Chemical Speciation of Lead Dust Associated with Primary Lead Smelting

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Abstract

The research presented in this article assessed geochemical factors relating to dust produced during primary lead smelting. Bulk dust samples and size-selective airborne dust samples were collected from four areas of a primary lead smelter and analyzed by X-ray diffraction and sequential chemical extraction. X-ray diffraction showed that the smelter dusts were composed primarily of sulfides, oxides, sulfates, and silicates of metal ores, with galena being the primary dust component. Sequential extraction revealed the solubility of lead compounds at less than 7% in the exchangeable and mildly acidic steps for the bulk dusts collected from four smelter areas. The later steps of the extraction procedure were more effective in dissolving the lead compounds associated with the bulk dust samples, with 43%, 26%, and 8% of the total lead, in the ore storage, sinter, and blast/dross smelter areas, respectively, being extracted in the residual step. Sequential extraction of coarse airborne dust samples from the ore storage and sinter plant showed that 1.2% and 4.1% of the total lead, respectively, was exchangeable. The finer particle size fractions from these areas of the smelter showed higher percentages of exchangeable lead. Of the course airborne dust from the blast/dross furnace processes, 65% of the total lead was exchangeable. However, the largest percentage of lead from these areas was associated with the finer particle-size fractions. If lead bioavailability is related to its solubility as determined through sequential extraction, the health hazards associated with lead exposure may be appreciably enhanced in the blast and dross furnace processes. **Key words**: bioavailability, lead dust, lead speciation, sequential extraction. **Environ Health Perspect** 106:565-571 (1998). [Online 11 August 1998]

Introduction

The research presented here was performed in a primary lead industry as part of a larger study designed to evaluate worker exposure to lead in terms of new health–related criteria. The aim of the overall study was to compare current worker exposure levels in terms of the relevant aerosol fractions of inhalable, thoracic, and respirable lead (1).

To completely assess the risk associated with lead aerosol exposure, the physical and chemical properties as well as the size distribution of the aerosol must be known. Absorption of lead from the respiratory and/or gastrointestinal tract is influenced by particle size, the pattern of regional particle deposition, and particle solubility. Particles larger than 3 µm in diameter deposit primarily in the nasopharyngeal and tracheobronchial regions of the respiratory tract and can be transferred by mucociliary transport to the esophagus and swallowed (2). Particles smaller than 3 µm have a greater probability of depositing in the alveolar regions of the respiratory tract. Bioavailability has been defined as the fraction of a compound in a matrix that is released from that matrix and

absorbed into the body's blood plasma (3). An important parameter relating to bioavailability is solubility, which is related to the ability of a compound to reach that location in the body where it can exhibit its inherent toxicity. Many factors determine the degree to which lead, when inhaled or ingested, can become soluble and enter the bloodstream. These factors include the site of contact, pH of the body fluid contacted, residency time, nutritional status, and numerous geochemical factors.

The major geochemical factors controlling the availability of lead from dust and/or soils include the species of lead, the size of the lead-containing particles, and the matrix incorporating the lead species (4). All species of lead compounds deposited in the deep lung region (alveoli) are thought to be completely absorbed into the bloodsteam (5-7). However, larger lead particles, which may have indefinite residency times in the upper regions of the respiratory tract or may be transferred from the respiratory tract to the stomach, will be absorbed at different rates based largely on speciation. Lead in the form of a sulfide is less bioavailable than lead carbonate or lead oxide (8).

The species of lead incorporated into soil vary depending on the source of lead. Soil mineralogy associated with lead smelter sites is complex, with lead existing as sulfides and multimetal oxides. Foster and Lott (9), in a study of lead speciation at a lead smelter, reported that galena was the major constituent of airborne lead particles from ore handling operations, and lead oxide species were the constituents of airborne particles associated with actual smelting operations such as the blast furnace and dross plant.

Chemical sequential extraction techniques have been developed to assess the solid-phase solubility or chemically extractable percentages of heavy metals occurring in contaminated soils, industrial and municipal sludges, and dusts. These techniques use chemical reagents of various strengths and pHs to leach metals from contaminated materials. The solutions are designed to interact with a solid contaminated material and liberate heavy metals on the basis of the solubility of the metal species within that solvent. Harrison et al. (10) suggested that mobility and bioavailability of metals decrease approximately in the order of the extraction sequence. Jenne and Luoma (11) showed that the bioavailability of heavy metals was inversely related to the strength of the metal-particulate binding in sediments. Other studies have demonstrated that compounds that are readily dissolved in weak acid are highly bioavailable (12,13).

The limitations of chemical sequential extraction techniques involve uncertainties as to the selectivity of the various extractants and readsorption of dissolved ions back onto the solid material. Chemical speciation and amount of material leached may result in a redistribution of metals within the leach fractions which is not representative of the sample. Despite these limitations, sequential extraction can provide qualitative information that may aid in the prediction of the bioavailability, mobilization, and transport of heavy metals (14). The research described in this paper was designed to assess the geochemical factors relating to lead in a primary production industry through the use of the Tessier sequential extraction method (15) with modifications developed by Harrison et. al. (10).

Methods

The workplace studied. The primary lead industry where this study was carried out processes concentrated lead, zinc, copper, and silver sulfide ores. Ores from mines around the world arrive at the smelter by truck or rail. Upon arrival, samples from each ore source are analyzed in the mill building to determine their elemental composition and moisture content. After sampling, ores are transported to a large ore storage building, where they are removed by overhead crane into either storage piles or large concrete feeder bins. Here materials are aggregated according to their chemical composition. These stored materials are subsequently routed by conveyor to the sinter plant where the ore is combined with fuel, ignited, and burned to produce fused "sinter" material (during which process the sulfur content is reduced). During sintering, the sulfides are oxidized to sulfates at approximately 700°C to produce a porous solid material composed primarily of bound lead oxides, lead sulfates, and lead silicate aggregates. The resultant sinter is then crushed and graded. The crushed sinter is mixed with coke and iron and transported to the top of the blast furnace into which oxygen-rich air is blown. In the blast furnace, the sinter is extensively reduced at l,000-12,000°C to produce molten lead, tin-arsenic-silver sulfides (speiss), copper-iron sulfide (matte), and iron silicate (slag). The molten material descends to the bottom of the blast furnace and collects in a settling basin, where the molten lead-rich fraction settles to the bottom and the lighter "slag" comes to the surface. The slag contains the iron which has been added, as well as zinc and lime. The lead fraction and slag are separated by draining the molten material out of the basin by ports located at different heights on the basin. Before cooling, small railcars are used to transport the slag for disposal and the lead-rich fraction to the drossing plant. In the drossing plant, elemental lead is separated from impurities not eliminated in the blast furnace. The molten material

from the blast furnace is poured into a large kettle, heated, and allowed to cool slowly. As the kettle cools, the impure "dross" fraction, rich in copper and arsenic, rises to the surface. This dross is skimmed off the top of the cooling kettle and transported to a large reverberatory furnace. The remaining pure lead is poured into molds and shipped to a refinery for further processing. The dross material in the reverberatory furnace is again heated and allowed to cool slowly. During cooling, three distinct layers are formed. The top "matte" layer is rich in iron and copper; the middle "speiss" layer is rich in arsenic. These two layers are tapped from the reverberatory furnace and shipped to a different smelter for copper extraction. The bottom layer contains pure lead and is returned to the drossing kettles for further extraction.

Sampling technique and locations within the smelter. Samples for lead speciation analysis were collected as both bulk dust and air samples. We collected bulk samples from four areas of the smelter: off-loading and ore storage, sinter plant, blast furnace, and dross furnace. The bulk dust samples were taken from dust-laden surfaces such as walkways or work surfaces using spatulas. The spatulas were cleaned using alcohol wipes after each collected sample to avoid cross-contamination. The collected material was placed in labeled petri dishes, sealed, and transported to the laboratory.

We collected air samples using a 28.3 l/min Andersen multistage cascade impactor placed in each of the four areas of the smelter described above. The Andersen was chosen for air sampling for two reasons: 1) large sample masses can be collected on the sampling stages because of the large sampler air volume rates, and relatively large sample masses are required for speciation analysis, and 2) a knowledge of the aerodynamic dimension of particles in the work environment is vital to understanding their potential health effects. The Andersen cascade impactor allows for the simultaneous determination of concentration and particle sizing information in one sample. The sampler is designed to reproduce to a reasonable degree the dust-collecting characteristics of the human respiratory system (*16*). The Andersen sampler is a static sampling instrument that consists of eight aluminum stages held together by three spring clamps and gasketed with O-ring seals. The eight stages of the impactor are preceded by a preseparator, designed to prevent particle bouncing and reentrainment errors, by limiting the access of larger particles to the sizing portion of the instrument. Cascade impactors operate on the principle of inertial impaction. A given stage consists of radial or circular slot openings and its accompanying impaction surface. The slot diameters become smaller at each successive stage proceeding through the impactor, resulting in successive increases in air velocity at each stage. Particle impaction is determined by its aerodynamic diameter (d_{ae}), with particles of larger d_{ae} being impacted on the upper stages and particles of smaller d_{ae} being impacted on the lower stages. For the Andersen sampler operated at 28.3 l/min, particle fractionation ranges from 10.0 to 0.4 µm. The particle size ranges for each stage of the Andersen sampler and their relationship to the human respiratory tract are shown in Table 1.

Table 1. Particle size ranges for each stage of the Andersen sampler and their relationship to deposition in the human respiratory tract

Andersen stage no.	Particle aerodynamic diameter (µm)	Respiratory tract region[a]
Preseparator	≥10	Nasopharyngeal
Stage 0	9.0–10.0	Nasopharyngeal
Stage 1	5.8–9.0	Nasopharyngeal and tracheobronchial
Stage 2	4.7–5.8	Nasopharyngeal and tracheobronchial
Stage 3	3.3–4.7	Nasopharyngeal and tracheobronchial
Stage 4	2.1–3.3	Tracheobronchial and alveolar
Stage 5	1.1–2.1	Alveolar
Stage 6	0.65–1.1	Alveolar
Stage 7	0.43–0.65	Alveolar

[a]Respiratory tract particle deposition has been estimated from mathematical models and human inhalation experiments There is no sharp distinction in particle deposition by particle size in the different regions of the respiratory tract Deposition of submicron particles (<1 µm) can occur in the nasopharyngeal region (24–27).

In this research, cellulose acetate filters of 82-mm diameter were placed on inverted stainless-steel impaction plates located on each stage. We used cellulose acetate filters because of their low trace metal background levels. Particles that reach the internal stages were assumed to stay on the impaction surface or filter. Air was drawn through the impactor by a 12-V AC Andersen pump operated at a calibrated flow rate of 28.3 l/min.

Air samples from the Andersen were combined to ensure that enough sample was available for speciation analysis. The samples from stage 0 were combined with stage 1 samples; samples from

stages 2, 3, and 4 were combined; and samples from stages 5, 6, and 7 were combined for each of the Andersen samples collected from the different smelter areas. Because of the small amount of material collected in the blast furnace area using the Andersen sampler, the blast and dross furnace air samples were combined into one sample group for analytical purposes. The bulk dust samples from these two areas were also combined into one sample group to maintain consistency with the air sample analysis.

Sample analysis. The bulk dust samples and the airborne dust collected on the first two stages of the Andersen sampler were analyzed by X-ray diffraction to determine the spectrum of metal compounds present in the dusts from the four smelter processes. Dust collected on the final six stages of the Andersen sampler was not analyzed by X-ray diffraction due to the small sample mass accumulated on these stages.

Next, both the bulk dust samples and the airborne dust samples from all the stages of the Andersen samples were analyzed by a series of sequential chemical extractions. The sequential chemical extractions, as well as the X-ray diffraction analysis described above, were performed at the Montana Tech of The University of Montana physical chemistry laboratory. One of the most thoroughly researched extraction techniques for studying chemical associations of metals in soils is the method of Tessier et al. (15). This procedure identifies specific classifications of heavy metal contamination as shown in Table 2. Unlike other procedures, this method separately defines a carbonate fraction. The extraction scheme used in our study is a modified version of the Tessier method after Harrison et al. (10) and is detailed in Table 3. The residual procedure was modified from the procedure of Harrison due to the potential explosiveness of $HClO_4$ in the presence of most organic materials. Extractions were performed in 50-ml polypropylene centrifuge tubes, using a mechanical shaker to mix the solutions. After each extraction, the mixture was centrifuged and the supernatant decanted into polythene bottles, acidified to pH less than 2, and stored in a refrigerator for analysis. All acid digestions were carried out in Teflon beakers and all plasticware was precleaned by soaking in 10% HNO_3. Lead analyses were performed by atomic absorption spectrophotometry.

Table 2. Classification, association, and extraction technique used during the Tessier sequential extraction method

Classification	Form or association	Extraction technique
Soluble	Metal precipitate; pore water	Release to pure water or river water
Exchangeable	Specifically adsorbed; ion exchangeable	Exchange with excess cations
Carbonate phases	Precipitate or co-precipitate	Release by mild acid
Fe-Mn oxide phases	Specifically adsorbed; co-precipitate	Reduction
Organic phases	Complexed; adsorbed	Oxidation
Residual phases	In mineral lattices	Digestion with strong acid

Table 3. Extraction fraction and chemical extraction procedure used by the Tessier et al. (15) sequential extraction method and modified by Harrison et al. (10)

Fraction	Procedure
Exchangeable	1.0 M $MgCl_2$, pH 7.0, 1 hr, 20°C, continuous agitation
Carbonate	1.0 M NaOAc, pH 5.0, 5 hr, 20°C, continuous agitation
Fe-Mn oxides	0.04 M $NH_2OH \cdot HCl$ in 25% acetic acid, 6 hr, 96°C, occasional agitation
Organic	0.02 M HNO_3 + 30% H_2O_2 (3:5 mixture), pH 2.0, 2 hr, 85°C, occasional agitation, further 30% H_2O_2 (3:8 mixture), pH 2.0, 85°C, occasional agitation, then 3.2 M HH_4OAc in 20% HNO_3 (5:11 mixture), 0.5 hr, 20°C, continuous agitation
Residual	(2 × 70% HNO_3, 10 ml) to dryness, 40% HF/concentrated aqua regia, (2:10 mixture) to near dryness, 1 ml concentrated aqua regia to dryness, residue taken up in 5 ml concentrated HCl and diluted to 50 ml or 250 ml with double deionized water

The limitations of sequential extraction were mentioned earlier. The sample:reagent ratio is important in determining whether complete leaching is achieved. These ratio values range widely (1:8 to greater than 1:100) in the reported literature because of sequential extraction modifications by numerous investigators in their application to differing test materials (17-20). A ratio of 1:70 was used in our study.

According to Tessier et al. (*15*), the sequential extraction method will dissolve heavy metals according to their chemical associations on the basis of the following classifications: 1) exchangeable or soluble metals that occur as weakly adsorbed ions on organic or mineral particle surfaces or forming soluble minerals (i.e., chlorides, hydroxides, borates, nitrates, and some oxides and sulfates), which are easily dissolved within an aqueous solution or exchanged by excess cations in solution; 2) metals associated with carbonate minerals that may form as particle coating, residues, or cements, which are liberated in the presence of a mildly acidic solution (note that some oxides or sulfates may also be liberated by these solutions); 3) metals associated with Fe-Mn oxide coatings in which the metal ions bond with amorphous Fe-Mn oxide materials, which may be liberated in the presence of a reducing solution; 4) metals associated with organic material and organo-metallic substances, which are liberated under highly oxidizing conditions (note that this step will liberate metals from humic or fulvic acids, bitumens, and some sulfide minerals); and 5) metals associated with the residual material following the previous four extraction steps (note that the metals may be held within insoluble phases such as silicate minerals, some oxides, sulfides, carbides, phosphides, clays, native metals, or encapsulated within amorphous solids of silica or alumino-silicate composition).

The last phase of the analytical chemistry was an analysis of the solubility of specific lead compounds through the sequential extraction method described above. Several mixtures of lead compounds and silica were prepared and subjected to the sequential extraction method. All of the mixtures were designed to match the lead content of the bulk dusts collected from the ore storage area of the smelter, which contained approximately 16% lead by weight. We used silica as a matrix for the dust compounds and imitated the variably high percentage of silicate minerals within the smelter dusts.

Results and Discussion

X-Ray diffraction. The X-ray diffraction analysis revealed smelter dusts composed of sulfides, oxides, sulfates, and silicates of ore metals and waste materials. A summary of the smelter dust mineralogy is shown in Table 4. Dust mineralogy is initially dominated by galena (PbS), which is the primary ore mineral processed at the smelter, and gradually evolves with the introduction of sulfates and complex oxides in association with other metals and metalloids as the material is sintered and roasted. Sintering and metal separation in the blast furnace is achieved at increasing temperatures and may result in the volatile off-gassing of many lead oxides, lead halides, and lead phosphate compounds, which, upon cooling, may contribute to the mineralogical composition of the dusts. In addition, X-ray diffraction patterns of the blast furnace and dross furnace bulk dusts showed peak broadening and sinuous background energy fluctuation, indicating that the dusts become increasingly amorphous and are probably derived from hot or rapidly cooling material as they enter the atmosphere.

Table 4. Mineralogical composition of the bulk dusts and coarse airborne dust fractions from different areas of the smelter based on X-ray diffraction analysis

Mineral	Chemical formula	Constituent
Ore storage area bulk dust sample		
Galena, syn	PbS	Major 1
Anglesite, syn	$PbSO_4$	Minor 2
Bindheimite	$Pb_2Sb_2O_7$	Minor 2
Lead bismuth titanium oxide	$PbBi_4Ti_4O_{15}$	Minor 2
Lead fluoride phosphate	$Pb_5(PO_4)_3F$	Minor 2
Lead phosphate	$Pb_9(PO_4)_6$	Minor 2
Lead silicate	Pb_4SiO_6	Minor 2
Lead tellurium oxide	Pb_3TeO_5	Minor 2
Lead tin fluoride	$PbSnF_4$	Minor 2
Phoenicochroite, syn	$Pb_2(CrO_4)O$	Minor 2
Strontium lead tin oxide	$Sr_2Pb_{0.7}5Sn_{0.25}O_4$	Minor 2
Zinc lead oxide	$Zn_xPb_{1-x}O$	Minor 2
Sinter area bulk dust sample		
Galena, syn	PbS	Major 1
Izoklakeite	$Cu_2Pb_{27}(Sb,Bi)_{19}S_{57}$	Major 1
Otjisumeite	$PbGe_4O_9$	Major 1
Plumbogummite	$PbAl_3(PO_4)(PO_3OH)(OH)_6$	Major 1
Unnamed mineral	$(Cu,Ag)Pb_6Bi_7Si_{17}$	Major 1
Coronadite	$PbMn_8O_{16}$	Minor 2
Heyrovskyite, syn	$Pb_{10}AgBi_5S_{18}$	Minor 2
Kombatite	$Pb_{14}(VO_4)_2O_9Cl_4$	Minor 2
Ourayite	$Ag_{25}Pb_{30}Bi_{41}S_{104}$	Minor 2
Phoenicochroite, syn	$Pb_2(CrO_4)O$	Minor 2
Vikingite	$AgPb_{25}Bi_3S_{7.5}$	Trace 3
Blast and dross furnace dust samples		
Galena, syn	PbS	Major 1
Lead fluoride silicate sulfate	$Pb_{10}(SiO_4)_3(SO_4)_3F_2$	Major 1
Lead oxide carbonate	$Pb_3O_2CO_3$	Major 1
Lead phosphate hydroxide	$Pb_5(PO_4)_3OH$	Major 1
Cadmium lead oxide	$CdPbO_3$	Minor 2
Lead fluoride arsenate	$Pb_5(AsO_4)_3F$	Minor 2
Phoenicochroite, syn	$Pb_2(CrO_4)O$	Minor 2
Vanadinite	$Pb_5(VO_4)_3Cl$	Minor 2

syn, synthesized.

Sequential chemical extraction of bulk dusts. The amounts of lead extracted by the individual extraction steps were compared for all of the bulk dust samples (ore storage, sinter, and blast/dross) as a percentage of the total lead extracted in each of the areas. The bulk dusts from the blast furnace and dross area were combined into one sample group. Figure 1 shows that the bulk dust samples from three different locations within the plant reacted similarly to the Tessier extraction chemicals with little regard to plant location or dust mineralogy. This may be an indication of the pervasiveness of coarse-grained PbS and its contribution to the sedimented dusts throughout the plant. The solubility of lead compounds was very low in the exchangeable and mildly acidic steps (<7% in all of the smelter areas), with the reducible, oxidation, and residual steps of the extraction procedure being much more effective at dissolving the lead compounds. It is interesting to note that the reducible fraction was highest in the dusts produced in association with the dross and blast furnaces (54%). This may be due to the presence of complex metalloid oxide compounds with lead. Furthermore, the abundance of PbS in the dusts, although pervasive throughout the plant, was greater in the ore concentrate and sinter dusts. The concentration of PbS gradually decreases as the ore is sintered and roasted. It is also apparent from Figure 1 that the residual fraction decreases in relation to the area of the smelter where the bulk dust was collected, with 43%, 26%, and 8% of the total lead in the ore storage, sinter, and blast/dross, respectively, being extracted in this step of the procedure. The bulk dusts collected from the blast and dross furnace areas were more soluble than the bulk dusts collected from the ore storage and sinter areas.
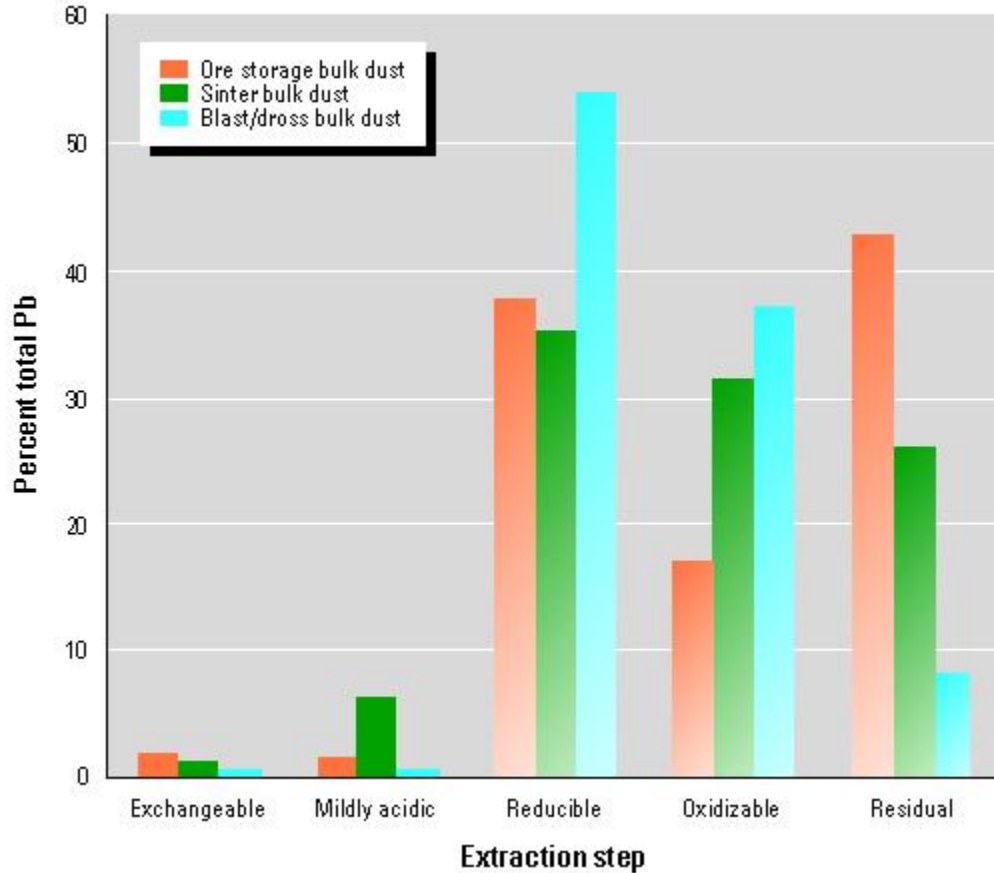
Figure 1. Percent total lead sequentially extracted from bulk dust by smelter process using the Tessier sequential extraction method (based on 0.50 g loose dust).

Sequential extraction of airborne dusts. The sequential extraction profiles for the airborne dust collected with the Andersen sampler from the different smelter processes are shown in Figures 2-5. The extraction profile for the ore-storage airborne dust samples, shown in Figure 2, indicates the sequential extraction of lead from the airborne dust was more effective for the finer particle sizes during the exchangeable and mildly acidic steps. Of the total lead on the Andersen stages 2-4 and 5-7, 32% and 39%, respectively, were exchangeable, compared to slightly more than 1% exchangeable lead for the coarser particles from stages 0-1. For the mildly acidic step, 6% and 19% of the total lead on the Andersen stages 2-4 and 5-7, respectively, were extracted, compared to less than 1% for stages 0-1. This may be a reflection of the coarser grain sizes of PbS particles which were derived from the ore.
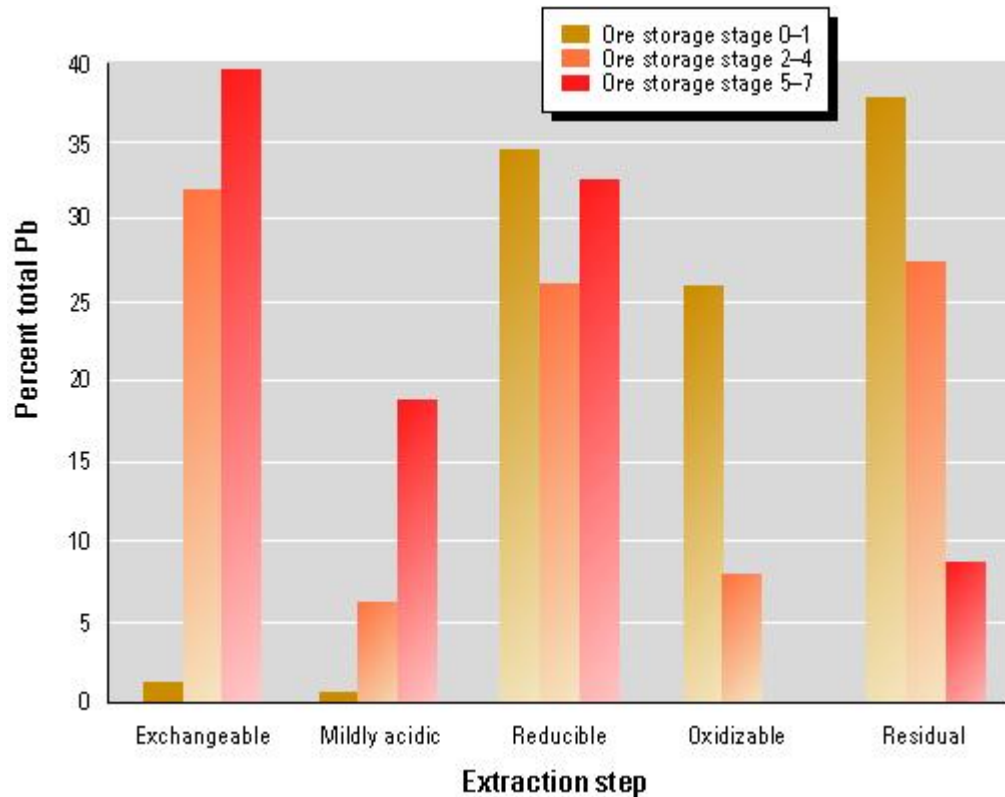
Figure 2. Percent total lead sequentially extracted by Andersen sampler stage from the ore-storage airborne dust samples.

A comparison between the bulk dust extraction profile shown in Figure 1 and the individual size fractions of dust from the ore storage Andersen samples, shown in Figure 2, indicates that the size fraction of the dust was an important factor in determining its solubility within the leach. The coarse fraction of the Andersen sampler (stages 0-1) most closely resembles the extraction profile of the ore storage bulk dust shown in Figure 1. This indicates that the extraction profile of the bulk dust was dominated by the coarser material within the dust and that the bulk of the lead resides within the coarse particle-size fraction of the dust from this area of the smelter.

The extraction profile for the sinter airborne dust samples is shown in Figure 3. As with the ore storage air samples, the finer particles were consistently more soluble, and the extraction profile for the coarser particle fractions from the Andersen air samples most closely resembles the extraction profile of the sinter bulk dust shown in Figure 1.
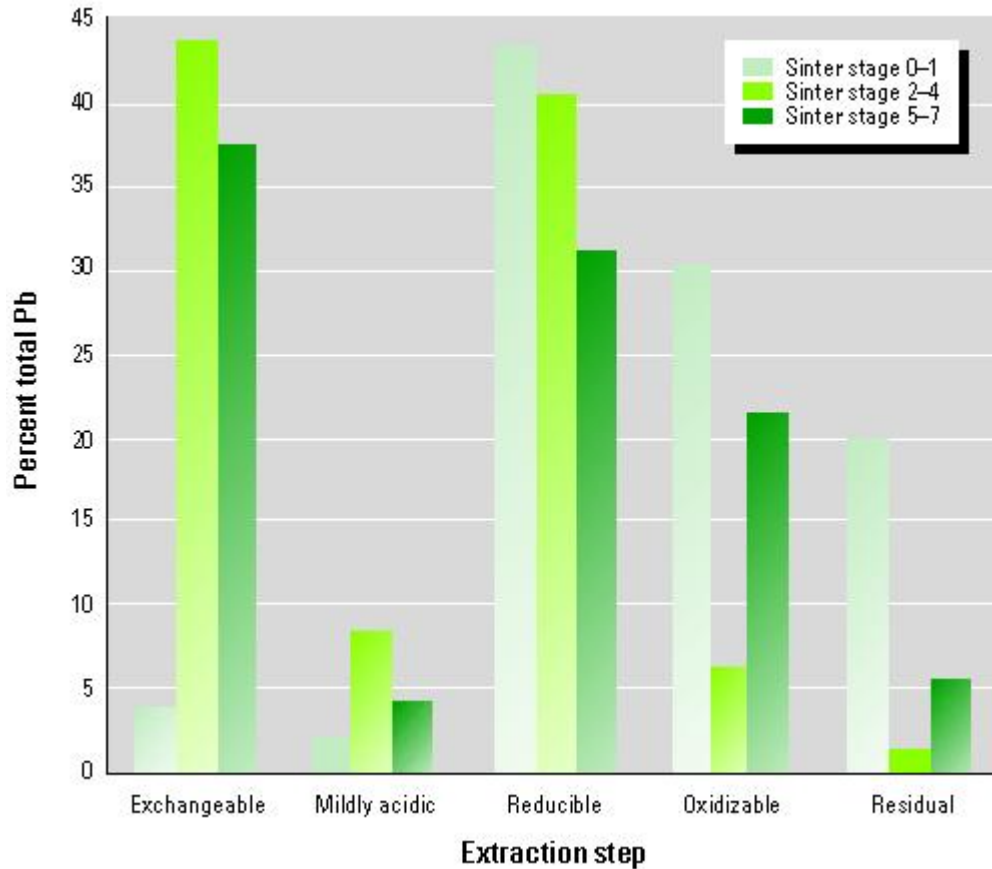
Figure 3. Percent total lead sequentially extracted by Andersen sampler stage from the sinter airborne dust samples.

Figure 4 shows the extraction profile for the combined airborne dust samples from the blast and dross furnaces. The highest percentages of total lead were extracted during the first three steps of the extraction procedure. The total lead from the Andersen stages 0-1, 2-4, and 5-7, 67%, 44%, and 36%, respectively, were exchangeable. Figure 4 also suggests that the contribution of transient dust emanating from other areas of the smelter may misrepresent the dust actually produced in the blast and dross areas in that the airborne dust collected was much more soluble in the larger particle-size fractions than that indicated by the bulk dust extraction profile from this same area (see Figure 1). This may be explained by an examination of the volume and extraction percentages of lead in the airborne dust from the blast and dross furnace areas, shown in Figure 5. Although the coarse dusts sampled in the blast and dross furnace areas were very soluble, Figure 5 shows that the largest percentage of blast and dross lead collected with the Andersen sampler was associated with the very fine particle-size fractions from stages 5-7. From these stages, 24%, 15%, and 22% of the total lead were extracted during the exchangeable, mildly acidic, and reducible steps, respectively. This compares to 9%, 0.66%, and 1.4% of the total lead extracted from stages 0-1 during these same extraction steps. An analysis of the volume and extraction percentage of lead in the airborne dust from the ore storage area (not shown) revealed approximately 99% of the total lead collected with the Andersen sampler to be associated with the coarse particle fraction from stages 0-1. In addition, essentially all of the lead from the ore storage area was extracted during the reducible, oxidizable, and residual extraction steps.
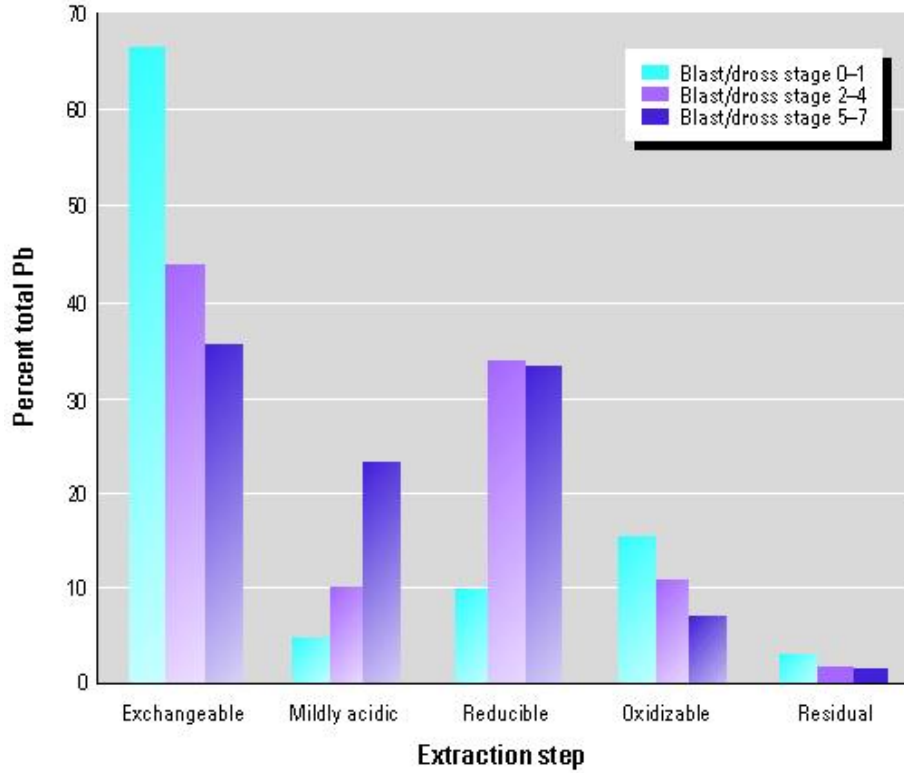
Figure 4. Percent total lead sequentially extracted by Andersen sampler stage from the combined blast and dross airborne dust samples.
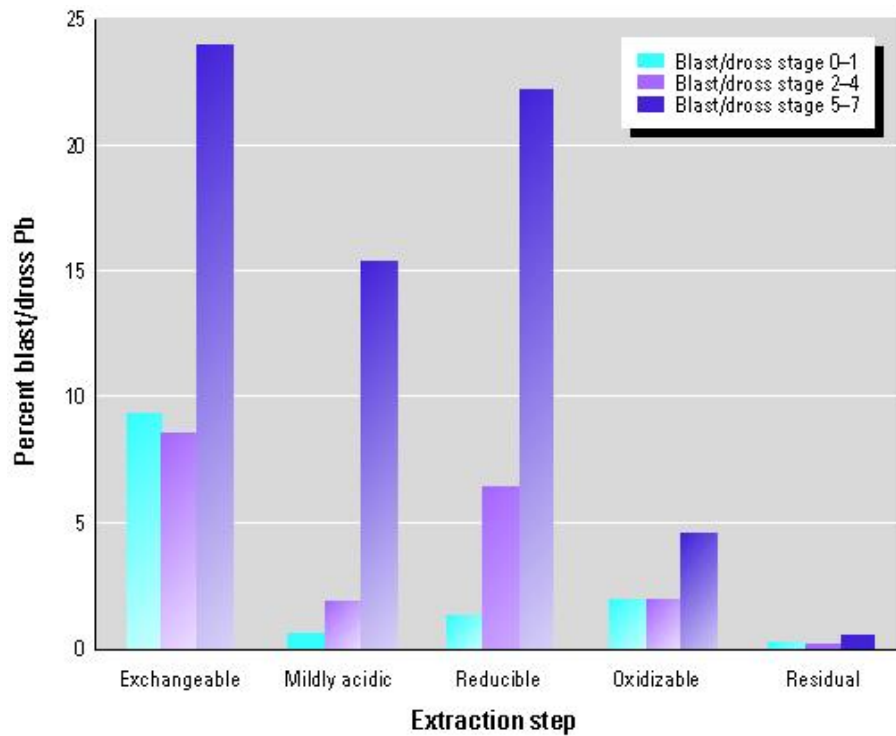

Figure 5. Percentage of the blast and dross lead sequentially extracted by Andersen sampler stage from the combined blast and dross airborne dust samples.

Comparison with PbO-silica, PbSO₄-silica, PbS-silica, and PbX-silica mixtures. The distribution of a given metal between various fractions can only be considered as operationally defined by the method of extraction. To determine the solid phase solubility of lead compounds through the extraction scheme used in our study, a series of lead oxide (PbO), lead sulfate ($PbSO_4$), and lead sulfide (PbS) mixtures with reagent-grade silica was prepared. The mixtures of reagent-grade PbO, $PbSO_4$, and PbS powder with reagent-grade silica powder were mixed to approximately 16% total lead. The three PbX-silica mixtures were then blended into a fourth mixture containing 16% total lead, and all four mixtures were dissolved by the Tessier method.

Figure 6 depicts the extraction of lead for the individual steps of the extraction procedure on these mixtures. During the exchangeable step, 70 mg of the lead oxide was extracted, with 28 mg and 5 mg being extracted in the mildly acidic and reducible steps, respectively. The lead sulfate was only slightly less extractable during the exchangeable step (65 mg), with 53 mg and 18 mg being extracted in the mildly acidic and reducible steps, respectively. The lead sulfide was primarily extracted during the oxidation (58 mg) and residual (19 mg) steps. The mixture of lead compounds and silica appears to be a compromise of the other three compounds, with the lead oxide and lead sulfate extracted during the first three steps and the lead sulfide extracted during the oxidation and residual step.
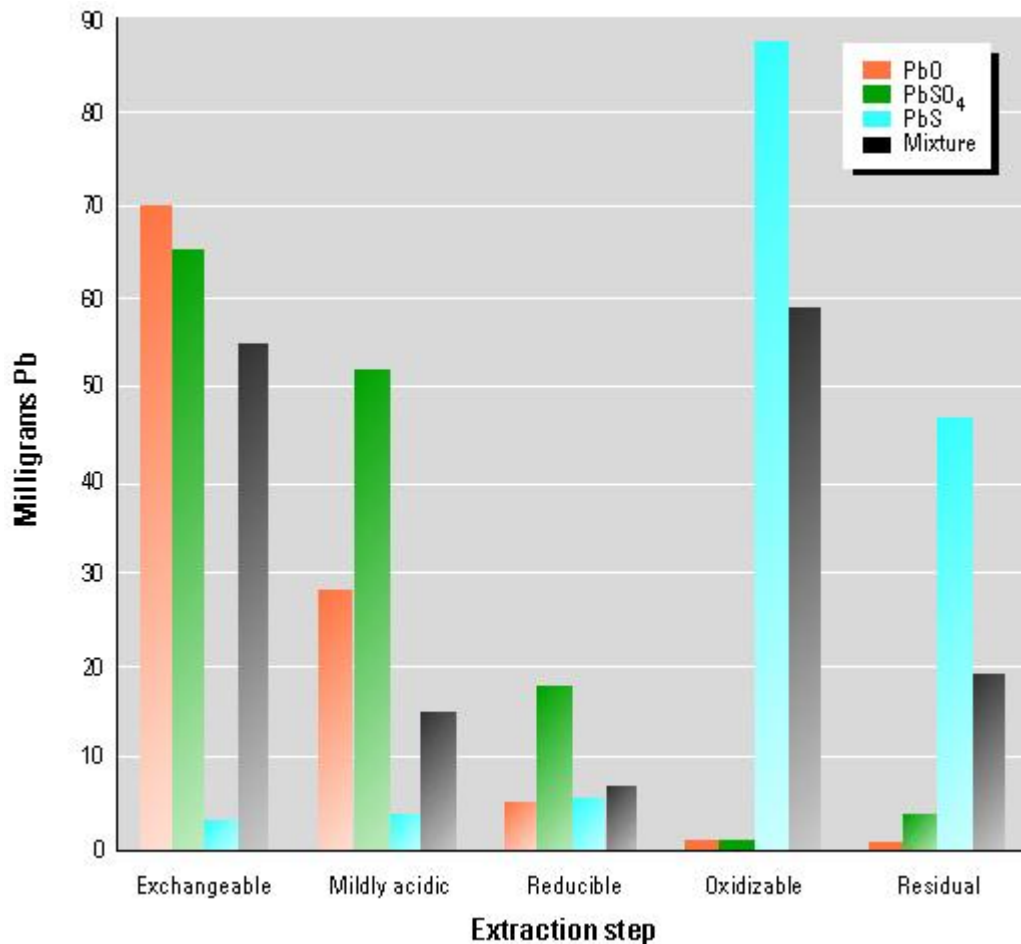

Figure 6. Milligrams of lead extracted from lead oxide-silica (PbO-SiO2), lead sulfate-silica (PbSO4-SiO2), lead sulfide-silica (PbS-SiO2) mixtures, and a composite mixture (PbX- SiO2) by the Tessier method.

Concluding Remarks

In most workplaces, aerosol exposures involve the inhalation of many different types of particles that are distinguished not only by their size but also by their chemical, physical, and biological characteristics. The combined distributions of particle size and species together determine the ability of the particles to reach given parts of the respiratory tract and their rate and intensity of action once they have arrived at the initial site of deposition. Currently, there is considerable interest in the various compounds that feature in aerosol exposure during the production and use of metals and in the setting of safe limits for their control. Whereas it is currently common practice to determine exposure in terms of the airborne concentration of the metal atoms that are present (e.g., by atomic absorption spectrophotometry), it is known that certain molecular forms are more harmful than others. In the production of nickel, for example, epidemiology has suggested that although water-soluble sulfidic and oxidic forms might be associated with lung and possibly nasal cancer, there is no such evidence for the metallic form (*21*). In such cases, the question of which chemical species is the most relevant to adverse health effects is therefore an important issue.

Our results of smelter lead dust speciation analysis for both the bulk dust samples and airborne dust samples confirmed that the lead dust mineralogy varies widely throughout the smelter, consisting of remnant sulfides and multimetal oxide phases. These findings are consistent with other studies that have reported galena as the major constituent in samples associated with ore handling, whereas lead oxide species (PBO_x, $PbO \bullet PbSO_4$) were the dominant species associated with smelter operations (*9*). Changes to the ore during the smelting process result in changes to the mineralogy of the airborne dust, which are reflected in the Tessier sequential extraction method. Oxides and sulfates of lead are predominantly dissolved during the exchangeable and mildly acidic steps of the sequential extraction procedure, with lead sulfides and silicate minerals predominantly dissolved in the oxidizable and residual steps.

Dusts produced in the ore storage and sinter areas of the smelter are coarser and react later in the extraction steps than do the dusts produced in the blast and dross furnace areas. The dusts produced near these furnaces contain a higher percentage of soluble lead oxide, lead sulfate, and soluble lead. The finer particle sizes appear to be more soluble regardless of the bulk mineralogy of the dust. This finding is also in agreement with other studies (*22*). Assuming that the mobility and bioavailability of lead are related to its solubility as determined through sequential extraction, the health hazards from lead exposure may be appreciably enhanced in the blast and dross furnace processes. These areas have higher percentages of exchangeable lead and higher lead concentrations contained in the finer particle-size fractions.

This research has implications pertaining to lead exposure to residential districts near the smelter. Entrainment of soil particles is an important route of lead transport contributing to the atmospheric burden around lead smelting facilities. Large particles (d_{ae} >2 μm) emitted from the smelter settle out of the atmosphere fairly rapidly and are deposited relatively close to the smelter. These larger settled particles can become more bioavailable as they are ground into smaller particles within the home environment. The smaller and more bioavailable particles emitted from the smelter may be transported many kilometers from the smelter (*23*). Lead particles emitted from the smelter would be primarily in the form of lead sulfur compounds, $PbSO_4$, $PbO \bullet PbSO_4$, and PbS.

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