Effectiveness and Mechanisms of High-Temperature Lead Capture by Various Aluminum-Silicate Minerals

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Abstract−The relative effectiveness of seven inorganic sorbents for the capture of gaseous lead chloride was investigated by using a high-temperature packed bed sorption reactor. The investigated sorbents were alumina, bauxite, andalusite, chamotte, kaolin, pyrophyllite and silica. Except for alumina, all other tested sorbents showed good potential for the capture of lead chloride, since they were good for limiting leachability of captured lead species. Combining the two sorbent criteria of increased metal uptake on sorption and reduced leachability by the toxicity characteristic leaching procedure (TCLP), kaolin and pyrophyllite appeared to be the most-promising sorbents for lead capture. From the analysis of post-sorption sorbent samples, three different capturing mechanisms for lead capture by high-temperature inorganic sorbents were suggested: 1) chemical reaction to form water-insoluble lead-mineral complexes such as $PbO \cdot Al_2O_3 \cdot 2SiO_2$, 2) physical adsorption of gaseous chloride to form water-soluble lead chloride ($PbCl_2$), and 3) formation of water-insoluble lead oxide (PbO) on sorbent surface.

Key words: Lead, High Temperature, Inorganic Sorbents, Sorption, Leachability, Reaction Mechanism

INTRODUCTION

The presence of volatile heavy metals in incinerator flue gases is of environmental concern because of their associated toxic properties. In most systems, volatilized metals ultimately end up as submicron particles that are difficult to control [Barton et al., 1990; Linak et al., 1993; Korzun et al., 1990]. Lead is considered one of the volatile hazardous metals that are easily emitted into the environment during waste incineration. Lead has a number of industrial applications, and due to the wide range of their use, lead compounds are present in various burnable wastes. There has recently been considerable interest in the potential use of mineral-based sorbents for the capture of gas-phase hazardous metals. Many volatile metals can be reactively scavenged by fly ash and earth elements such as calcium, aluminum and silicon, etc. [Chen et al., 1998; Evans et al., 1999; Ho et al., 1991, 1992, 1996; Mahuli et al., 1997; Masseron et al., 1999; Uberoi et al., 1989, 1991a, b; Wang et al., 1999; Yang et al., 1999, 2001a, b]. Metals bound to larger sorbent particles will be more effectively collected by air pollution control systems. Studies suggest that chemical reactions between the metal and mineral-based sorbent dominate over physical adsorption, offering the additional advantage of reduced potential for metal leaching from sorbents [Evans et al., 1999; Shin et al., 2001]. Previous works have studied the reaction of a lead and kaolinite. Uberoi et al. proposed from the result of X-ray diffraction (XRD) of lead-sorbed kaolinite flake that reaction formed a water-insoluble product, lead aluminum silicate ($PbO \cdot Al_2O_3 \cdot 2SiO_2$). More recently, advanced experiments using laboratory-scale or pilot-scale down-flow combustor were performed to

examine the post-flame reaction between lead vapor and kaolinite [Masseron et al., 1999]. Their works show that lead capture by kaolinite was reduced at higher temperature and in the presence of chlorine.

This study investigated the relative effectiveness of various aluminum-silicate minerals including kaolinite as high-temperature sorbents of lead vapor in the presence of chlorine. In addition to metal capturing, an ideal sorbent would retain captured metal species in the sorbents when they are disposed of [Uberoi et al., 1991]. Accordingly, the primary objective of this study is to evaluate seven aluminum silicate minerals with respect to 1) the degree to which they capture lead when they are exposed to the flowing flue gas containing lead chloride ($PbCl_2$) vapor, and 2) the degree to which they retain captured lead in the sorbent structure when they are subjected to the toxicity characteristic leaching procedure (TCLP) extraction [U. S. EPA., 1992]. The additional objective of this study is to understand the high-temperature sorption mechanisms from the XRD (X-ray diffraction) analysis and the microscopy of raw and lead-captured sorbent samples.
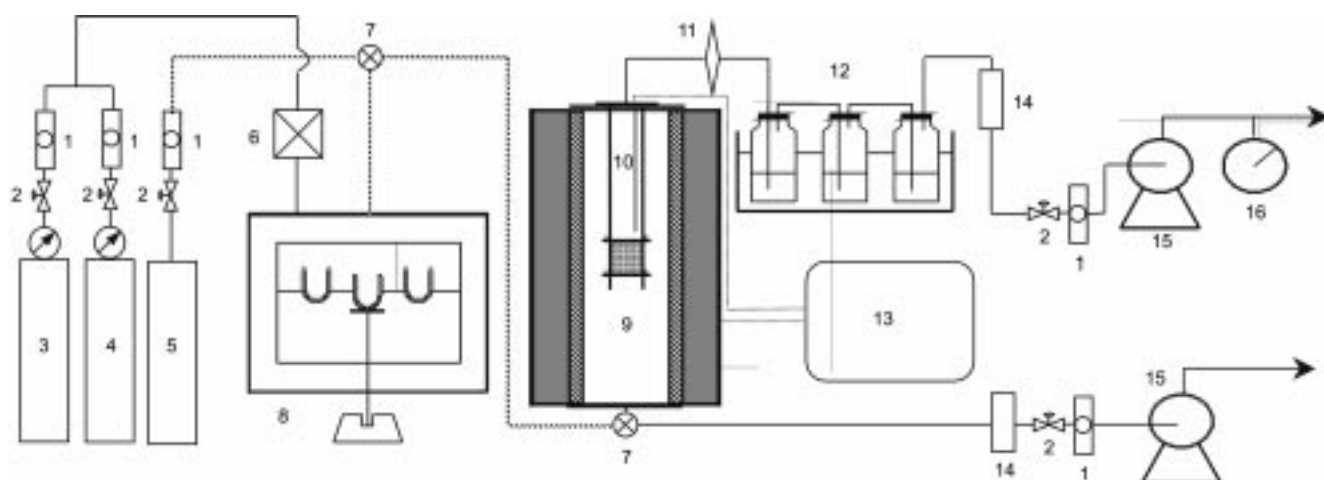
EXPERIMENTAL

1. Experimental System

The high-temperature sorption tests comprising this study were performed by using a packed bed sorption reactor. The principle of the tests is to pass a simulated flue gas, which includes vapor-phase $PbCl_2$, through a high-temperature bed of calcined mineral particles. The experimental system, as shown in Fig. 1, mainly consists of a flue gas supplying system, a sorption reactor assembly, and a vapor collection train. The flue gas supplying system included a thermo-gravimetric furnace (MAC-500, from LECO Inc.) for metal vaporizing and a gas mixer. The sorbent bed reactor assembly consists of a 1,373 K ceramic tube furnace and a stainless steel sorbent

Fig. 1. Schematic diagram of experimental system.

1. Flow meter	7. Valve	13. Controller
2. Needle valve	8. Thermo gravimetric furnace	14. Silicagel bed
3. N_2	9. High temperature sorption bed	15. Vacuum pump
4. O_2	10. Thermocouple	16. Dry gasmeter
5. Steam generator	11. Filter	
6. Gas mixer	12. Impingers	

bed holder assembly. The ceramic tube furnace is a 2-inch ID custom-fabricated single-zone furnace. The sorbent bed holder with a 1-inch ID and a 1.5-inch length is made of a stainless steel tube and 300-mesh stainless steel screens. The flue gas exhaust tube of the sorbent bed reactor assembly is connected with metal scrubbing train [Carrol et al., 1995].

2. Materials Used

Seven inorganic sorbents were tested for lead capture. Bauxite, kaolin and silica were first selected based on the most promising results from the literature and our previous studies [Uberoi et al., 1989, 1991a, 1992b; Yang et al., 1999, 2001a, b]. Four inorganic sorbents (alumina, andalusite, chamotte and pyrophyllite) were added to make up a mineral-spectrum ranging from pure alumina to pure silica. The approximate mineral compositions and major mineral species of tested seven sorbents are given in Table 1. Mineral particles in the size range of 35-48 mesh were selected and calcined at 1,173 K, then stored in a heated oven at 423 K until used. Lead sources were powdered high-purity $PbCl_2$ (Aldrich Co., >99.9%).

3. Experimental Procedure

Table 1. Approximate mineral composition of tested mineral sorbents

Tested sorbent	Approximate composition (%)		Major mineral species
	Al_2O_3	SiO_2	
Alumina	>99.5	-	Corundum (Al_2O_3)
Bauxite	89	7	Corundum (Al_2O_3)
Andalusite	58	39	Andalusite ($Al_2(SiO_4)O$)
Chamotte	40	55	Mullite ($Al_6Si_2O_{13}$)
Kaolin	33	52	Kaolinite($Al_2Si_2O_5(OH)_4$)
Pyrophyllite	18	76	Pyrophyllite($Al_2SiO_4O_{10}(OH)_2$)
Silica	-	>99	Quartz (SiO_2)

All experiments were performed with a $PbCl_2$ vapor-carrier gas of 20 LPM (liter per minute). The major composition of the simulated flue gas entering the sorption bed was 12% of O_2, 5% of CO_2 and 1% of H_2O by volume, with the remainder consisting of nitrogen. The concentration of $PbCl_2$ vapor in the simulated flue gas was controlled with prior knowledge of the averaged vaporization rate, which was determined from the weight loss of the sample $PbCl_2$ in the vaporizing furnace [Yang et al., 1999, 2001a, b]. At the start of each experiment, the temperature of the sorbent loaded sorption bed was raised to 973 K. Powdered lead chloride was loaded on the crucible and the thermogravimetric furnace was heated to 973 K with a maximum heating rate of 99 K per minute. All flue gas generated during preheating of the thermo-gravimetric furnace was directly passed through multiple metal sampling trains. The weight of the loaded crucibles was continuously measured by using a turntable and a microbalance with a sensitivity of 5 μg. When the vaporization rate of lead chloride in the thermo-gravimetric furnace became nearly constant with time, the flue gas path was changed to pass through the heated packed bed of sorbent. The concentration of $PbCl_2$ vapor in the simulated flue gas was controlled to be 110 ± 10 ppm.

4. Sample Analysis

After each sorption test at 973 K, the total quantity of captured lead was first determined by the weight increase of the sorbent. TCLP extraction tests and higher-temperature desorption tests at 1,073 K were then performed for post-sorption samples. The structural and morphological changes of the sorbent samples at the stage of lead sorption were investigated by the powdered XRD analysis (Philips, X'pert MPD) and the SEM photographs (JEOL, JXA 8600) of calcined sorbents and lead-sorbed sorbents [Wi et al., 2002].

RESULTS AND DISCUSSION

1. Lead Uptakes

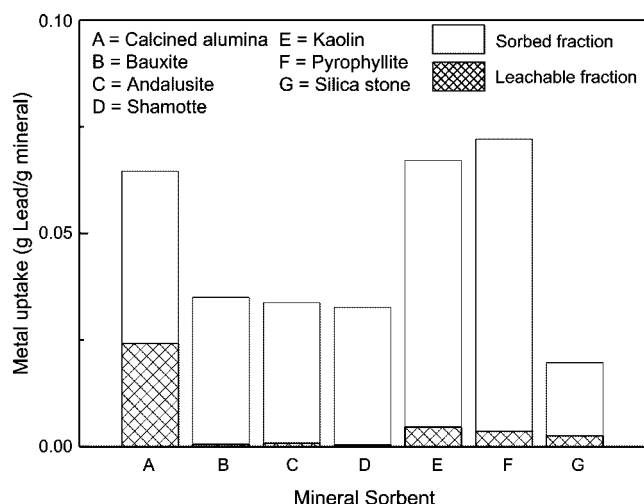Fig. 2. Lead uptake of inorganic sorbent by passing simulated flue gas through packed bed of 35-48 mesh mineral sorbent particles at 973 K (110 ppm PbCl$_2$ for 250 min).

Fig. 3. Powdered XRD patterns of (a) raw and (b) lead-sorbed bauxite.

The results of lead sorption and TCLP extraction are shown in Fig. 2 and Table 2. Alumina, kaolin and pyrophyllite have higher lead uptakes on sorption than other four minerals. Pure alumina shows a relatively high lead uptake but about 40% of lead captured by alumina was water-soluble. Therefore, pure alumina appeared to be inadequate as high-temperature lead-capturing sorbents because of their high leachability of captured lead. Pure silica showed the smallest lead uptake among tested seven minerals. However, captured lead species by pure silica was not easily leached by TCLP extraction, relative to pure alumina. Compared to pure alumina and pure silica, all other lead-captured aluminum-silicate minerals were relatively good for limiting leachability of captured lead species. Fractional lead leachability (F_L), which represents the ratio of leached lead quantity by TCLP extraction to the total captured lead quantity on sorption, of five aluminum-silicate minerals were in the range of 0.012-0.067. These small leachability values for post-sorption aluminum silicate minerals and pure silica suggested that most lead species in post-sorption sorbents except for alumina were present as water-insoluble lead species and much smaller amount of water-soluble lead species was included in the post-sorption samples. Combining the two sorbent criteria of increased metal uptake on sorption and reduced leachability by TCLP, kaolin and pyrophyllite appeared to be the promising sorbents for lead capture.

In order to get quantitative information on the captured lead species, desorption tests were performed under oxygen-deficient atmosphere (>99.999 N$_2$) at 1,073 K, at which temperature PbCl$_2$ vaporizes with a significant vapor pressure. Fractional desorption (F_D), which is shown in Table 2, represents the ratio of the desorbed lead to the total lead in the post-sorption sample. Andalusite was the best of seven tested sorbents at limiting lead volatility at 1,073 K. The vaporization of captured lead species on silica was also very lim-
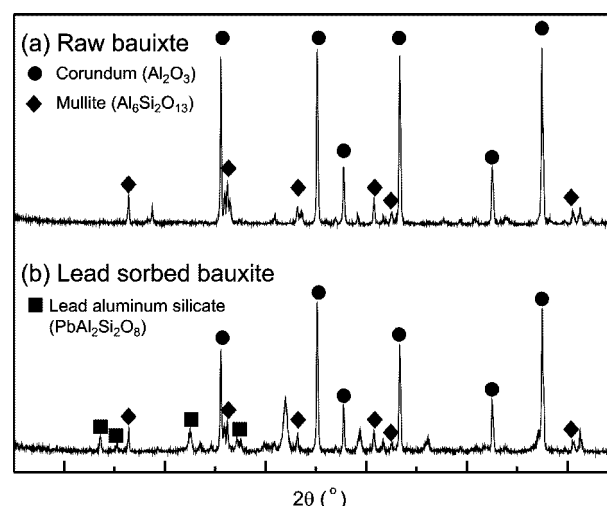
ited, in spite of its relatively large fractional desorption. Less than 1% of captured lead by silica as well as by andalusite was desorbed at 1,073 K. In every case except for silica, easily leached lead species was easily desorbed, and fractional desorption, F_D, was larger than fractional leachability F_L. This suggested that leaching of some water-soluble lead species, PbCl$_2$, could be limited by mineral sorbent matrices.

2. Capturing Mechanisms

It was suggested from the results of TCLP extraction tests that water-insoluble lead species such as lead aluminum silicate (PbO·Al$_2$O$_3$·2SiO$_2$) and/or lead oxide (PbO) were present in the post-sorption sorbent samples, together with a smaller amount of water-soluble lead chloride (PbCl$_2$). In order to get further information on the captured lead chemical species, powdered XRD pattern analyses of raw and lead-captured sorbent samples were performed and the results are shown in Figs. 3-7. As expected, water-insoluble lead aluminum silicate (PbO·Al$_2$O$_3$·2SiO$_2$) was found in all lead-sorbed aluminum-silicate sorbents. These suggested that any minerals including both Al$_2$O$_3$ and SiO$_2$ could capture lead vapor to form lead aluminum silicate (PbO·Al$_2$O$_3$·2SiO$_2$). However, the powdered XRD patterns of lead-sorbed alumina and silica show no new peaks, which can be assigned to any condensable lead species. However, lead oxide (PbO) and lead chloride (PbCl$_2$) with melted amorphous structures, which could not be found by XRD, must be present in post-sorption alumina and silica.

Fig. 8a-f shows the results of SEM microscopic analysis and EPMA quantitative analysis of raw and lead-sorbed alumina, chamotte and silica samples. The cross-sectional views of pre- and post-sorption alumina samples (Figs. 8a and 8b) show lead species in the post-sorption alumina are mostly distributed in the pores of alumina sorbent sample. The captured lead species by alumina ap-

Table 2. Leachable fraction (F_L) and fractional desorption (F_D) of post-sorption mineral sorbent

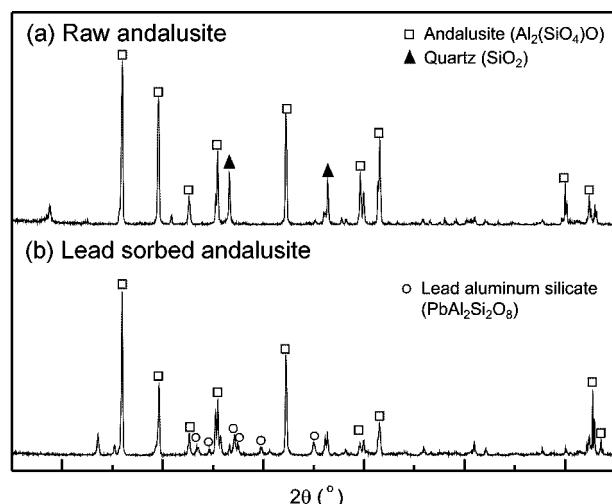|	Alumina	Bauxite	Andalusite	Chamotte	Kaolin	Pyrophyllite	Silica stone
F_L	0.375	0.014	0.024	0.012	0.067	0.049	0.129
F_D	0.631	0.040	0.007	0.026	0.100	0.224	0.008

Fig. 4. Powdered XRD patterns of (a) raw and (b) lead-sorbed andalusite.

Fig. 6. Powdered XRD patterns of (a) raw and (b) lead-sorbed kaolin.

Fig. 5. Powdered XRD patterns of (a) raw and (b) lead-sorbed chamotte.
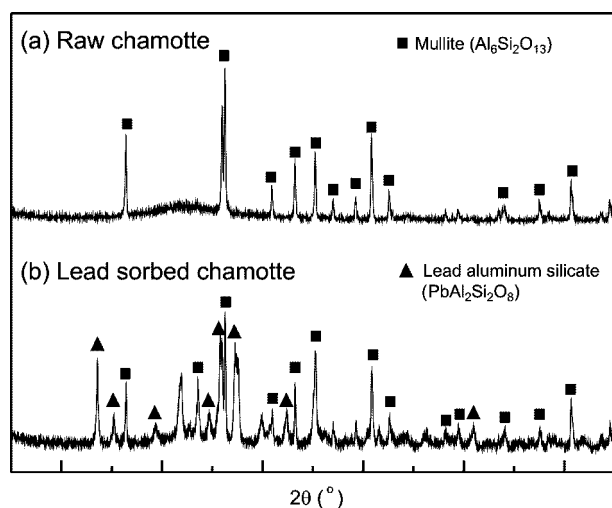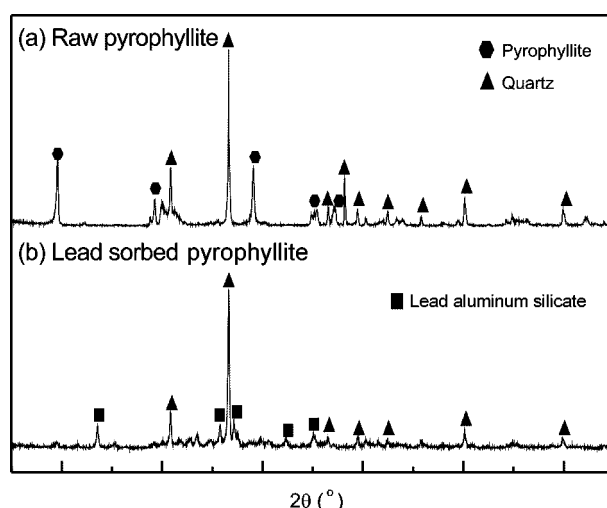

Fig. 7. Powdered XRD patterns of (a) raw and (b) lead-sorbed pyrophyllite.

peared to be not chemically combining with Al_2O_3. They appeared to be physically adsorbed in the pores of raw alumina. The results of EPMA quantitative analysis of lead-sorbed alumina are in agreement with this suggestion. The chemical composition of lead-sorbed alumina (LA in Fig. 8b) by EPMA quantitative analysis was 80.6% of lead (Pb), 17.1% of chlorine (Cl), and remainder consisting of aluminum (Al). It could therefore be known by stoichiometric estimation that about a half of the captured lead species is present in the form of $PbCl_2$ and others are present in the form of PbO. The results are in consistent with the results of TCLP extraction and volatility tests.

The lead distribution in the selected aluminum silicate, chamotte, is quite different from that in the alumina. As shown in Figs. 8c and 8d, sorbed lead species by chamotte are evenly distributed in the sorbent structure. Captured lead species by chamotte must be chemically combining with the sorbent mineral. In addition, no chlorine was included in the captured lead compounds. Lead chloride vapor sorption by chamotte occurs due to the chemical reaction to form a
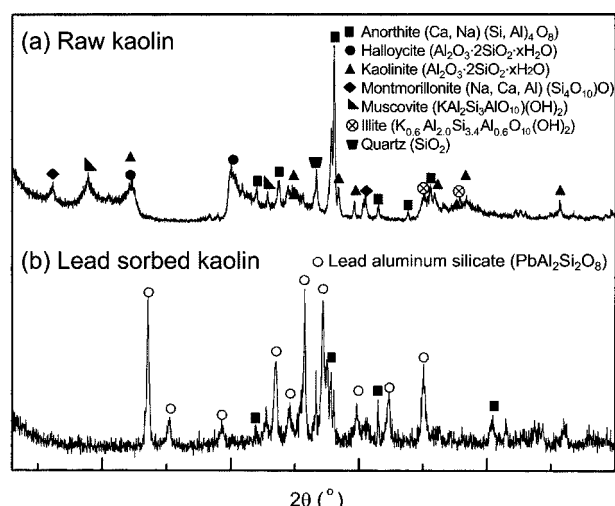
water-insoluble product, lead aluminum silicate ($PbO \cdot Al_2O_3 \cdot 2SiO_2$), which is assigned in the XRD patterns of lead-sorbed chamotte.

It can be seen in Figs. 8e and 8f that captured lead on silica was concentrated on the surface of silica particles. Very small quantity of chlorine was included in the captured lead species by silica. Therefore, it could be known that most lead species was present in the form of lead oxide (PbO), which is water-insoluble. The results of EPMA analysis of pre- and post sorption samples are generally in agreement with the results of TCLP and volatility tests.

CONCLUSION

All the seven tested sorbents which have a mineral spectrum range from pure alumina to pure silica could capture gaseous lead chloride at high temperatures. Except for alumina, all other six sorbents were good for limiting leachability of captured lead species. Combining the two sorbent criteria of increased metal uptake on sorption and reduced leaching by TCLP, kaolin and pyrophyllite ap-

Raw particle   Lead-sorbed particle
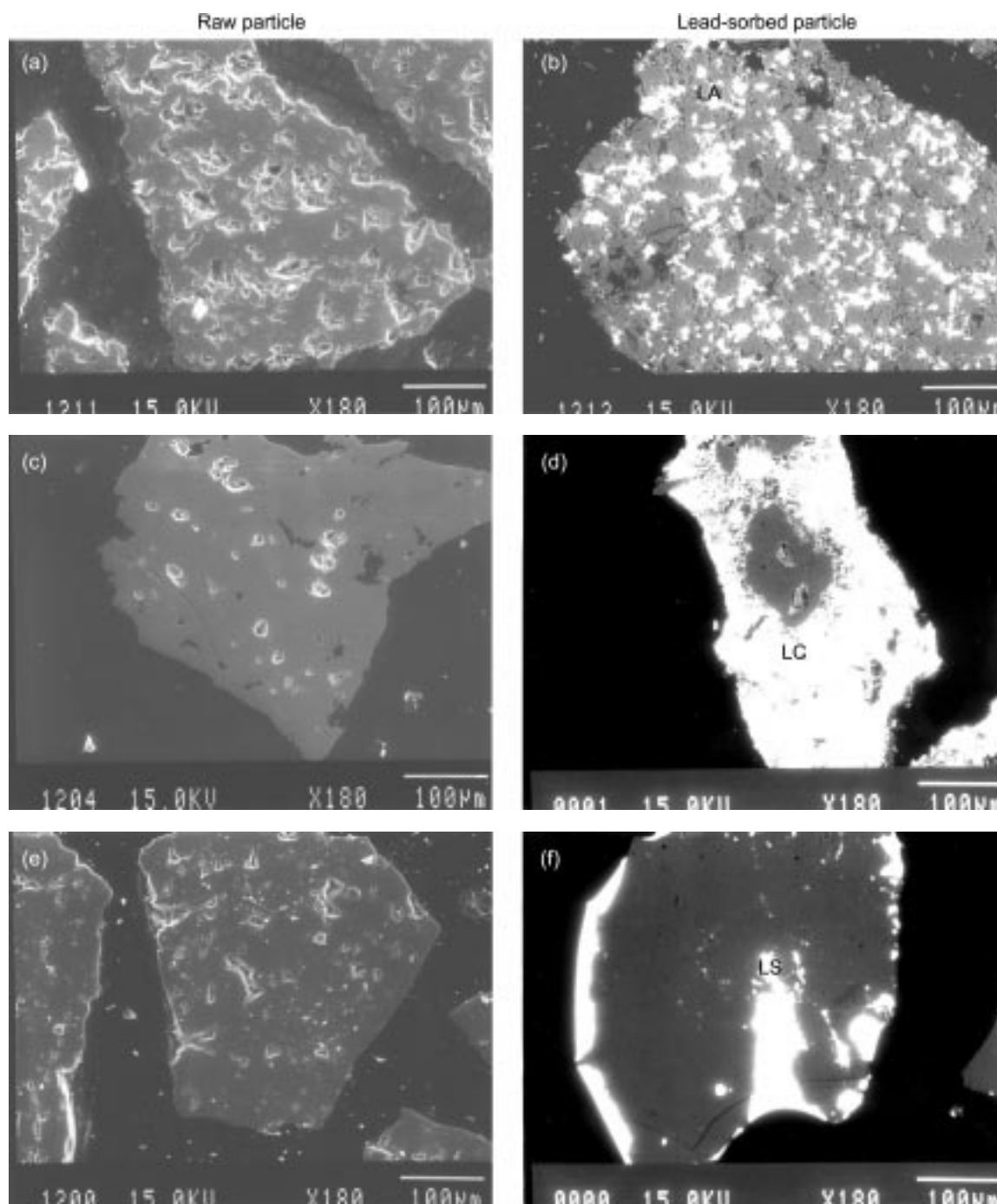
Fig. 8. SEM photograph of selected raw and lead-sorbed sorbents: (a) raw alumina, (b) lead-sorbed alumina, (c) raw chamotte, (d) lead-sorbed chamotte, (e) raw silica and (f) lead-sorbed silica.
LA - Lead sorbed alumina (Al: 2.28%, Pb: 80.58%, Cl: 17.14%)
LC - Lead sorbed chamotte (Al: 26.30%, Si: 31.12%, Pb: 37.19%)
LS - Lead sorbed silica (Si: 17.35%, Pb: 81.11%, Cl: 1.54%).

peared to be the most-promising sorbents for lead capture. High temperature lead sorption by tested mineral sorbents occurred by three mechanisms: 1) chemical reaction of gaseous lead chloride with sorbent minerals to form water-insoluble lead aluminum silicate ($PbAl_2Si_2O_8$); 2) condensation of gaseous chloride to form water-soluble condensate ($PbCl_2$); and 3) formation of water-insoluble lead oxide (PbO) on the sorbent surface by the dechlorination of $PbCl_2$. Field tests at commercial incinerators with the injection of powdered sorbents will be performed for practical application of the present results.

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