INTERACTION BETWEEN LIGHT/HEAVY METALS AND Al–Si PHASES FORMED FROM COMBUSTIBLE SOLID RESIDUES

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This paper discusses the characteristics of inorganic solid particles with an emphasis on the relationships between the light/heavy metals and the ash matrix Al–Si compounds during ash solidification. The electron probe microanalysis (EPMA) of the final ash shows the distribution of major elements Al and Si in different phases such as crystalline mullite, corundum, and aluminosilicate glass. It also illustrates that the majority of the Cr coexists with the corundum phase, while Cd, Pb, Na, and K coexist with mullite and aluminosilicate glass. A quantitative analysis of the EPMA results indicates that the surface of the ash particle contains 15.8% (concentration ratio) more of Na and 14.3% more of K than at the core. However, the concentration ratio of Pb and Cd is more at the core (11.8% and 13.2%, respectively) than the surface. The $^{27}$Al and $^{29}$Si solid-state nuclear magnetic resonance spectroscopy (NMR-MAS) and X-ray diffractometry studies also support the formation of three phases in the final ash. The formation of mullite and aluminosilicate amorphous phases is indicated by the presence of $^{27}$Al NMR peaks at 50 ppm (AlO$_4$ tetrahedral group), 8 ppm (AlO$_6$ octahedral group), and a broad $^{29}$Si NMR peak at –99 ppm. The $^{23}$Na NMR spectra show a broad peak around –28.7 ppm due to the Na$^+$ present to compensate SiO$^-$. During ash evolution, Cr$^{3+}$ replaces Al$^{3+}$ in its octahedral sites of corundum/mullite, while Pb$^{2+}$ and Cd$^{2+}$ either fill oxygen vacancy in mullite or form stable compounds with the glass phase. The results clearly indicate the interaction between light/heavy metals and ash Al–Si matrix compounds.

Keywords: Sludge combustion; Encapsulation; EPMA; NMR-MAS; Aluminosilicates; Surface free energy

INTRODUCTION

Ash residue obtained after the incineration of paper mill sludge may be considered a potential environmental pollutant as it contains heavy toxic metals such as chromium, cadmium, and lead (Linak and Wendt, 1993; Koziński, Saade, and Zheng, 1996; Somppi et al., 1998). When the ash material is disposed off by landfill, these toxic metals can be leached out under uncontrolled conditions, resulting in a negative impact on the environment. Minimization of metal leachabil-
ity from the residue thus becomes necessary, and hence the study of the behavior of heavy metals during waste combustion becomes more significant. In other words, the chemistry of light and heavy metals during ash formation is important as it resolves the ash characteristics. Rink, Koziński, and Lighty (1995) observed Cd and Pb encapsulation within a Si–Al–Ca-based glassy structure during fluidized bed incineration of pulp and paper sludge. This was effected by the melting and rapid cooling of the residues. The chemical reaction of heavy metals with Al or Al–Si compounds to form heavy metal-aluminate or -aluminosilicate is the primary reason for their immobilization. Previous research (Yoon et al., 1996; Koziński and Zheng, 1998) discussed the behavior of metals at high temperatures during waste or fuel combustion. However, the chemistry and mechanism of their interaction with an aluminosilicate matrix during combustion and solidification were not well established, so the present work focuses on the chemistry and mechanism of light/heavy metal interaction with an aluminosilicate matrix during ash solidification. We describe a structure for ash containing aluminosilicate glass as a major phase, with embedded crystalline mullite and corundum phases. The presence of alkali and heavy metals within these three phases suggests a mechanism for their interaction and allows us to propose a detailed hypothesis for metal immobilization/replacement within inorganic material. We explain why microstructural and crystallographic evidence suggests that the metals change their environments. In conclusion, we suggest some practical implications of the proposed structure.

**EXPERIMENTAL PROCEDURE**

A multizone temperature reactor (Koziński and Zheng, 1998), a Cahn 171 thermogravimetric furnace (TGF) (sensitivity 1 µg), was used for the combustion of simulated ash pellet. Ash formed during combustion was simulated by significantly larger ash pellets (2–4 mm) to obtain quantitative information on metals and to provide proper heating conditions. A detailed study of the real ash (obtained during deinking waste combustion) and the simulated ash pellets revealed almost identical chemical and structural characteristics (Koziński and Zheng, 1998; Ramesh and Koziński, 2000). The major components of the pellet were SiO₂ (50.1%) and Al₂O₃ (24.0%), along with minor compounds of CaO (3.7%), MgO (1.2%), NaOH (2.8%), KOH (0.9%), and TiO₂ (1.2%). It was doped with Cr (13,120 ppm), Cd (14,210 ppm), and Pb (13,140 ppm). High concentrations of the heavy metals in the ash pellet were preferred as the previous studies (Koziński and Zheng, 1998) contained only small amounts of these metals (<3000 ppm) and therefore lacked information on the metals’ behavior during ash melt
solidification (no Cl, S, or F were present in the system). The pellets were then heated up to 1500°C on a platinum foil in an oxidative environment (airflow 140 mL/min) at an average rate of 40°C/min, remained in this high-temperature zone for 600 s, and were subsequently cooled in N₂ at ~500°C/min to avoid thermal shock and surface oxidation. It was previously demonstrated that these conditions yield ash particles with encapsulated and immobilized heavy metals. Ash samples were collected at various temperatures during heating and solidification. In this article we restrict discussion to the initial pellet and samples withdrawn at 1000°C (heating), 1500°C, 1000°C (quenching), and 25°C (cooling).

The reason for applying an average heating rate of 40°C/min was to simulate the ratio of the heating time scale (inverse of heating rate) to the diffusion time scale (proportional to particle radius). It is true that in most combustion systems the heating rate is approximately three or four orders of magnitude higher than the one applied in our experiments (Niessen, 1995). However, the size of the fly ash particles formed during combustion is usually 0.1–10 µm. By having a slower heating rate for a larger ash pellet used in this study, the heating/diffusion time scale ratios were comparable. In other words, the Lewis numbers existing in most practical waste combustors and in our system were matched such that the temperature profiles and gas concentration profiles were similar. In addition, we observed quantitatively similar radial distributions of metals in ash collected from both a large pilot-scale combustor (7.5 m × 0.5 m unit) and from the TGF (Ramesh and Koziński, 2001a, b). It suggests that the kinetics associated with metal transformations in both systems did not cause different behavior of metals. Thus both the kinetics and the heating/diffusion time scales existing in large combustors and in our system are comparable, and they are adequate.

The authors realize that in general, the TGF technique may not be satisfactory for the simulation of the fly ash formation process. However, it certainly is a good technique for simulating metal migration within ash particles, which we studied.

The furnace–foil–sample assembly was also tested to verify the presence of mass transfer limitations, and the configuration was established, and used, that minimized the influence of these limitations (Ramesh and Koziński, 2001a). The heating process was taking place in the entire volume of the sample; therefore the intrapellet spatial temperature gradient was not significant. The influence of the foil location, sample conditions, and gas flow through the furnace on the measurements was carefully verified in separate experiments (Ramesh and Kozinski, 2001b).
INSTRUMENTAL ANALYSES

The microstructural changes and distribution/concentration of metals were carried out using electron probe microanalysis (EPMA) analysis: A Jeol 8900 SuperProbe equipped with five wavelength-dispersive spectrometers was used (Ramesh and Kozinski, 2001b). The formation of different phases was identified by a Rigaku X-ray diffractometer, with a 12-kW high-intensity rotating Cu anode. $^{27}\text{Al}$, $^{29}\text{Si}$, and $^{23}\text{Na}$ solid-state nuclear magnetic resonance spectroscopy with magic angle spin (NMR-MAS) was used to examine the effect of a high concentration of heavy metals on the Al and Si structural environments and alkali metal chemistry in the ash pellet. A Chemagnetics CMX-300 solid-state NMR spectrometer was used for this study. The $^{29}\text{Si}$ spectra were taken at 59.5 MHz with a 3-s recycle delay, while $^{27}\text{Al}$ spectra were taken at 78.1 MHz with a recycle delay of 0.5 s, using external standards of tetra methyl silicates and aluminium nitrate, respectively. The $^{23}\text{Na}$ spectra were taken at 79.3 MHz, with a recycle delay of 0.1 s, using sodium chloride as an external standard. Single pulses of appropriate length ($\pi/4$ for $^{29}\text{Si}$ and $<\pi/6$ for $^{27}\text{Al}$ and $^{23}\text{Na}$) were applied (Ramesh and Kozinski, 2001b).

RESULTS

Mineralogy of the Ash

The results obtained from the X-ray Diffraction (XRD) pattern of the initial pellet showed the presence of individual major compounds (alumina and silica). At 1400°C the ash consisted of an assemblage of crystalline mullite, corundum, and alkali, or the alkaline aluminosilicate glass phase, which was evident from its characteristic hump at 18°–35° 2θ. The samples obtained at 1500°C, 1000°C (solidification), and 25°C (after cooling) revealed similar phases (Ramesh and Kozinski, 2001a). It was also observed from our previous studies (Ramesh and Kozinski, 2001a, c) that the XRD pattern of a simulated pellet with high and low amounts of heavy metals is almost identical, indicating no major change in the chemistry of the ash pellet.

Microstructure and Inorganic Particle Distribution

The EPMA images of the ash pellet obtained at various temperatures evidently show the microstructural changes and quantitative distribution of the major elements (Al, Si), heavy metals (Cd, Pb, Cr), and light metals (Na, K). These results are shown in Figures 1, 2, and 3, respectively.
FIGURE 1  Electron probe microanalysis (EPMA) analyses of the simulated ash pellet microstructure obtained at various temperatures via mapping of Al and Si regions (size of each image is 500 × 500 µm).

FIGURE 2  EPMA analyses of the simulated ash pellet microstructure obtained at various temperatures via mapping of heavy metal (Cr, Cd, and Pb) regions (size of each image is 500 × 500 µm).
Microstructure of Al–Si

The initial pellet contains distinct and separate powder particles of randomly distributed Si and Al compounds, as indicated by regions A and B in Figure 1, respectively. When the sample is heated to 1000°C, it undergoes a solid-state reaction, and the images show two different phases (Si, regions C and D; Al, regions E and F). Region D, with a low concentration of Si, corresponds to the formation of aluminosilicate spinel, as a small amount of Al is also coexisting in this region (indicated by F). Regions C and E correspond to nonreacted silica and alumina phases, respectively. At 1500°C the specimen contains several phases corresponding to Al, Al and Si (high), and Al (high) and Si. Regions K and G, where Al (high concentration) and Si coexist, represent the mullite phase formed from the initial spinel observed at 1000°C. The spinel may produce mullite crystals and silica at 1200°C. Silica can subsequently react with alumina, generating a silica-rich aluminosilicate amorphous glass phase, marked as H and J, where Si (high concentration) and Al coexist. Region L, where only Al is present, is due to the corundum phase, which exists as platelets embedded in the glass phase. Si is absent in this region (I). Thus at 1500°C the pellet consists of three phases, mullite, corundum, and aluminosilicate glass, which is consistent with the XRD results. During ash solidification (1000°C and 25°C) the three main phases prevail, with higher concentrations of amorphous aluminosilicate at the expense of mullite and corundum.

FIGURE 3 EPMA analyses of the simulated ash pellet microstructure obtained at various temperatures via mapping of light metal (Na, K) regions (size of each image is 500 × 500 µm).
**Microstructure of Cd, Pb, and Cr**

The behavior of heavy metals Cr, Cd, and Pb is shown in Figure 2. The initial pellet contains individual particles of Cr, Cd, and Pb (regions A, B, and C, respectively). At 1000°C (during heating), no phase change was visible, but the elements were more dissipated inside the pellet, indicating the beginning of the solid-state reaction with the major constituents (Al and Si). At 1500°C, distinct and different phases were formed. Cr revealed a major single phase marked as D (Fig. 2). It is interesting to note that in this region, Al also coexists (region L in Fig. 1). So the majority of the Cr present in the ash at 1500°C is associated with Al in the corundum phase (a very small amount is dispersed in mullite). In contrast, Cd and Pb form two different phases. Regions E and G are rich in Cd and Pb, while regions F and H consist of coexisting Cd and Pb at very low concentrations. It is important to note that the regions E (Cd-high) and G (Pb-high) in Figure 2 correspond to Al–Si regions H, G, K, and J in Figure 1. Therefore the majority of the Cd and Pb mainly coexist with the mullite and aluminosilicate glass phases. Moreover, it is also clear that regions F (Cd-low) and H (Pb-low) in Figure 2 correspond to the corundum and Cr-rich phases (L in Fig. 1 and D in Fig. 2, respectively). The results reveal that although most of the Cd and Pb coexists with mullite and glass, a very small amount of Cd and Pb also coexists in the corundum-chromium phase.

**Microstructure of Na and K**

The distribution of light metals, such as Na and K, is shown in Figure 3. As can be seen from the figure, the initial pellet shows random distribution of Na and K throughout the ash pellet. When the sample is heated to 1000°C, there is not much change in the phases of these two metals. However, at 1500°C these two light metals show two different phases, as illustrated in Figure 3 (regions D, E, F, and G). Regions D and F indicate that the phases consist of a relatively high concentration of Na and K, respectively. At the same time, regions E and G show the less concentrated phases of Na and K, respectively. Similar to Cd and Pb, the high concentrated regions of Na (D-high) and K (F-high) in Figure 3 correspond to the Al–Si regions H, G, K, and J in Figure 1. It indicates that these two metals mainly coexist with the mullite and aluminosilicate glass phases. Only small amounts of Na and K are distributed with the corundum-chromium phase. During solidification (at 1000°C and 25°C) the trend in chemical distribution is preserved, while the concentration of the phases formed at 1500°C increases. The pellet, however, becomes significantly less porous (see Figs. 1–3).
Radial Distribution and Quantitative Analysis of Light and Heavy Metals

EPMA studies were also carried out to establish the quantitative radial distribution of light and heavy metals in the ash material collected at various temperatures (25°C (initial sample), 1000°C, 1500°C (solidification), and 25°C (after cooling)). The concentration ratio of the Na, K, Pb, and Cd present in the surface and core of the ash material was calculated based on the quantitative measurements of X-ray intensities or counts. For this study the pellet was cut in half, and the metals were analyzed at the cross sections, as described previously (Koziński and Zheng, 1998). In the half cross section the concentrations of Na, K, Pb, and Cd were analyzed in three areas located in the particle core, the middle, and the outer section (the size of each area was 200 × 200 µm). From the total concentration in these three regions the concentration ratios of Na, K, Pb, and Cd at the surface and core of the pellet were calculated for each temperature. The results are shown in Figs. 4a–4d. As can be seen in Figures 4a and 4b, the concentration ratio of the Na and K at the surface increases with the temperature. The surface of the final ash material obtained after the solidification contains 15.8% and 14.3% more...
Na and K, respectively, than the core. Unlike light metals, the surface concentration ratio of the Pb and Cd decreases as the temperature increases (Figs. 4c and 4d). The core of the final ash material contains 11.8% and 13.2% more Pb and Cd, respectively, than the surface. The above results indicate a clear difference in the behavior of Na/K and Pb/Cd ions due to the variation in the chemical activity of light and heavy metals in the molten ash.

STRUCTURE OF ALUMINOSILICATE MATRIX

Si Structural Environment

The solid-state $^{29}$Si NMR spectra obtained for the initial ash pellet showed a sharp, single peak at –109 ppm due to an ordered structure of silica (Fig. 5a).
When heated to 1000°C, the sharp $^{29}$Si peak changed into a broad signal at −99 ppm (Fig. 5b) due to the formation of Si–Al spinel. At 1500°C it gave a peak centered at −95 ppm (Figs. 5c and 5d), which is typical of both an amorphous material (aluminosilicate glass) and mullite aluminosilicate. This milieu of Si did not change, either during further heating or during solidification (Fig. 5e). The decrease in chemical shift value ($\delta$), from −109 ppm (initial sample) to −95 ppm (final sample) at a higher temperature, is due to the inclusion of AlO$_4^-$ in the silica network to form aluminosilicate compounds. The $Q^d$ environments of Si changed into $Q^d$(2Al) or $Q^d$(3Al) environments (as in aluminosilicates), where the presence of Al substitution increased the deshielding effect, causing chemical shift toward the low field (Engelhardt and Michel, 1987). When the sample was cooled down to room temperature, there was not much change in its $\delta$ value, which remained at −95 ppm (Figs. 4d and 4e). Thus a very significant variation in the Si environment occurs during ash solidification. The results also indicate that Si is present in the tetrahedral environment in both the initial SiO$_2$ powder and in the aluminosilicates formed after the thermal treatment.

**Al Structural Environment**

The initial pellet gives a single peak at 10 ppm (Fig. 5f), which corresponds to the octahedral aluminium (AlO$_6$ in alumina). The $^{27}$Al spectrum of the sample obtained at 1000°C (Fig. 5g) gives a broad peak at 10 ppm due to the formation of spinels. At 1500°C the spectra show two resonance peak maxima at 50.0 ppm and 8.0 ppm, indicating the presence of AlO$_4$ tetrahedral and AlO$_6$ octahedral structures, respectively (Figs. 5h–5i). The tetrahedral peak is characteristic of a mullite structure, while both mullite and corundum phases contribute to the octahedral peak. Domination of the AlO$_4$ over the AlO$_6$ sites may be due to the partial replacement of Al$^{3+}$ from the octahedral symmetry of the corundum and mullite by Cr$^{3+}$. It would be compatible with the EPMA results where Cr and Al coexist together in the phases formed at 1500°C (see Figs. 1 and 2). During solidification the $^{27}$Al NMR spectra expose mainly an AlO$_4$ peak (Fig. 5j). However, there is still some six-coordinate Al present in the sample, indicating that chromium replaces most of the Al$^{3+}$ from its octahedral symmetry in both mullite and corundum. When the ash solidifies, the peak due to the octahedral symmetry becomes very weak. This result is consistent with the results obtained by the microprobe analysis (Fig. 1, solidification at 1000°C and 25°C), where the concentration of Al in the corundum phase decreases as the sample solidifies. In fact, the replacement of Al$^{3+}$ by Cr$^{3+}$ from its octahedral symmetry in corundum/mullite seems to begin during the 600 s residence time at 1500°C and to continue during the solidification.
**Na Structural Environment**

Studies were also carried out to find the environment of an alkali metal (Na) present in the ash sample using $^{23}$Na solid-state NMR spectra. The initial powder sample gives a single peak at $-14.0$ ppm (Fig. 5k) due to the presence of well-ordered crystalline Na$_2$O. When the sample is heated to higher temperatures of $1000^\circ$C and $1500^\circ$C (Figs. 5l–5n), the peak is shifted to a higher field of $-28.1$ ppm. Also, the peak width increases to $\sim 50$ ppm for samples at a higher temperature, indicating the formation of amorphous compounds. This is also indicative of the formation of alkali aluminosilicates, where the Na$^+$ ion compensates the SiO$^-$ ion present in the alluminosilicate matrix. The presence of Cd, Cr, and Pb, even at higher concentrations, did not influence the $^{23}$Na spectra. When the sample is cooled down to room temperature after heating it to $1500^\circ$C, there is not much change in the Na environment present in the aluminosilicate sample (Fig. 5o). Thus the $^{23}$Na resonance remains unchanged during the solidification.

**VOLATILIZATION OF HEAVY METALS**

Studies were carried out to examine the evaporation of volatile heavy metals during the thermal treatment of a simulated ash pellet. The experimental setup of a TGF reactor is shown in Figure 6. The reactor consists of an alumina tube (30 mm diameter) placed inside an electrical furnace. As can be seen from the figure, a known amount of the sample was taken in a platinum foil, which was then placed inside an alumina crucible. The sample was heated to $1000^\circ$C, $1200^\circ$C, and $1500^\circ$C, and the temperature of the sample, pt-foil, and crucible assembly was measured by using a B-thermocouple. An alumina disc was suspended above the crucible to capture all the volatilized heavy metals at a high temperature. The height of the alumina disc was adjusted in such a way that its temperature zone was kept around $150^\circ$C, and the temperature of the disc was measured using a K-thermocouple. An alumina disc was suspended above the crucible to capture all the volatilized heavy metals at a high temperature. The height of the alumina disc was adjusted in such a way that its temperature zone was kept around $150^\circ$C, and the temperature of the disc was measured using a K-thermocouple. This was so that the heavy metals volatilized at $1000^\circ$C, $1200^\circ$C, and $1500^\circ$C, on reaching the alumina disc, could easily condense and absorb at its bottom as the disc was in a low-temperature region. The disc was removed after each experiment and was treated with 5 mL of aqua regia in order to dissolve the absorbed heavy metals. The disc was then carefully washed with distilled water, and all the extracts were collected, mixed together, and diluted to a known volume. The concentration of Cd, Cr, and Pb present in the mixture was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), using Cd = 3610, Pb = 2203, and Cr = 2677 Å emission lines. The results are shown in Figure 7. It is clear from the results, at $1000^\circ$C and $1200^\circ$C, that
FIGURE 6  Thermogravimetric furnace experimental setup for the volatilization study of heavy metals during the heating of the simulated ash pellet.

FIGURE 7  Volatilization of heavy metals during the heating of simulated ash at various temperatures.
the volatilization of all three heavy metals is very low. However, there is a significant volatilization of heavy metals at 1500°C. Among the heavy metals, Pb shows a higher value (13.4%) than Cd (4.8%) and Cr (2.9%).

DISCUSSION

Heavy and Light Metal Environment during Ash Solidification

The EPMA and solid-state NMR results clearly indicate that the final ash consists of the three distinct phases, namely mullite, corundum, and a major amorphous aluminosilicate. Spinel (another aluminosilicate) is formed at ~1000°C and transforms into mullite crystals and SiO$_2$ at temperatures above 1250°C (Ramesh and Koziński, 2000, 2001a). Subsequent dissolution of Al$_2$O$_3$ by alkali and alkaline metals containing Si-rich melt leads to the formation of a glassy aluminosilicate matrix in which the corundum and mullite phases are embedded. Since SiO$_2$, formed from spinel, is progressively reincorporated into the aluminosilicate network, at 1500°C, there is therefore practically no free silica present. Only the presence of Al-rich mullite (3Al$_2$O$_3$·2SiO$_2$) and amorphous Si-rich glassy aluminosilicate was detected (see Fig. 1, 1500°C, regions G, K, H, and J). At a high temperature the metal ions present at the surface of the ash pellet evaporate (Fig. 7) and thus make a concentration gradient between the surface and the core of the pellet. This in turn triggers the diffusion of light and heavy metals from the ash core to the surface. Thus the diffusion of small ions of Na$^+$ and K$^+$ (with a size of 0.5 and 0.9 Å, respectively) and large ions of Pb$^{2+}$ and Cd$^{2+}$ (1.19 and 1.09 Å, respectively) initiates changes in the metals’ distribution. As was previously observed (Koziński and Zheng, 1998), the mobility of light metals is about two orders of magnitude higher than the mobility of heavy metals ($10^{-9}$ vs. $10^{-11}$ m$^2$/s). This forces K$^+$ and Na$^+$ toward the surface, while Pb$^{2+}$ and Cd$^{2+}$ are mainly concentrated inside the ash melt core. As these light and heavy metals are mostly distributed within aluminosilicate glass or mullite phases (see Figs. 2 and 3), it can be viewed that the aluminosilicate phases at the surface are rich in Na and K (Figs. 4a and 4b), while the core contains higher amounts of Pb and Cd (Figs. 4c and 4d). The formation of alkali-rich aluminosilicate phases was also confirmed by the presence of broad $^{23}$Na spectra at 28.1 ppm (Figs. 5m–5o). Unlike Pb$^{2+}$ and Cd$^{2+}$ ions, Cr$^{3+}$ (0.62 Å) diffusing inside the ash melt replaces Al$^{3+}$ (0.54 Å) in AlO$_6$-rich sites in mullite and corundum. It is possible because of the similarity in both ions’ sizes and charges (Partyka, 1997; Ramesh and Koziński, 2001a). Our data suggest that Cr$^{3+}$ shows preference in replacement of
Al$^{3+}$ from its octahedral symmetry, rather than the tetrahedral. The replacement of Al$^{3+}$ begins at a high temperature and continues during ash solidification. Larger ions, such as Pb$^{2+}$ and Cd$^{2+}$, cannot replace Al$^{3+}$ because the laws of stereochemistry cannot be violated. Instead, they can probably occupy the vacancy of 5–6 Å in size created by the oxygen deficiency in mullite. Low concentrations of Cd and Pb in the corundum phase (see Fig. 2) may be attributed to the inclusion of small amounts of Cd/Pb into the pores in corundum. However, high concentrations of Pb and Cd in the aluminosilicate matrix firmly indicate either that they occupy the sites in mullite, or they form glass with Si-rich amorphous aluminosilicate. The replacement of Al$^{3+}$ by Cr$^{3+}$ in the corundum and mullite phases is strongly supported by the NMR and EPMA results reported above. In addition, the relaxation times of the $^{29}$Si (NMR-MAS) resonance obtained during solidification are much shorter than during heating (3 vs. 60 s) due to the presence of paramagnetic species (such as Cr$^{3+}$) incorporated in the matrix. While metal rearrangements begin at high temperatures, it is clear that a significant portion of the intermetallic interactions responsible for the final ash structure takes place during solidification. For example, intraparticle metal concentration profiles are established mostly when ash solidifies. Apart from the difference in the diffusion of the light and heavy metals in the ash melts, it is believed that the influence of surface tension or surface free energy on the diffusion of these metals may be the primary reason for their final radial distribution.

**Surface Free Energy**

The diffusion process in aluminosilicate melts may be divided into self-diffusion and chemical diffusion. Self-diffusion involves the movement of the various species, and there is no net flux or chemical potential gradient established. The presence of a chemical potential gradient or concentration gradient influences the chemical diffusion. As the surface elemental evaporation (Fig. 7) initiates the concentration gradient between the core and the surface (Ramesh and Koziński, 2001a), the process of chemical diffusion of light and heavy metals inside the particle occurs. Apart from this, the presence of a chemical potential gradient in the aluminosilicate melts initiates the diffusion of the light and heavy metals. The origin of this chemical potential gradient is the excess free surface energy, which influences the diffusion of the surface-active metals, such as Na and K, to the surface. In general, the relationship between the surface tension and surface free energy of the multicomponent system is given as (Rusanov, 1996)

$$
\sigma = f^8 - \sum_i \Gamma_i \mu_i^f,
$$

(1)
where $\sigma$ is the surface tension, $f_s$ is the surface free energy, and $\Gamma_i$ and $\mu_i^\phi$ are the surface excess and chemical potential of the $i$th component, respectively. The above equation also implies that for a single-component system, surface tension is equal to surface free energy.

The surface tension of the ash melt is expected to be reduced, due to the diffusion of the surface active metals, to the interface or surface of the liquid-solid. Sodium and potassium are very effective surface active metals and are considered as efficient network modifiers (Dunn, 1986). The interaction of Na and K with a silicate network, which also enables their diffusion through the silicate melts, proceeds via the breaking of the Si–O–Si bonds as $\text{M}_2\text{O} + \text{Si–O–Si} \rightarrow \text{Si–OM} + \text{MO–Si}$ (where M is Na or K). This chemical diffusion through the silicate network leads to the excess concentration of these metals on the surface of the ash particles. The surface excess of the single metals can be calculated from the equation (Turkdogan, 1980; Chattoraj and Birdi, 1984)

$$\Gamma_i = -\frac{C_i}{RT} \frac{d\sigma}{dC_i} , \text{ mol cm}^{-2}$$

where $C_i$ is the concentration of the solute and $d\sigma/dC_i$ is the flux.

The combined effect of high temperature and an increase in the concentration of the surface active metals at the ash surface (Na and K) leads to the reduction of its surface free energy. To diminish the surface tension or free energy, the system uses the excess energy on the kinetic motion of the smaller ionic particles, such as $\text{Na}^+$, $\text{K}^+$, and so on, assisting their diffusion toward the surface. Heavy metals, because of their surface-inactive properties as well as their lower diffusion velocity (due to their bigger ionic size), reside mostly at the core of the ash particles. This in turn enables the heavy metals to interact efficiently with the Al–Si matrix present in the core of the ash melt. Since their residence time inside the core is longer, it stimulates better interaction. This mechanism ensures the encapsulation of the heavy metals in the ash particle and thus prevents their leachability (Ramesh and Kozinski, 2001d).

**CONCLUSIONS**

Our results show that the ash formed from the thermal treatment of the simulated pellet (model of deinking sludge) consists of three main phases: mullite, corundum, and aluminosilicate amorphous glass. They initially form at a high temperature, but the final structure, including intraparticle metal rearrangement, takes shape during solidification. A quantitative analysis of the radial distribution of light and heavy metals in the ash particle indicated that (1) the surface of the ash particle contains 15.8% and 14.3% (concentration ratio) more Na and K, respec-
tively, than the core and that (2) the core contains 11.8% and 13.2% more Pb and Cd, respectively, than the surface. This result clearly indicates surface predominance of alkali metals over heavy metals. Surface free energy of the ash particle is believed to be the primary reason for the diffusion of heavy and light metals. The diffusion of surface active metals reduces the surface free energy of the ash particles during solidification. This affects the diffusion and intermetallic rearrangements inside the ash particle. Our model also suggests possible explanations for a number of important phenomena. For example, the disappearance of the octahedral 27Al NMR peak is due to the replacement of Al3+ from its corundum and mullite AlO6 site by Cr3+ ions. Other toxic metals (Pb and Cd), not being able to replace Al3+, occupy mainly the oxygen vacancy in mullite crystals. The proposed structure for the ash particle may help to understand the observed pattern of the metals’ rearrangement. Results of this study also suggest the possibility that elemental surface versus core segregation may be a general phenomenon in inorganic particles derived from high-temperature processes followed by solidification, for which diffusion and subsequent condensation of elements is likely to occur. The observed inclusion of chromium into the corundum phase, and the firm binding of the Pb and Cd inside the aluminosilicate matrix network, promote their immobilization within the inorganic particles.

REFERENCES


