

A REVIEW OF SLAG CHEMISTRY IN LEAD RECYCLING

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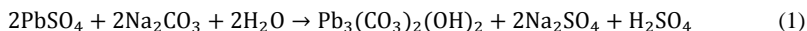
Abstract

A critical review of the technical literature on slag chemistry in lead recycling is presented. Laboratory methods used to improve our understanding of these systems is described. Ongoing investigations in the Kroll Institute for Extractive Metallurgy are presented.

Introduction

In 2015, about 86% of smelted North American lead came from secondary sources (1,800,000 short tons). Of that, 95% came from spent lead-acid batteries. The other 14% of production came from smelting of primary lead (290,000 st). No primary smelting occurred in the United States, although lead concentrates are still produced. Compared to 1980, the percentage of secondary output has increased from 50% and the proportion from batteries has risen from 70% [1]. Given the importance of lead battery recycling to the US lead supply this paper presents a review of lead slag chemistry and behavior, past experimental methods to study lead slags, and recent advances at the Kroll Institute for Extractive Metallurgy.

A description of the lead battery recycling process shown in Figure 1 is required. The contents of a lead-acid battery are the sulfuric acid and lead sulfate battery paste, the metallic and oxidic lead grid parts, the plastic battery casings, and the silica separators. Although the methods have changed over the years and vary from plant to plant, the batteries must initially be broken and separated. Acid is recovered and sold, casings are melted and extruded into new plastics, and separators are fluxed in the furnaces and the grid parts are fed to the reverberatory furnace. Historically the paste was also directly fed to the reverb, where it would form a matte phase, but due to concerns with sulfur dioxide generation, the paste material is now desulfurized. This is commonly done with soda ash and leads to a marketable sodium sulfate product. The lead continues to the furnace as a carbonate:



In the reverb, lead is reduced, while impurities like antimony, arsenic, and tin are slagged. Dross can form when lead sulfide crystallizes out of the cooling bullion. The reverb process leaves much lead oxide in the slag, so it is then sent to a blast furnace for reduction. The lead products are then impurity-free “soft” lead and impurity-containing “hard” lead.

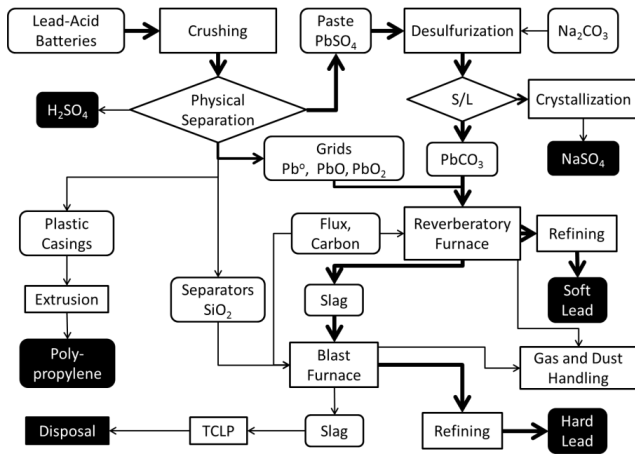


Figure 1. The Lead-acid Battery Recycling Process.

Historical Blast Furnace Slags

Operation of a Lead Blast Furnace

The first smelting metallurgists brought the blast furnace to the western US from Germany [2]. An objection to early reverb furnaces was considerable valuable metallurgical losses to smoke. Blast furnace baghouses are able to retain this value. Thus, the blast furnace came into use.

A lead blast furnace operates at a lower temperature and with a lower coke requirement than an iron blast furnace [3]. They are generally rectangular with tuyeres along the long side. Magnesia brick typically composes the crucible lining. Because the conditions are not strongly reducing, iron oxide is maintained in the slag. Scrap iron will reduce the lead according to:



There can be up to four products from the lead blast. The crude lead bullion contains the lead. Sulfur, if desulfurization is not used, will create a matte that will attract the copper. Antimony and arsenic in excess may react with iron to form a speiss, which will contain cobalt and nickel. Lead and antimony can both be reduced by iron:



Any less-noble impurities will slag out, but because the change in free energy about 900°C is only slightly negative, substantial lead oxide will also be contained in the slag. With no desulfurization (historical practice), CaO-FeO-SiO₂ slag will melt around 1200°C and the lead at

330°C. When modern desulfurization occurs, the sodium content creates a $\text{Na}_2\text{O-FeO-SiO}_2$ slag. Both are corrosive and are contained in the lower part of the hearth with water cooled steel plates onto which the slag solidifies and forms a lining. It should be removed as quickly as possible because it can only cool and create operational troubles.

Changes in Slag Characteristics Caused by Additives

The effects of many additives to slags have been determined qualitatively through years of practice [4]. Keeping the slag easy to handle without containing too much lead has always been and continues to be the smelter's biggest struggle. While the thermodynamic and metallurgy of lead systems hasn't changed over the last hundred or so years, the constraints to the metallurgists have. Conversion to lead carbonate has a significant change in the chemistry of the final slag and leads to little to no matte production. While desulfurization decreases lead losses, the slags can contain enough to not pass the TCLP. A similar result can be achieved with modern addition of barite.

Lime rejects lead sulfide from the slag and reduces it to metallic lead. Replacing lime with barite gives a lower temperature and more-fluid slag. Barite also mitigates difficulties with magnesia and zinc oxide. However, modern practice would stray from adding more barite to the system, because when it ends up in the slag it can lead to failure of the TCLP. Barium produces a deep green flame over the slag and matte, a stony appearance, and a large amount of matte.

Too much alkaline earths or too much zinc can "freeze" a blast furnace [2]. A low silica high-lime slag is a dangerous sign that the furnace is about to freeze. Magnesia will produce a stony slag that fuses hard, raises the formation temperature, and makes the slag "pasty."

A slag that is curdy, short, brittle, rapidly cooling, and does not leave a string on the bar has too much lime. Low silica a high iron or lime slags will not fuse but instead become curdy. These slags break short, do not make strings, produce round drops, fall quickly, form a heavy shell, quickly chill matte boxes, are bad for the tuyeres, tap hard, and are prone to freezing up the furnace.

When lime is substituted by alumina, the formation temperature of the slag is raised. But when alumina replaces silica, the temperature is lowered. This is due to alumina's amphoteric nature in slags. A 'lazy' slag with an oily stream contains a "safe" amount of silica. Low silica and high magnesia and zinc cause a curdy, fast-cooling slag. The shell spits as the slag in the pot darkens in color. Alumina increases the viscosity of the slag and makes it stringy and wavy.

Iron and manganese raise the formation temperature, but reduce lead and other sulfides and prevent lead oxide from combining with silica. Iron slags zinc oxide. Zinc will be signified by white smoke and volcanoes on top of the cooling slag exhibiting a yellow (sulfur-like) coat.

Potash and soda produce tough slags with high amount of lead. High copper will cause more lead to be contained in the matte. A high copper matte can be a valuable product; either re-smelted or sold.

Wrinkly, fish-scale-like liquid slags will produce a thick brittle shell and freeze up the furnace. A slag with a warty surface and inclusions of unfused particles into the underside of the shell is produced when fines sink through the furnace.

Characterization of Lead Slags

Beyke characterized slags from three secondary operations: (A) one using a reverb then blast furnace, (B) one using only a blast furnace, and (C) one using a reverb and blast furnace after desulfurizing the feed [5]. Nominal slag compositions were 15-30 wt% CaO, 25 to 25% FeO, and 30-35% SiO₂, with minor concentrations of 1-3 wt% Pb, 2-4% S, and 1-8% Na. The mattes were 25-25 wt% Pb, 35-45% Fe, and up to 25% S.

Slag A contained silicates of calcium and iron as the major phases, magnetite, and metallic lead. SEM images showed that the lead was not found as a silicate, but as entrained metallic particles. The associated matte contained pyrrhotite and magnetite with spheres of metallic lead often rimmed with galena.

Similar dominant phases were found for slag B, except that the metallic lead particles were larger (25 μm up from lows of 2-3 μm). They also contained subparticles containing other elements: antimony, calcium, and chlorine (from casings). The matte was more complex, with iron oxides and sulfides growing around galena unassociated with metallic lead.

The desulfurization process resulted in no matte to accompany the third slag, which contained approximately 3% S – in the same region as slags A and B. Phase identification was difficult because of the amorphous, glassy quality of the slag. In this slag, the lead particles were embedded in iron oxides, sulfides, and sulfates.

Slags in the Laboratory

Jak and Hayes summarized many types of experiments that are performed in order to study various characteristics of slags [6]. A common theme among these experiments is that laboratory-based binary or ternary phase systems can only be at best an approximation of their industrial counterparts. These diagrams are much easier to represent using two- and three-dimensional diagrams.

When designing these experiments, material selection and sample preparation must be done carefully in order to obtain equilibrium (and not metastable) phases at the desired conditions. Containment of experiments and their products must be carried out with solubility, nobility, and reactivity of those materials and products in mind. This can often limit the materials and atmospheres available for experiments.

Table I. Methods and Suitability for Study of Oxide Systems. From [6].

Methods	Suitability for oxide systems
STATIC METHODS	
Electrochemical	Thermodynamic props (e.g. a_i , ΔG , ΔS)
Vapour Pressure	Knudsen – low metal vapour pressure, non-aggressive slags
	Reactive gas equilibration – low metal vapour pressure – PO_2 control
	Isopeistic equilibria - high metal vapour pressure
X-Ray powder Diffraction (XRD)	Phase detection/identification; Extensive solid solutions – lattice parameters at temperatures
Hot stage microscopy	Liquidus of low vapour pressure systems, transparent liquids
Calorimetry	Enthalpies, ΔH
	- of formation
	- of solution
	- of phase transition
Equilibration/quench/analysis techniques	Liquidus of high viscosity liquids (e.g. high silica slags); solid state phase equilibria
DYNAMIC METHODS	
Thermogravimetric Analysis (TGA)	Gas/solid; Gas/liquid reactions
Differential Thermal Analysis (DTA)	Rapid phase transitions (m.p. of congruently melting compounds)
	Liquidus/solidus of low viscosity liquids

Part of that design can be done using computer simulation methods. These new computer modelling techniques combined with critical examination of previous data can bring to light inconsistencies and inaccuracies with even the most highly-regarded of data sets. Software which analyze multiphase equilibrium systems with databases include Thermo-Calc, FACT, ChemSage, MTDATA, and GEMINI2. Solution models and data assessment has been performed by SGTE (Scientific Group Thermodata Europe). FACTSage and ChemApp combine thermodynamic databases in a more user friendly experience, while Thermo-Calc and DICTRA combine thermodynamic databases with kinetic models. The Flood- Grjotheim model and the above packages were discussed by Gaye and Lehmann [7].

According to Jak and Hayes, electron probe X-ray microanalysis (EPMA) is the preferred technique for phase identification and measurement, with XRD as a complimentary method. Energy-Dispersive Spectrometry (EDS) is not suitable for accurate phase determination, but Wavelength Dispersive Detectors (WDD) may be used for accurate chemical analysis.

Experimental Methods for Lead Slag Characterization

Battle and Hager studied the viscosity of lead slags using a rotational viscometer [8]. Their setup used an alumina crucible and a quartz reaction vessel and operated between 1150 and 1350 °C in

a nitrogen environment. They also performed partitioning experiments, cautioning against the use of their data outside the composition ranges specified.

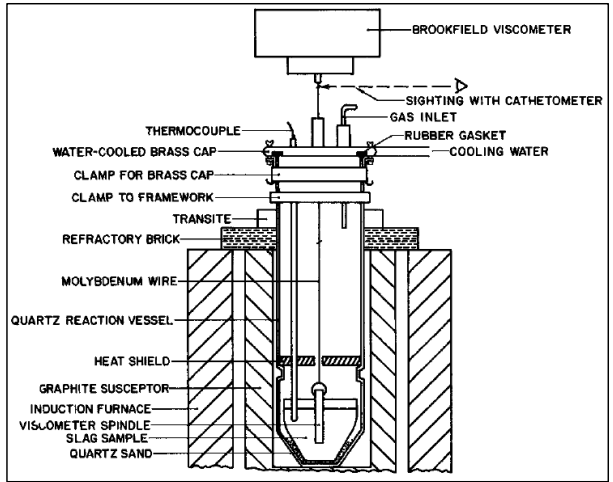


Figure 2. Experimental Setup Used by Battle and Hager, [8].

Reddy and Zhang also created and studied lead slags with a viscometer, this time employing a graphite crucible and argon environment from 1050-1300 °C [9].

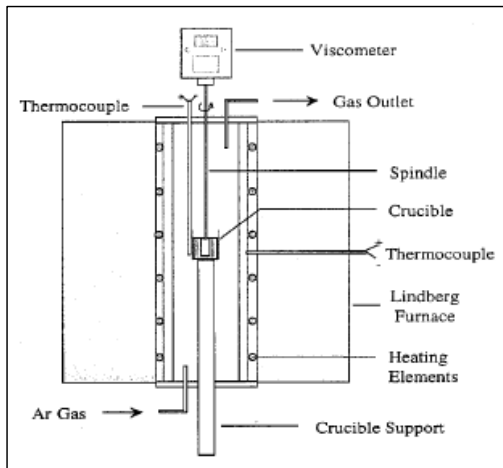


Figure 3. Experimental Setup Used By Reddy and Zhang, [9].

Their work focused not only on the temperature dependence of viscosity, but on the composition dependence, particularly the effect of similar actors whose characteristics may be lost when grouped simply as “chain breakers” and “chain modifiers” [10].

An Archimedeian spindle can be used to calculate the density of these slags at molten temperatures. The weight change of the immersed spindle (designed to minimize surface effects) relates to the exerted on the spindle, from which the density can be calculated. Such a design was used when examining the vitrification of iron phosphate containing radioactive wastes [11].

Fisher and Bennington examined the partitioning behavior of minor elements [12]. Minor element (silver, cadmium, zinc, and cobalt) distributions were found to be insensitive to changes in calcium ferrite slag composition over the ranges examined in that study. The composition did affect melting and fluidity characteristics, however. The calcium ferrite slags held <1wt% lead, which was much better than the 6% in iron silicate slags.

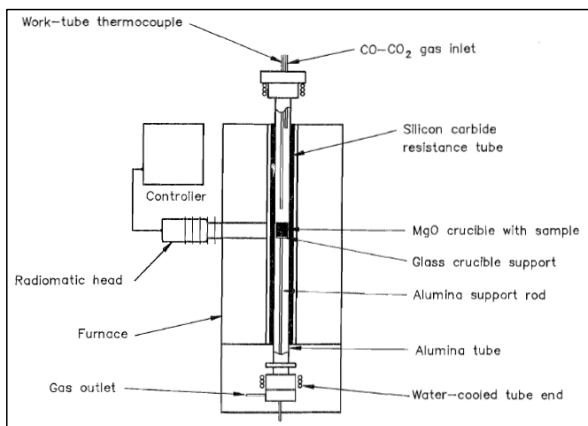


Figure 4. Experimental Setup Used By Fisher and Bennington, [12].

Hollitt measured Lead oxide activities in conventional and direct smelting slags at 1200°C [13]. Much higher coefficients than previously reported were obtained and were attributed to interactions between iron and lead oxides. The authors stated that the most suitable methods for measuring the activities of PbO are those using a stabilized zirconia solid electrolyte. Assuming ideal solution behavior of the silicates allowed for significant interactions between dissolved oxides. Gas-phase PbO vapour equilibrium was considered in the experimental setup. While the slags were 2.3 wt% Pb, the dissolved lead was only 0.64 wt%, with the rest being prills of metallic lead.

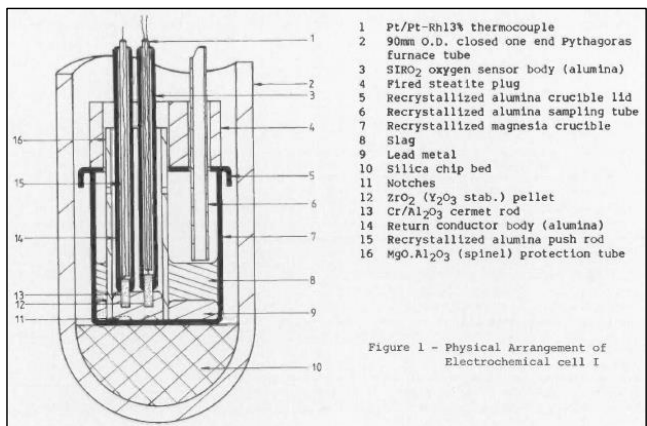


Figure 5. Experimental Setup Used By Hollitt, [13].

Environmental Concerns of Slag Constituents

As was discussed earlier, constraints for operation of a blast furnace and disposal of waste generated are different in the modern era as composed to those of a hundred years ago. In the United States, the Environmental Protection Agency sets the regulatory limits for certain toxic elements and compounds [14].

Table II. TCLP Inorganic Elements

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

The Toxicity Characteristic Leaching Procedure (TCLP) is the standard determinant for toxic elements that slags must pass to be disposed of in landfills. It involves a buffered or non-buffered acetic acid leach, depending on sample composition [15]. However, alternatives have been put forward because industrial wastes are not typically disposed of in common landfills. One such, the Synthetic Precipitation Leaching Procedure was developed to simulate acid rain using a combination of nitric and sulfuric acid. [16]

Slags of the CaO-FeO-SiO₂ system have been tested to determine the behavior of such toxic elements [17]. Slags were constructed and doped with arsenic, antimony, cadmium, chromium, and zinc, and leached according to the TCLP. When slow-cooled slags were analyzed, they were found to be crystalline with toxic elements distributed among the lower melting point phases. The cadmium was found to volatilize during the melt. According to that research, arsenic and antimony are best contained in basic slags while zinc and chromium are stabilized in acidic melts.

Ongoing investigations at the Kroll Institute for Extractive Metallurgy

The Kroll Institute for Extractive Metallurgy is researching the fundamental characteristics of Na₂O-FeO-SiO₂ slags. The testwork being performed consists of high-temperature viscosity and density measurements; partitioning of species between metal, slag, and vapor phases; and leachability of elements according to the TCLP.

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