THE MICROSTRUCTURE OF Pb-DOPED SOLIDIFIED WASTE FORMS USING PORTLAND CEMENT AND CALCITE

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Abstract : An electron probe microanalysis (EPMA) investigation can provide quantitative and qualitative insight into the nature of the surface and bulk chemistry on solidified waste forms(SWF). The proportion of Pb in grain areas is below 0.3 wt. %, and the proportion near the border of the grain slightly increases to 0.98 wt. % but in the inter-particle areas farther from the grain, the concentration of Pb markedly increases. It is apparent that very little Pb diffuses into the tricalcium silicate(C_3S) particles and most of the Pb exists as precipitates of sulfate, hydroxide, and carbonate in the cavity areas between C_3S grains. Calcite additions on Pb-doped SWF are also observed to induce deeper incorporation of lead into the cement grains with EPMA line-analysis of cross-sections of cement grains. The line-analysis reveals the presence of 0.2~5 weight % Pb over 5 µm from cement grain boundaries. In the inter-particle areas, the ratio of Ca, Si, Al and S to Pb is relatively similar even at some distance from the grain border and the Pb (wt. %) ratio is reasonably constant throughout the whole inter-particles area. It is apparent that the enhanced development of C-S-H on addition of calcite can increasingly absorbs lead species within the silica matrix.

Key Words : solidification, $CaCO_3$, Lead, EPMA, Calcium-Silicate-Hydrate (C-S-H)

INTRODUCTION

Cement has been used worldwide for the solidification and stabilization (S/S) of hazardous and radioactive wastes. Cement-based solidification creates solidified waste forms (SWF) which have the physical and chemical properties of the cementing materials.[1] Since the alkalinity of cementitious materials greatly reduces the solubility of many hazardous inorganics, their use prevents pollutants from migrating into the environment by rendering the toxic contaminants physically immobile and chemically bound to the encapsulating solid.[2-4] Portland cement is one of most common S/S

agents, in part because of its ability to set and harden under water (a hydraulic cement).[5,6]

The system of solidified waste forms (SWF) with the chemistry of cement, especially when combined with hazardous wastes, has been considered a "black box" due to the complexity of the system and inadequacy of analytical tools.[7] Indeed, the mechanism of hydration is still a very active and controversial area with the lack of understanding of such basic processes limiting development of S/S technology.

On the other hand, electron microscopy can provide very valuable insight into the structure and morphology.[7] EPMA can be a valuable approach and has reached a high degree of sophistication with literally thousands of compounds being identified by their visual characteristics. EPMA

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typically applies for metallurgical studies, failure analysis, thin film analysis, particulate analysis, mineral analysis, ceramic analysis, and many others.

In the study of cement-based S/S, the use of EPMA can provide quantitative and qualitative insight into the nature of the surface and bulk chemistry. The correlation between Pb and other components to elucidate the fixation mechanism of lead wastes is observed to be the higher relative quantities of Si, Ca, Al, and S to Pb by line-analysis of cross-sections of cement grains. In addition, the elemental analysis of lead through cross-sections of cement grains with pore areas can help to investigate the mechanisms such as precipitation, adsorption and intrusion on the S/S of Pb wastes.

EXPERIMENTS

Materials

Ordinary Portland cement was purchased from Sangyong Cement in Korea and used in all studies. The cement has the following mineralogical composition: (i) 41.7% of tricalcium silicate (Ca$_3$SiO$_5$: C$_3$S), (ii) 27.9% of dicalcium silicate (Ca$_2$SiO$_4$: C$_2$S), (iii) 12.7% of tricalcium aluminate (Ca$_3$Al$_2$O$_6$: C$_3$A), (iv) 9.4% of calcium aluminoferrite (Ca$_4$Al$_2$Fe$_2$O$_{10}$: C$_4$AF), and (v) 2.9% of calcium sulfate (CaSO$_4$·2H$_2$O).

Calcite used was of high grade crystalline form ($\geq$95.0% CaCO$_3$) with $\leq$4.0% MgCO$_3$ and $\leq$1.5% acid insolubles. Its specific gravity was 2.7 and its BET specific surface area was 5.2 m^2/g. It was ground such that it exhibited an average diameter (D$_{50}$) of 1.8μm, maximum particle size of 8μm, and residue on 20 μm screen of no more than 0.005%. The addition of up to 5% calcite to cement clinker has been recommended by the American Society for Testing and Materials (ASTM), the Canadian Standards, and many countries in Europe.[7] Calcite addition to cement (i) acts as a partial substitute for gypsum as a set controller, (ii) results in some reduction in the energy costs for grinding clinker, and (iii) results in improvements in some characteristics of the hardened concrete.

The wastes were prepared from lead nitrate which precipitated to form hydroxide sludge on adjusting the pH to 8.5 with 6.0 N sodium hydroxide and then dried at 104°C for 24 hours. The major crystalline phases present were identified by X-ray diffraction to be lead nitrate hydroxide, [Pb$_2$(NO$_3$)(OH)$_3$] and lead oxide nitrate hydroxide [Pb$_6$O$_3$(NO$_3$)$_2$(OH)$_4$].

Varying ratios of dry Pb waste and cement were mixed with water at a water/solid (cement, calcite and Pb wastes) ratio (W/S) of 0.3. After thorough mixing the samples were introduced into polyethylene cylindrical moulds measuring 20 mm diameter × 40 mm height and removed after 24 hours. The curing was carried out in humid air at 20°C for 28days. The samples are denoted KCiPbj where i is the calcite content, j is the Pb-doped waste content.

Electron Probe Microanalysis (EPMA)

Electron Probe Microanalysis was undertaken using a Cameca SX50 instrument. The Cameca SX50 is a fully automated instrument employing four wavelength dispersive spectrometers and one energy dispersive x-ray analyser for the detection and nondestructive analysis of almost all elements from boron (B). Quantitative analysis was carried out on the bulk matrix and micro-constituents, such as inclusions and grain boundaries. X-ray elemental line scans were carried out across constituents of interest. X-ray and electron images were acquired, stored and processed to produce colored hard copies. This instrument is controlled by a Windows based SAMx operating system and interface which enables procurement of line scans and elemental area maps. Specimens can be imaged using either secondary or backscattered electrons.

Samples were prepared with a flat and well polished surface, finished to <1 micrometer, and were physically compatible with the specimen stage. The specimen stage is top referencing and thus the specimen surfaces were flat with perpendicular sides. Samples were one-inch diameter rounds.
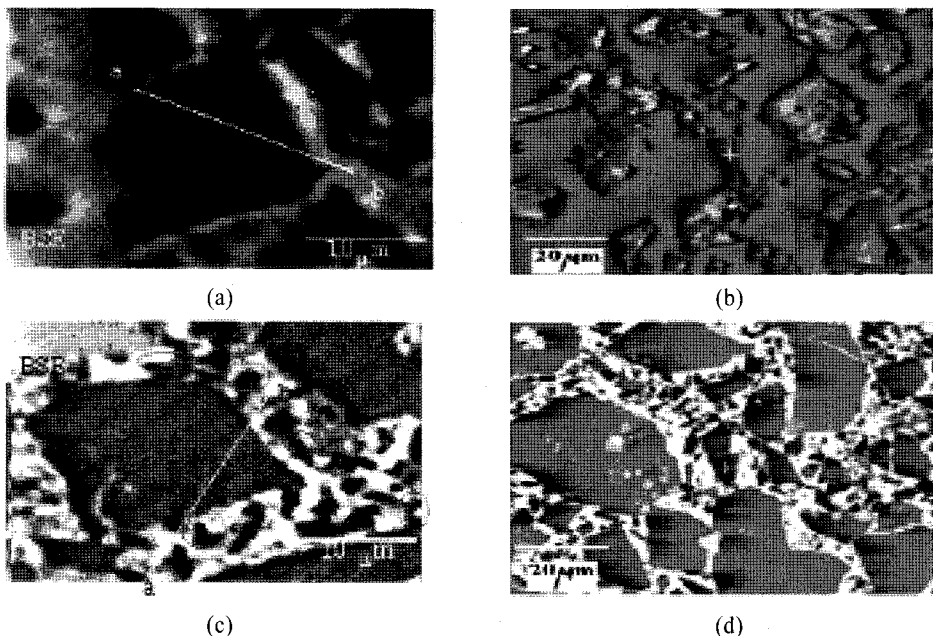
(a)

(b)

(c)

(d)

Figure 1. Backscattered electron image of (a) KP10 in a whole area of ×2,000 magnification and (b) KP10 (×1,000 magnification) (a) KC5P10 (×2,000 magnification) and (b) KC5P10 (×1,000 magnification).

Odd shaped samples were mounted in epoxy resin. Samples for EPMA were provided with a coating of carbon.

The characteristic X-rays of Pb (Pb-M_α), Ca (Ca-K_α), Si (Si-K_α), Al (Al-K_α), Fe (Fe-K_α) and S (S-K_α) were generated with a tightly focused electron beam (probe current; 100nA) at an acceleration voltage of 15keV. The intensities of characteristic X-rays generated by the elements in the sample were measured according to their wavelengths by the following crystal spectrometers: TAP for Al and Si, PET for Pb, Ca, and S, LiF for Fe. Both stage and beam image acquisition scans may be carried out to provide elemental concentration maps of both large areas and minute constituents, such as phases, inclusions and grain boundaries. It was possible to process the results obtained using HiMax, Matlab or Visilog software.

RESULTS AND DISCUSSION

The Effect of Pb Wastes and Calcite on the S/S

It investigated, in the early study, that Pb-doped solidified waste forms(SWF) with Portland cement (i.e., KP10: cement 90% + Pb waste 10%) produced less unconfined compressive strength(UCS), compared to UCS of the pure cement.[8] This may be due to retardation effect of lead in the hydration of cement.[9,10] SWFs containing Pb have almost no compressive strength within the first 14 days, but after 28 days curing, approximately 20% of the UCS was increased, as compared to the pure cement. In addition of 5% calcite Pb-doped SWF(KC5P10: cement 85% + Pb waste 10% + calcite 5%) resulted in 2-3 times increase of the UCS, as compared to samples without calcite (KP10).[8]

Electron microscopy by backscattering image (BSE) fitted in the EPMA provides the structural insight of SWF, and then supporting interpretation of these findings on compressive strength of Pb-doped SWF. The BSE image of Pb-doped SWF (KP10) as shown in Figure 1 (a) and (b) shows a large area of loose structure between cement particles. The larger the inter-particle areas

are, the greater is the probability of capillary and gel pores in KP10. This accounts for the lower strength of Pb-doped solidified samples associated with the retardation effect of Pb in cement hydration. As shown in Figure 1c and 1d, the addition of calcite in the S/S of Pb wastes produces a denser structure probably due to the increase in rate and extent of formation of calcium silicate hydrate (C-S-H) and other

hydrated minerals compared to the Pb-doped SWF without calcite. This provides evidence of the accelerating effect of calcite in producing a denser material.

The Structure of SWFs with Pb Waste

Great flexibility and accuracy in analyzing unknown samples of arbitrary composition can be provided via quantitative matrix correction pro-
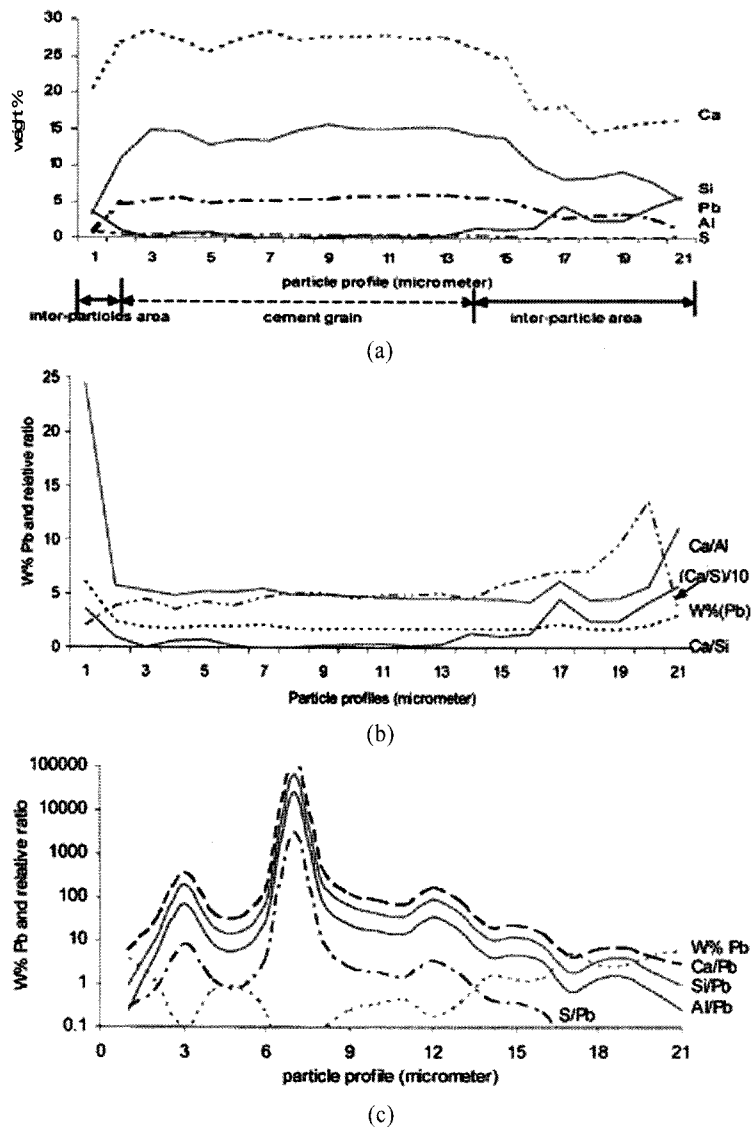

Figure 2. EPMA line-analysis of KP10 through the line of 'a' and 'b' in the BSE of Figure 2. (a) Line-analysis of each element (b) line-analysis of Pb *wt.* % with the ratio of Ca:Si, Ca:Al and Ca/S (C) line-analysis of around cement grain with ratio of Ca:Pb, Si:Pb, Al:Pb, S:Pb and *wt.* % Pb.

cedures by an EPMA line-analysis, which is a technique enabling quantitative visualization of the spatial distribution of elemental constituents through a focused beam of high energy electrons (5 - 30 KeV). The fixation mechanism of lead within cement grain has been examined by quantitative measurement of Pb, Ca, Si, Al and S across the tricalcium silicate(C_3S) particles (i.e. the line of a and b in Figure 1 (a)) in the EPMA line-analysis of non-crushed SWFs as shown in Figure 2. In KP10 Ca, Si and Al concentrations rapidly decrease on moving from the particle borders to the inter-particle area. These results are almost identical to those of the EPMA elemental maps examined in the early EPMA mapping analysis.[11]

Pb is present at very low proportions of below 1 wt. % for 10% Pb-doped SWFs within the C_3S particle. The proportion of Pb in grain areas is below 0.3 wt. %, and the proportion near the border of the grain slightly increases to 0.98 wt. % but in the inter-particle areas farther from the grain, the concentration of Pb markedly increases. It is apparent that very little Pb diffuses into the C_3S particles with most of the Pb present as precipitates of sulfate, hydroxide, and carbonate located in the cavity areas between C_3S grains.[11]

As shown in Figure 2 (b), the ratios of Ca to Si and Ca to Al sharply increase on moving away from the particle. These high ratios result particularly from low Si and Al content in the inter-particle regions. As shown in Figure 2 (c), profiles of the proportion of Ca, Si, Al and S to Pb exhibit distinct maxima in the interior of the C_3S particle with value of the Ca/Pb ratio exceeding 100,000. These results again highlight the limited extent of diffusion of Pb into the clinker substances and/or C-S-H with the majority of the Pb located between the cement grains where Pb ions are presumably incorporated into some form of calcium-lead-silicate-hydrate (C-Pb-S-H). Since the ratio of S to Pb is almost zero in the inter-particles area, sulfate probably dose not play a major role in fixing Pb within the C-S-H gel in these regions.

The hypothesized formation of calcium lead silicate hydrate (C-Pb-S-H) is consistent with the results of other studies. Bishop[12] has argued that lead (in a similar manner to chromium) is re-precipitated in the silicate matrix in the form of hydroxide after the hydration of cement. Even after the consumption of all of the alkalinity from the specimen in a leach test, lead was largely retained in the silicate matrix. The silicate matrix including lead was described as a "metallic calcium silicate hydrate", by Bhatty[13] suggest that the metal hydroxide is simply encapsulated in a silicate matrix that prevents its removal except by destroying the matrix.

Many researchers have described the structure of calcium-metallic ions-silicate-hydrate (C-Me-S-H) to elucidate the fixation (sorption) mechanism of metal ions in the interactions between C-S-H and metal ions.[7,14] Moroni and Glasser[15] examined the reaction of the Si component of cement with U(VI) and proposed the formation of CaO-UO_3-SiO_2-H_2O (C-U-S-H) of solubility lie in the low range, $10^{-8} \sim 10^{-9}$ mol/l. Atkin and Glasser,[16] in a study involving thermodynamic modeling of cement chemistry, argued that strontium is liable to substitute for Ca in cement phases in the long term. They also found that sorption on C-S-H is a significant form of iodine immobilization, and showed that uranium can also react with cement to form compounds with Ca and Si. Substitution of nickel and cobalt at the C-S-H surface probably for Ca^{+2} ions has been reported by Komarneni et al.[17] Based on these works, metallic ions should be immobilized in the structure of C-Me-S-H through interactions between C-S-H and the metal ions by sorption, substitution and incorporation, etc.

The Structure of Pb-doped SWF with Calcite

In the Pb-doped SWF containing calcite(Figure 3), the Si % exhibits a much lower decrease in inter-particle areas compared to that of KP10. At about 2 μm from the borders into cement grain, the w % of Ca and Si is very much reduced, and rises again to values similar to those in the centre of the cement grain around the surface. Up to about 5 wt. % of Pb is present in the

areas-surface 2-5 μm of the cement grain, and 0.2~5 $wt.$ % of Pb into 5 μm. Al and S are observed to have a higher $wt.$ % in the inter-particle areas than those within the cement grain.

The proportion of Ca, Si, Al and S to Pb in KC5P10 inside the cement grains is much lower than that in KP10. As shown in the graph of $wt.$ % Pb, lead components intrude/incorporate deep into the cement grain with larger quantity

than those in KP10. At the same time, Ca, Si, Al and S components located inside the cement grains diffuse extensively into inter-particle areas due to the accelerating effect of calcite. In the inter-particle areas, the ratio of Ca, Si, Al and S to Pb are relatively similar even at some distance from the grain border and the Pb ($wt.$ %) ratio is reasonably constant throughout the whole inter-particles area.
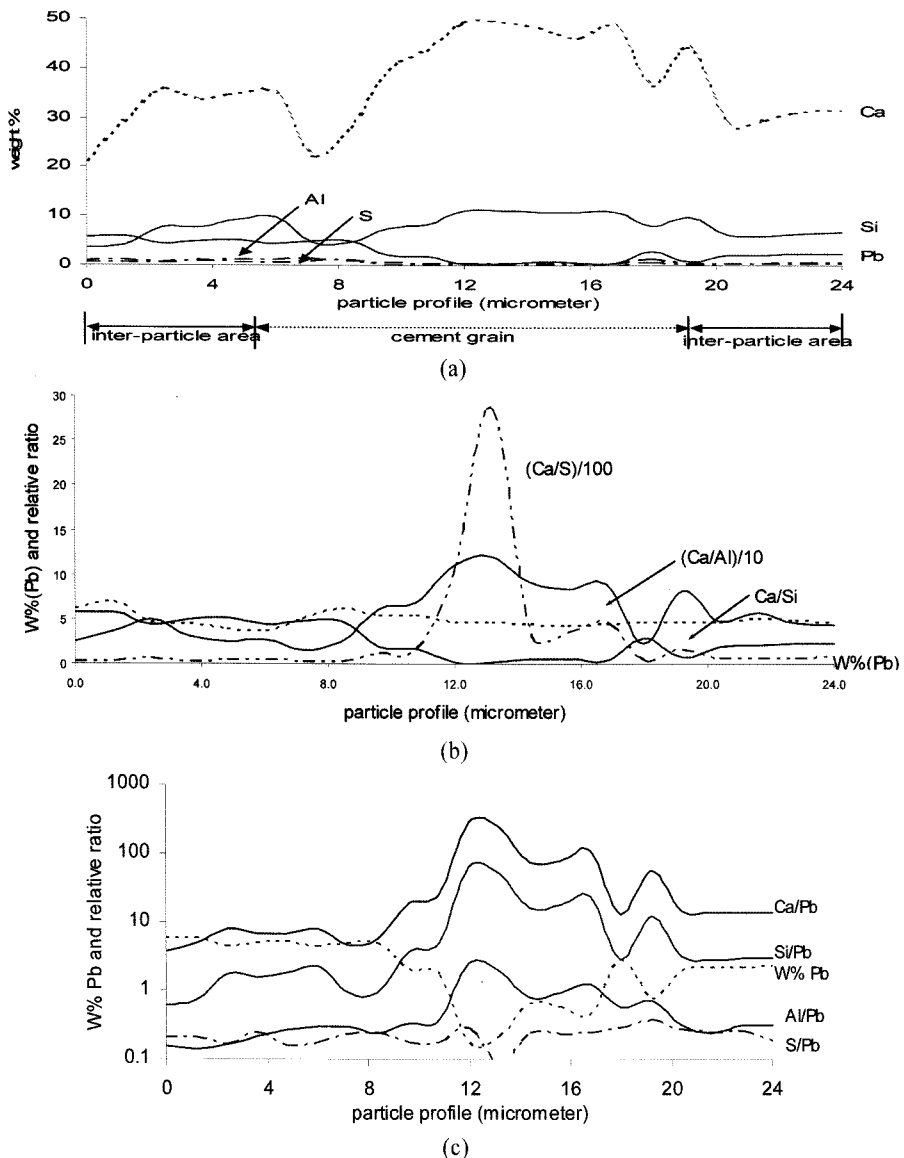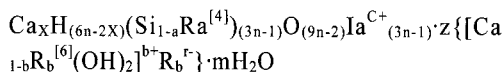

Figure 3. EPMA line-analysis through the line of 'a' and 'b' in the BSE of Figure 4. (a) Line-analysis of each element (b) line-analysis of Pb $wt.$ % with the ratio of Ca:Si, Ca:Al and Ca/S (C) line-analysis of around cement grain with ratio of Ca:Pb, Si:Pb, Al:Pb, S:Pb and $wt.$ % Pb.

It is thus apparent that calcite addition improves the development of higher silicate even in the inter-particle areas on the S/S of Pb wastes. The enhanced development of C-S-H on addition of calcite can increasingly encapsulate lead species within the silica matrix.

On addition of calcite, the ratio of Ca to Si is relatively uniform throughout the sample while the ratios of Ca to Al and Ca to S are significantly lower in the inter-particle areas than within grains. Al and S are probably further encapsulated in a non-stoichiometric form of C-S-H via Si substitution. Richardson and Groves[18] argued the following compositional formula of C-S-H gel involving substitution for Si^{4+}:

$$Ca_XH_{(6n-2X)}(Si_{1-a}Ra^{[4]})_{(3n-1)}O_{(9n-2)}Ia^{C+}{}_{(3n-1)}\cdot z\{[Ca_{1-b}R_b{}^{[6]}(OH)_2]^{b+}R_b{}^{r-}\}\cdot mH_2O$$

where R[4] is a trivalent cation, such as Al^{3+} or Fe^{3+}, in tetrahedral co-ordination; $R^{[6]}$ is a trivalent cation, Al^{3+} or Fe^{3+}, in octahedral co-ordination; I^{c+} is an interlayer ion, charge balancing the R^{3+} substitution for Si^{4+} (such as a monovalent alkali cation or Ca^{2+}); R^{r-} is most likely to be OH^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$.

It is also reasonable to suggest that the presence of calcite will enhance further dissolution of silicate ions as well as calcium ions. At the same time, the migration of calcium and silicate ions occurs naturally with a stronger concentration gradient from the cement grain to inter-particle areas through the membrane made of Pb precipitates. From the early hydration, the stronger concentration of calcium and silicate ions provides higher pH in the hydration of Portland cement in accordance to formula Eq. (1) below illustrated:

$$3CaO\cdot SiO_2 + H_2O \leftrightarrow 3Ca^{2+} + SiO_4{}^{4-} + 2OH^-,$$
$$Log\ K_{sp} = 0.47 \qquad (1)$$
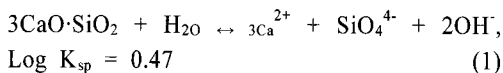
The change of pH is especially significant for the solubility of lead that exhibits the property of amphoterism. Most lead hydroxide salts exhibit minimum solubility through a narrow pH range of pH 7.5-10, and are markedly dissolved below

pH 6 and above pH 12.[14]

As a result, the original Pb wastes, $Pb_2(NO_3)(OH)_3$ and $Pb_6O_3(NO_3)_2(OH)_4$, in the presence of calcite will be dissolved/diffused more quickly due to the high pH in cement grain as well as in all inter-particles area. The dissolved Pb ions ($Pb(OH)_4{}^-$ above pH 12.8) produce C-Pb-S-H through re-precipitation/incorporation with/into C-S-H gel. The C-Pb-S-H structure in Pb-doped solidified samples with calcite (KC5P10) will be more calcium-rich and silicate-rich than in Pb-doped solidified samples without calcite (KP10) due to earlier/larger dissolution of C_3S as a result of the accelerating effect of calcite.

CONCLUSION

An EPMA line-analysis provides great flexibility and accuracy in analyzing unknown samples of arbitrary composition via quantitative matrix correction procedures. The fixation mechanism of lead within cement grain has been examined by quantitative measurement of Pb, Ca, Si, Al and S across the C_3S particles in the EPMA line-analysis of non-crushed solidified waste forms (SWF). Pb ions in Pb-doped SWF(KP10) are found at the cavity and broad inter-particle areas, but calcite addition makes preferential deposition of lead at the specific locations of higher intensity of Ca, Si, S as well as Pb in the inter-particle areas. Pb is present at very low proportions of below 1 *wt.* % for 10% Pb-doped SWFs within the C_3S particle. Profiles of the proportion of Ca, Si, Al and S to Pb exhibit distinct maxima in the interior of the C_3S particle with value of the Ca to Pb ratio exceeding 100,000. These results again highlight the limited extent of diffusion of Pb into the clinker substances and/or C-S-H with the majority of the Pb located between the cement grains where Pb ions are presumably incorporated into some form of calcium-lead-silicate-hydrate (C-Pb-S-H).

In calcite-additional SWF(KC5P10), the correlation between Pb and other components, , to elucidate the fixation mechanism of lead wastes is observed to be the higher relative quantities of Si,

Ca, Al, and S to Pb compared to KP10. Calcite addition on Pb-doped SWF is observed to produce a denser structure probably due to the increase in rate and extent of C-S-H and other hydrated minerals compared to Pb-doped SWF without calcite by backscattered electron images fitted in the EPMA. The presence of calcite on Pb-doped SWF also is observed to make deeper incorporation of lead into the cement grains up to over 5 μm with the high intensity of 0.2~5 *wt.* % Pb by line-analysis of cross-sections of cement grains compared to below 0~1*wt.* % Pb intensity in Pb-doped SWF without calcite.

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