST ON OLIVINE SAND

Metal	Concentration (mg/L)	Matrix Spike Recovery (Accuracy)
Copper	37.2	1.102
Iron	1.86	0.84
Lead	39.9	NA
Tin	<0.10	1.162
Zinc	118	1.016

TABLE C-3. X-RAY DIFFRACTION RESULTS OF BULK OLIVINE SAND

Phase	Formula	PFD Number	Structure	Relative Abundance
Quartz	SiO ₂	33-1161	Hexagonal	Major Phase
Forsterite	Mg ₂ SiO ₄	34-189	Orthorhombic	Minor Phase
Litharge	PbO	5-561	Tetragonal	Possible Trace

X-RAY DIFFRACTION ANALYSES

The olivine sand was analyzed by x-ray diffraction (XRD) to determine major crystalline phases. Results of analyzing a sample of the bulk material are shown in Table C-3. Additionally, the olivine sand was size fractionated by ultrasonically cleaning a sample of the sand in acetone for about 10 minutes. Then, the suspended material was decanted and the acetone was evaporated. Both the decanted material and the sediment were analyzed by XRD after they were fully dried. Results are

**TABLE C-4. X-RAY DIFFRACTION RESULTS OF DECANTED MATERIAL
FROM OLIVINE SAND**

Phase	Formula	PFD Number	Structure	Relative Abundance
Calcite	CaCO ₃	5-586	Rhombohedral	Major Phase
Quartz	SiO ₂	33-1161	Hexagonal	Secondary Phase
Illite-1M	aluminosilicate	29-1496	Monoclinic	Minor Phase
Smectite-Kaolinite	aluminosilicate	29-1490	NA	Minor Phase
Kaolinite-1Md	Al ₂ Si ₂ O ₅ (OH) ₂	29-1488	Monoclinic	Minor Phase
Lead	Pb	4-686	Cubic	Possible Trace
Forsterite	Mg ₂ SiO ₄	34-189	Orthorhombic	Possible Trace
Litharge	PbO	5-561	Tetragonal	Possible Trace

shown in Tables C-4 and C-5. Although these test results cannot be considered definitive, they do reveal some information about the abundance of the phases present and the relative size of the particles. The bulk sand is composed of quartz and Mg-rich olivine (forsterite). When the clay-size fraction was removed by washing, XRD spectra of the sediment were made less complex, thus permitting possible identification of tetragonal lead(II) oxide as a trace component (see Table C-4). The decanted material contains mostly clay-size particles. The mineralogic makeup consists of calcite, quartz, and clays, in that order of abundance (see Table C-5). Smectite is a group clay mineral name that includes montmorillonite and bentonite. Kaolinite is also known as fire-clay or china-clay. Note that both elemental lead and lead(II) oxide may be present in the decanted fraction.

SCANNING ELECTRON MICROSCOPY

Samples of the olivine and green sands were analyzed by scanning electron microscopy (SEM), equipped with an energy dispersive x-ray spectroscopy (EDS) analyzer. Figure C-1 shows a secondary electron image (normal SEM image) of some olivine sand grains at 3,500x magnification. Figure C-2 shows the same view as a backscatter image. In backscatter mode the brighter areas

**TABLE C-5. X-RAY DIFFRACTION RESULTS OF SEDIMENT
FROM OLIVINE SAND**

Phase	Formula	PFD Number	Structure	Relative Abundance
Quartz	SiO ₂	33-1161	Hexagonal	Major Phase
Forsterite	Mg ₂ SiO ₄	34-189	Orthorhombic	Minor Phase

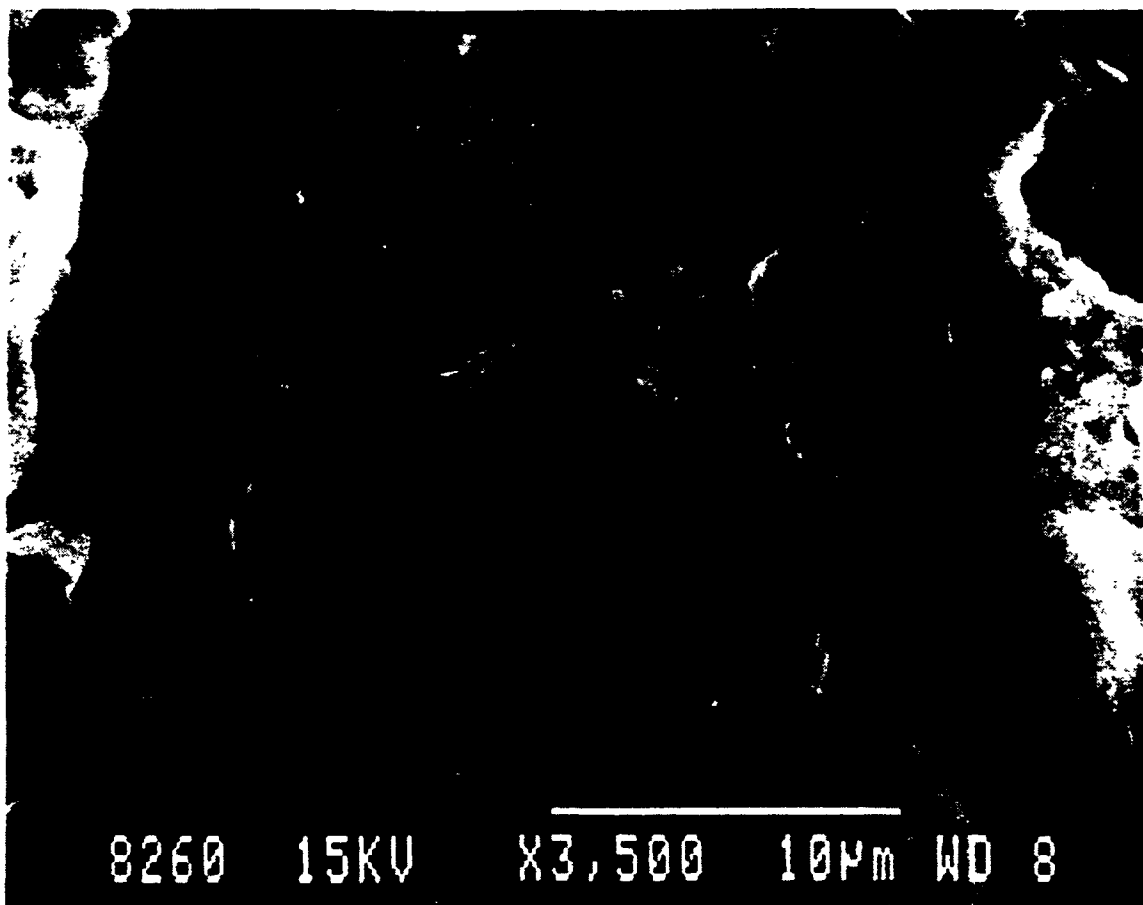


Figure C-1. Secondary electron image of olivine sand grains at 3,500x magnification.

represent regions of higher atomic densities. Thus, the bright areas shown in Figure C-2 are indicative of lead-rich or other heavy metal-rich regions. SEM photographs also were taken of the decanted material from the olivine sand wash. Figure C-3 shows a secondary electron image at 3,500x magnification which mainly consists of clay-size material. Figure C-4 shows a backscatter image of the same view. The single luminous particle in Figure C-4 is believed to be Pb metal or PbO, based on chemical analysis (see EDS results below). In Figure C-3 the lead-rich particle appears undifferentiated from its surroundings, because of the considerable mass of clay material present.

The lead-rich areas in the green sand from foundry B are more ubiquitous than those observed in the olivine sand. Figure C-5 shows a secondary electron image at 5,000x magnification which mainly consists of clay-size material. Figure C-6 shows the same view as a backscatter image. The lighter areas in Figure C-6 may reveal lead-rich particles, but the majority are too small to be distinguished in the photograph. It appears as though the lead is surface-adsorbed onto clay particles.

Chemical analyses were performed using the EDS analyzer. Table C-6 gives results of analyses of the unwashed olivine sand for a bulk view of the sample and for a single particle. In the bulk analysis, the x-ray beam was distributed over a wide area. In photo #E8260 (see Figure C-1), the x-ray beam was focused to cover the lead-rich area. The data in Table C-6 show a large relative

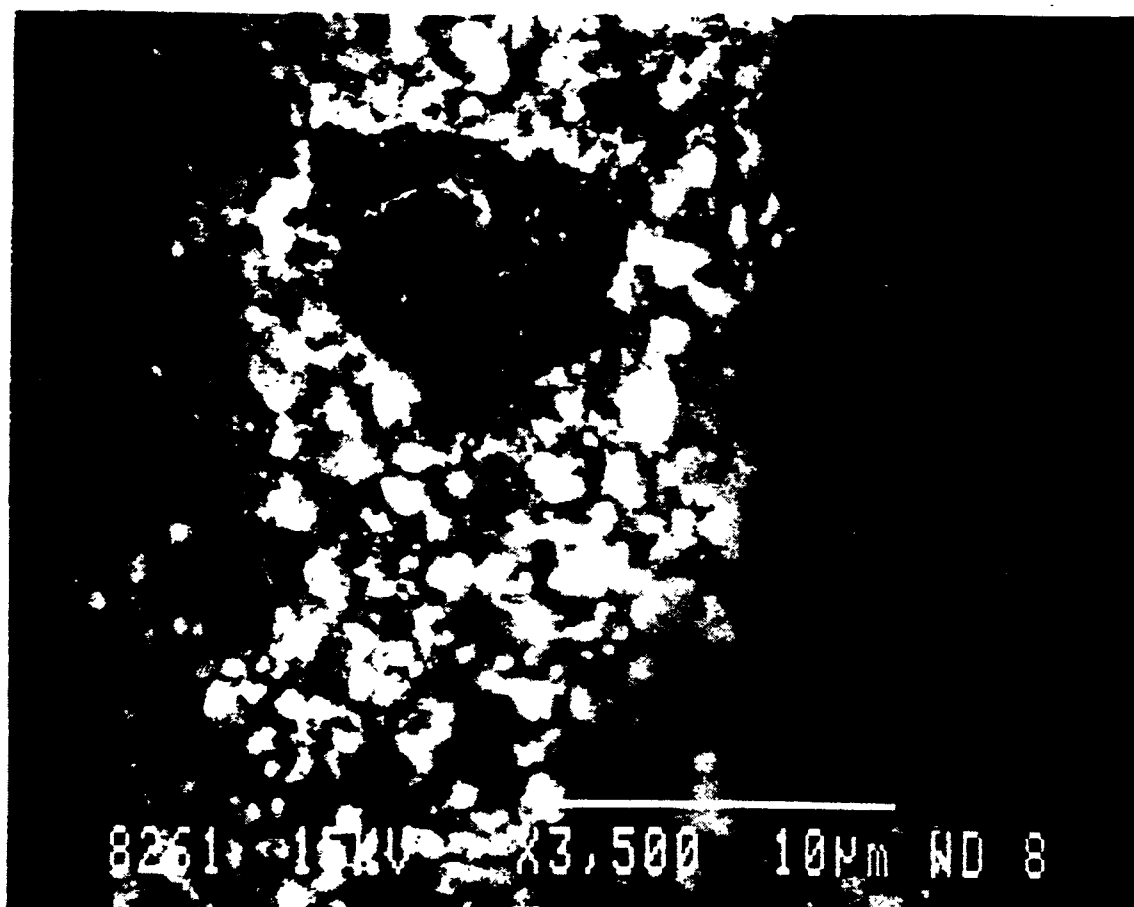


Figure C-2. Backscatter electron image of same view as in Figure C-1.

increase in lead in the closeup area, compared to the bulk composition (22:1). Copper and zinc show a much smaller relative increase in the closeup area (1.5:1). Because oxygen is not analyzed directly, it is not certain whether the lead enrichment is due to elemental lead or to lead oxide.

Table C-7 gives results of analyses of the decanted material from the washed olivine sand for a bulk view of the sample and for a single particle. Analysis of the particle in photo #E8292 (bright area in Figure C-4) shows considerable enrichment in lead (80:1) and a large increase in copper (8:1). The decanted material from the silica sand also shows relative enrichment in lead for a specific particle, as shown in Table C-8.

X-RAY PHOTOELECTRON SPECTROSCOPY

A sample of unwashed olivine sand was analyzed by x-ray photoelectron spectroscopy (XPS). The spectra reveal major silicon-oxygen phases and, possibly, a small lead peak ($4f_{7/2}$) may be observed at a binding energy of 138 eV. However, the spectral intensity is too low, due to the low lead content of the sample, to accurately determine the oxidation state of lead. If the binding energy value of 138 eV is accurate, this result is indicative of an oxidized form of lead, rather than

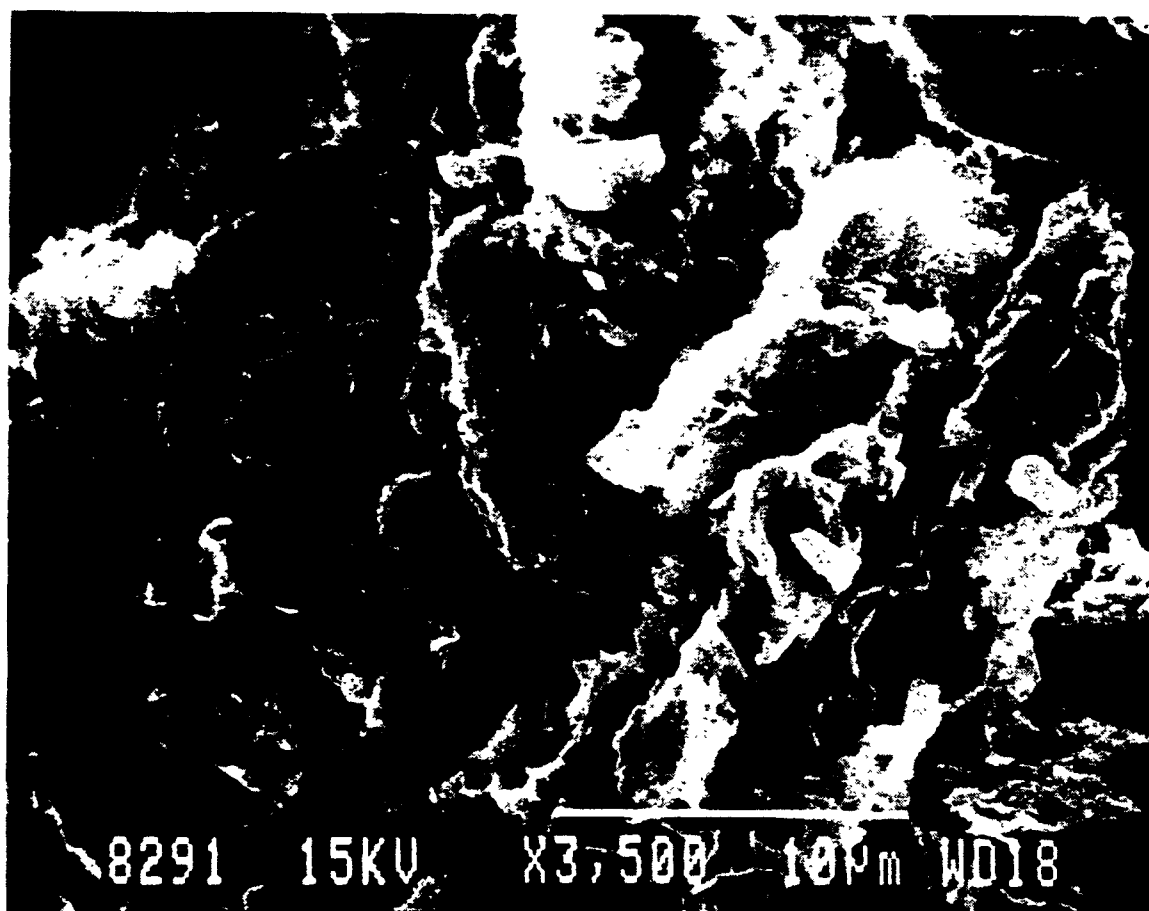


Figure C-3. Secondary electron image of decanted fraction of olivine sand at 3,500x magnification.

elemental lead. To correctly assess the lead oxidation state(s) would require concentrating lead-rich particles, such as by fractionating the sample by density. If fact, this technique would be an asset to the SEM and XRD analysis methods as well.

Because XPS detects only the top 20Å or so of the sample surface, the result could be skewed if the surface material is different from the bulk composition. For example, it is possible that only the outer surface of an elemental lead particle may be oxidized, whereas beneath the lead is in its elemental state. In addition, part or all of the oxide surface may become converted to lead hydroxide or lead carbonate by exposure to moist air. In these circumstances argon ion sputtering could be used to sequentially remove thin outer layers of the sample to obtain depth profile analyses. The depth profiling technique is often used to examine surface compositions of reactive materials.

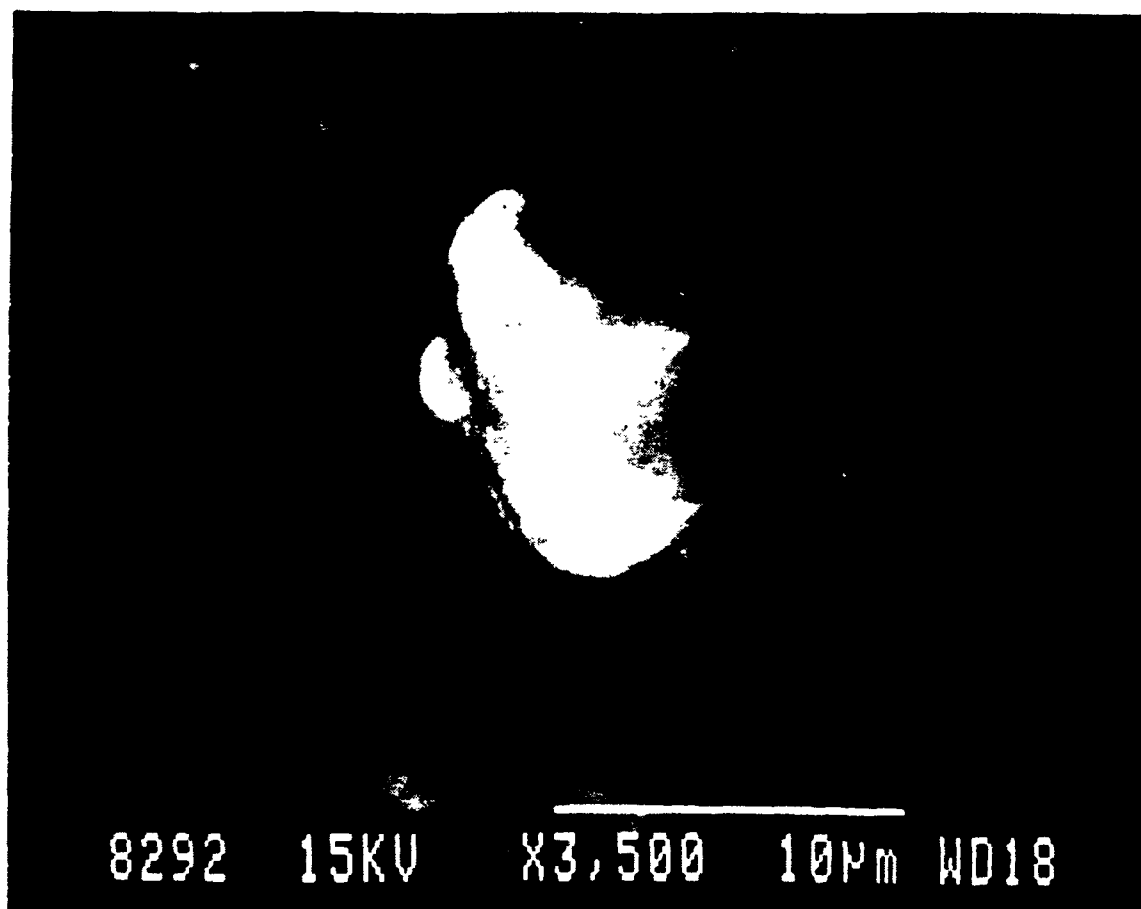


Figure C-4. Backscatter electron image of same view as in Figure C-3.

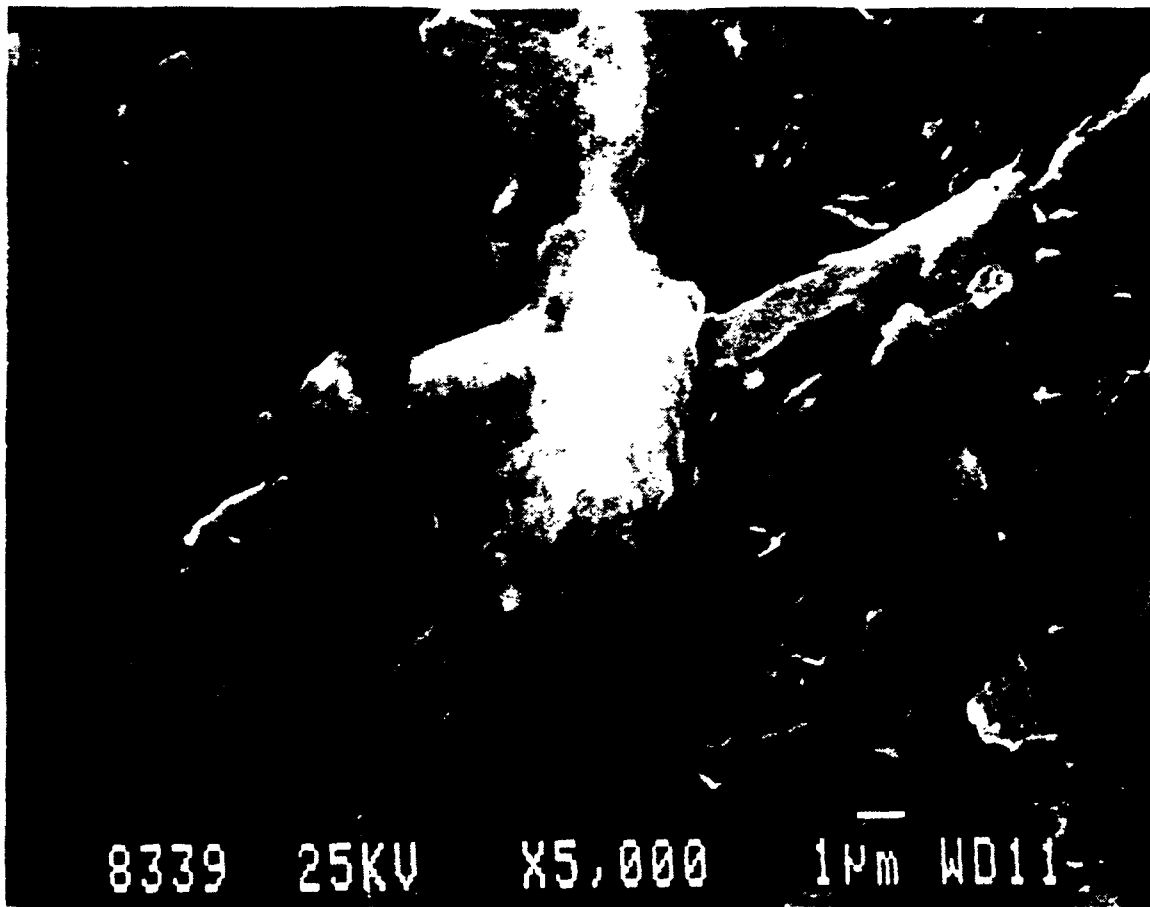


Figure C-5. Secondary electron image of green sand at 5,000x magnification.

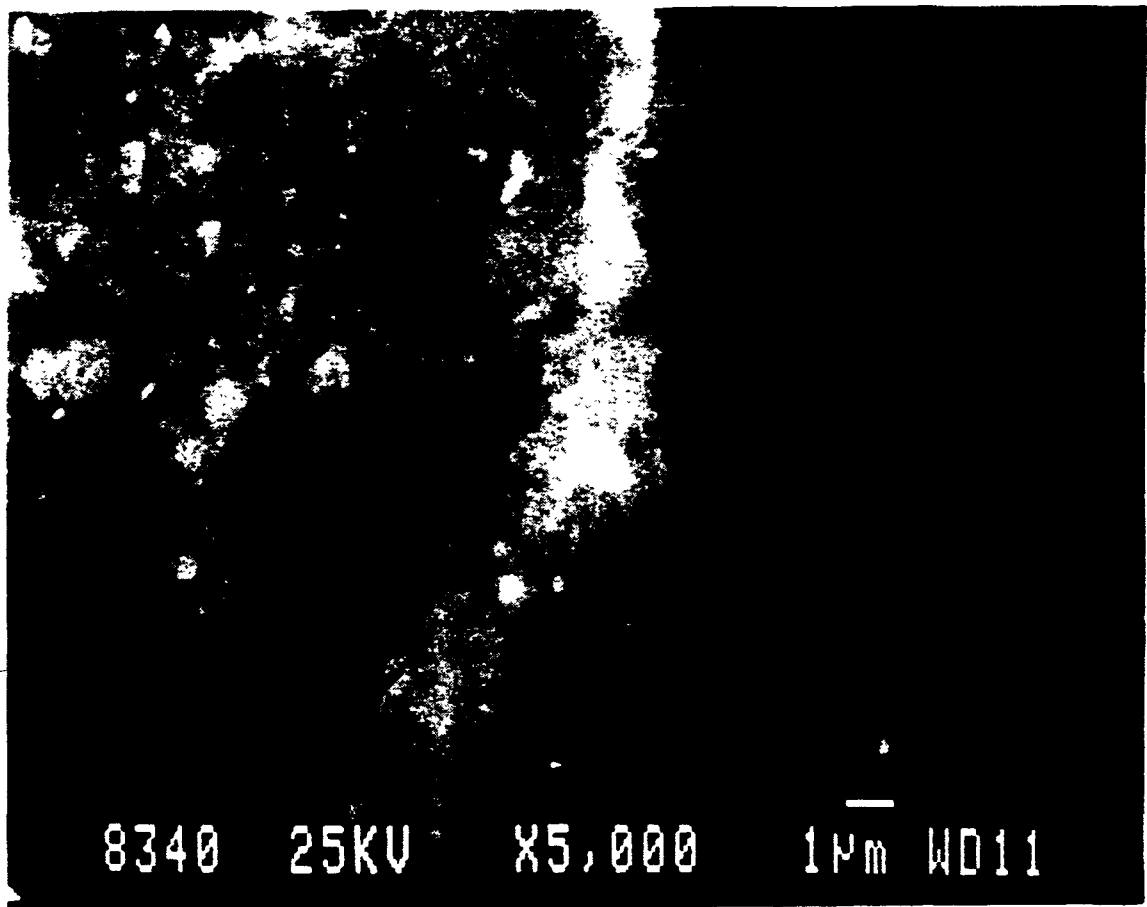


Figure C-6. Backscatter electron image of same view as in Figure C-5.

**TABLE C-6. RESULTS OF SEM/EDS INVESTIGATION
OF UNWASHED OLIVINE SAND**

Element	Atom %	
	Bulk	Photo # E8260
Mg	11.17	4.74
Al	15.01	17.16
Si	58.02	52.6
Pb	0.29	6.5
K	0.57	0.55
Ca	4.24	5.52
Ti	0.28	0.28
Cr	0.21	0.00
Fe	4.78	4.62
Cu	0.91	1.39
Zn	3.85	5.43
S	0.67	1.21

**TABLE C-7. RESULTS OF SEM/EDS INVESTIGATION
OF OLIVINE SAND-DECANTED MATERIAL**

Element	Atom %	
	Bulk	Photo #E8292
Mg	6.69	4.4
Al	18.2	9.56
Si	58.85	26.34
S	0.94	0.64
Pb	0.45	36.06
K	0.83	0.25
Ca	5.39	3.34
Ti	0.28	0.00
Fe	3.88	4.38
Cu	1.25	10.1
Zn	3.24	4.94

**TABLE C-8. RESULTS OF SEM/EDS INVESTIGATION
OF SILICA SAND-DECANTED MATERIAL**

Element	Atom %	
	Bulk	Single Particle
Mg	3.20	3.90
Al	18.59	20.05
Si	63.16	58.81
S	1.83	0.85
Pb	0.71	4.73
K	0.59	0.50
Ca	1.54	1.52
Ti	NA	NA
Fe	2.14	1.98
Cu	0.91	1.01
Zn	7.33	6.65



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
RISK REDUCTION ENGINEERING LABORATORY

DATE: February 22, 1994

SUBJECT: Iron Chemistry in Lead Contaminated Materials

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Attached is the final report from Battelle on the RARE project. Please look it over and let me know your thoughts on where we go from here. Thanks.

Attachment

