Sorbents for Removal of Lead Compounds from Hot Flue Gases

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Since strict regulations have been placed prohibiting the placement of hazardous wastes in landfills, incineration is emerging as the principal and most attractive alternative for disposal of hazardous wastes. Incineration of waste offers various advantages including conversion of toxic organic components of hazardous wastes to harmless or less harmful forms, reduction in volume, and means of energy recovery (Palmer et al., 1988). Unfortunately, since metals are not destroyed during the incineration process, toxic metal particles or vapors are generated as byproducts when wastes containing these metals are incinerated. A significant fraction of volatile compounds of toxic metals like lead, mercury, cadmium, arsenic, and selenium, are emitted as vapor or fine particles (Palmer et al., 1988). Nonvolatile toxic metal compounds are released with the ash and also require safe disposal.

Lead and lead compounds are very toxic and have been found to have a significant effect on the neurophysical performance of humans, specially children (Jaworski, 1987). Lead salts of long chain organic acids are used as stabilizers for nearly all plastic material, except those used for food processing (Cole and Kressin, 1984). Compounds of lead are also consumed in large quantities for production of storage batteries and pigments. When wastes containing lead are incinerated, a wide variety of lead compounds are generated. The chemical form and concentration of these compounds depend on a number of factors including waste composition and operating conditions (Barton et al., 1988). Using chemical equilibrium analysis, it has been shown that when chlorine-containing wastes are incinerated, lead compounds exist predominantly as PbO, $PbCl_2$ and $PbCl_4$ in the flue gas (Mathews, 1988). In the presence of sufficient sulfur, $PbSO_4$ may also be formed. For safe incineration of lead-containing wastes, the concentration of lead compounds in the flue gas has to be reduced to tolerable levels as specified by the environmental regulation agencies. A promising technique for the removal of lead compounds from flue gases is that of passing the lead laden flue gas through a fixed bed of an appropriate sorbent.

Some studies have been undertaken on the reaction of lead compounds with different solids. The chemical reaction of lead oxide with kaolinite, an aluminosilicate clay, has been previously studied by heating the powders of these compounds to high temperatures (Holland et al., 1976). Cantwell et al. (1972) demonstrated that alumina pellets can be used as lead traps for control of particulate lead emission from automobile exhausts. In general, the desired characteristics in any material used for removal of toxic vapors in incineration processes include high-temperature stability, rapid adsorption, and conversion of lead compounds to forms that are stable, less toxic, and easily disposable. The purpose of this study is to screen various materials as effective sorbents for removal of lead compound vapors from hot flue gases. Possible sorption mechanisms for materials found most promising are also discussed.

Experimental Approach

In the first part of this study, several naturally available materials and model compounds were evaluated as potential sorbents for removal of gaseous lead compounds from hot flue gases. The model compounds included silica (MCB grade 12 silica gel) and alpha alumina (Du Pont Baymal colloidal alumina, technical grade). The naturally available materials included kaolinite, bauxite, emathlite, and lime. The composition of these sorbents is given in Table 1. Aluminosilicate type materials have been found to be reactive with various metal vapors (Punjak et al., 1989; Lee and Johnson, 1980). Since lime is used for removal of gaseous sulfur compounds from hot flue gases, a high lead capturing efficiency would make it a very attractive choice for simultaneous removal of sulfur and lead compounds. Sorbent particles, 60–80 mesh in size, were calcined at 900°C for two hours and stored under vacuum until used. Lead chloride was used as the source and the flue gas had a composition of 15% CO_2, 3% O_2, 80% N_2, and 2% H_2O.

A schematic of the experimental setup is shown in Figure 1. The main components of this system are a Cahn recording microbalance, a quartz reactor, a movable furnace, and analyzers for determining the composition of the gaseous products. The lead source is suspended by a platinum wire from the micro-

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Table 1. Composition of Sorbents (As Received)*

	Bauxite** wt. %	Kaolinite*** wt. %	Emathlite† wt. %	Limestone‡ wt. %
SiO_2	11.0	52.1	73.4	0.7
Al_2O_3	84.2	44.9	13.9	0.3
Fe_2O_3	4.8	0.8	3.4	0.3
TiO_2	—	2.2	0.4	—
CaO	—	—	5.0	97.2
MgO	—	—	2.6	1.5
K_2O	—	—	1.2	—
Na_2O	—	—	0.1	—

*Volatile-free basis
**Paranam bauxite from Alcoa Corporation
***Burgess Pigment Company
†Mid-Florida Mining Company
‡Pfizer Incorporated

balance, which monitors the weight change during the experiments. A fixed bed of the sorbent particles was made by placing 100 mg of the sorbent particles on a 100-mesh stainless-steel screen in a quartz insert. Independent control of temperatures in the upper part of the reactor containing the lead source and the lower part containing the sorbent was obtained by using a two-zone heater. All experiments in this study were performed with the source at 495°C and the sorbent at 700°C.

Each experiment was initiated by first starting the carrier gas flow to purge the system. The preheated furnace was then raised to heat the sorbent particles. Heating of the lead source was subsequently started to vaporize $PbCl_2$ which was carried by the flue gas through the sorbent fixed bed. After a predetermined amount of the source compound had vaporized, the adsorption was terminated by lowering the furnace and diverting the gas flow through the auxilliary vent on the reactor. The percentage of lead adsorbed was determined from the amount of lead delivered (microbalance measurement) and the lead content of the sorbent at the end of the experiment. To measure the lead content of the sorbent, the samples were dissolved in a $H_2O/HF/HNO_3$ (2/1/1 proportion by volume) mixture. The lead content of the solution was determined by atomic absorption spectroscopy. Separate water leaching experiments were performed to determine the water soluble fraction of adsorbed lead. The leaching of lead was conducted at 40°C in an ultrasonic bath for two hours. The lead content of the solution was subsequently determined by atomic absorption spectroscopy. Leaching experiments conducted for longer time periods indicated that the two-hour period was adequate to leach out most of the water soluble lead. X-ray diffraction analysis was used to identify the principal crystalline phases formed during lead adsorption/reaction.

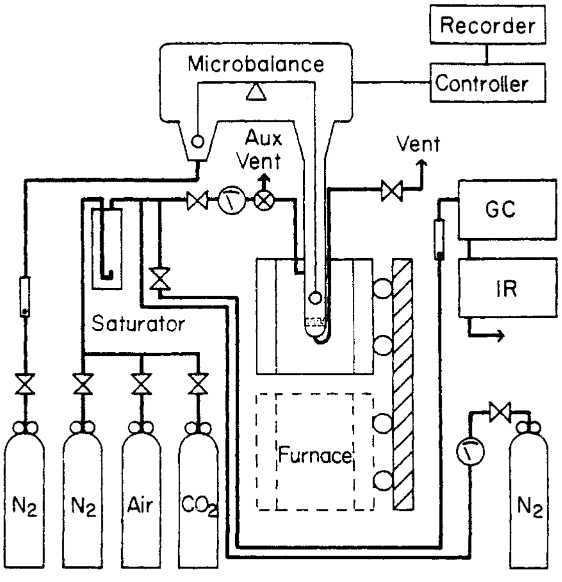

Figure 1. Apparatus.
GC = gas chromatograph; IR = nondispersive infrared analyzer

Results and Discussion

The results obtained from the screening experiments are given in Figure 2. Multiple experiments were conducted for most of the sorbents and good reproducibility was obtained. Since all experimental parameters except the sorbent type were kept constant, the amount of lead adsorbed is a good indication of the sorbent effectiveness for lead removal from hot flue gases. The most obvious feature of these results is the difference in abilities of the sorbents to capture lead from the flue gas passing through them. Both model compounds, silica and alumina, showed similar effectiveness for lead removal. Of the other sorbents tested, bauxite and kaolinite had high lead capture efficiencies while lime captured only a small fraction of lead from the flue gas. These results show that although SiO_2 and Al_2O_3 alone are good for lead removal, the combined presence of both greatly enhances the overall capacity for lead removal. To prevent ground water contamination when the spent sorbents are disposed, the water solubility of lead compounds adsorbed by these sorbents is also a very important factor in choosing an appropriate sorbent. Most of the lead captured by silica and kaolinite was found to be water insoluble. Bauxite, emathlite and alumina had larger fractions of water soluble lead while almost all the lead adsorbed by lime was found to be soluble in water. Based on the overall capacity for lead removal, and water solubility of the product, kaolinite and bauxite seem to be the most promising naturally occurring materials for lead removal

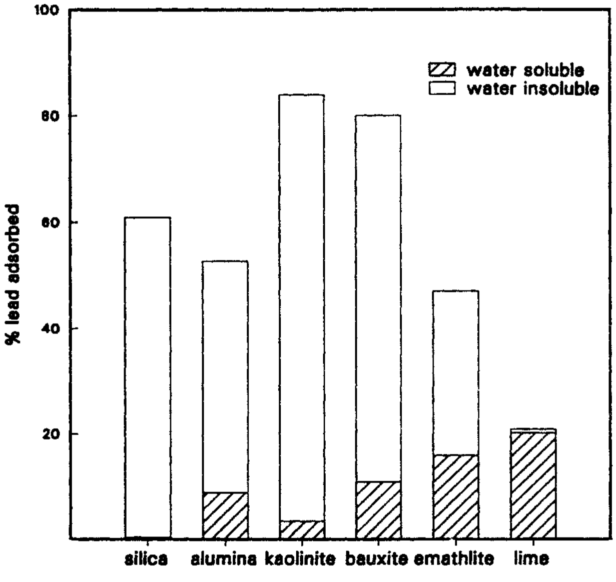

Figure 2. Lead removal efficiencies of various sorbents.
T = 700°C
Source = $PbCl_2$

from flue gases. These sorbents were therefore further studied to understand the mechanism of lead sorption.

The porosity of the sorbents was determined by mercury porosimetry. Bauxite had an initial porosity of 0.56 while kaolinite had an initial porosity of 0.50. X-ray diffraction (XRD) analysis was used to identify the final products formed by sorption of lead chloride on kaolinite and bauxite. As shown in Figure 3, analysis of kaolinite particles exposed to lead vapors indicated the formation of a lead aluminum silicate compound, $PbAl_2Si_2O_8$, which is water insoluble. XRD results showed that this compound existed in two crystalline forms: hexagonal and monoclinic. Based on XRD and water leaching results, the following reaction scheme is proposed for capture of lead:

$$\underbrace{Al_2O_3 \cdot 2SiO_2}_{\text{metakaolinite}} + PbCl_2 + H_2O \rightarrow PbO \cdot Al_2O_3 \cdot 2SiO_2 + 2HCl\uparrow \qquad (1)$$

where metakaolinite is the dehydration product of kaolinite. Sorrel (1962) also observed the formation of this compound when a solid mixture of lead compounds and kaolinite was heated to high temperature. Based on the stoichiometry of the overall reaction, 1 kg of kaolinite can adsorb 0.94 kg of lead, forming a product which is water insoluble and therefore safely disposable. Since $PbCl_2$ is soluble in water under our leaching experimental conditions, the water soluble fraction of adsorbed lead could be due to physisorption of lead chloride on the kaolinite particles. A scanning Auger Microprobe survey of particles after lead adsorption did show a chlorine signal, indicating that some lead chloride was physisorbed. However, it appears that lead chloride exists in a glassy form in the particles and is therefore not detected in XRD analysis.

XRD analysis of bauxite particles exposed to lead vapors indicated the formation of the same lead aluminum silicate compound as for kaolinite, but only the hexagonal crystalline structure was observed (Figure 3a). The amount of SiO_2 present in bauxite is not enough to combine with all Al_2O_3 to form an aluminosilicate compound. Based on the stoichiometry of Eq. 1 and the amount of SiO_2 present, bauxite should have an ultimate reaction capacity of 0.20-kg lead/kg bauxite. As shown in Figure 2, bauxite adsorbed a larger fraction of water soluble lead as compared to kaolinite. This can also be explained by the fact that bauxite has more Al_2O_3 than kaolinite. Since adsorption on alumina results in a larger fraction of water soluble lead as compared to silica, it seems that the excess Al_2O_3 in bauxite adsorbs some $PbCl_2$ by the same mechanism as alumina, resulting in a larger fraction of water soluble lead. Although no other crystalline phase was observed, an Auger Microbe survey did show a chlorine signal, indicating that some $PbCl_2$ might be physisorbed on bauxite particles appearing in a glassy form.

The above results have important implications in choosing sorbents for lead capture. Lime, a good sorbent for sulfur compounds is not very effective as a lead adsorbent. Although bauxite and kaolinite captured approximately the same amount of lead from the flue gas in our experiments, kaolinite has a larger ultimate capacity for lead removal and a smaller water soluble fraction of lead captured. The results indicate that for both kaolinite and bauxite, the sorption process is not just physical condensation, but rather a combination of chemical reaction and adsorption. No pore plugging is expected in our experiments since the sorbent conversion was quite low. Experiments for longer duration are needed to determine whether pore plugging occurs during sorption at high conversions. In practice, however, sorbent use at high conversions is limited by the slower rate of lead capture. In the final selection of sorbents, and design of a process, further information is needed on the intrinsic kinetics of the adsorption/reaction under different operating conditions.

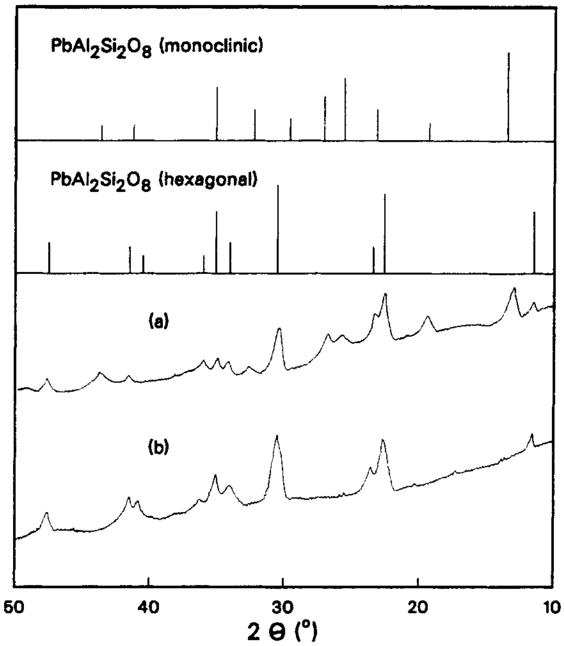

Figure 3. X-Ray diffraction patterns of fully saturated sorbents.
a = kaolinite; b = bauxite

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