ELECTRON PROBE MICROANALYSIS (EPMA) INVESTIGATION OF LEAD LOCATION ON THE SOLIDIFICATION/STABILIZATION OF PB WASTES

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Abstract : The location of lead on the solidified waste forms (SWF) has been investigated by electron probe microanalysis (EPMA) which provides quantitative and qualitative insight into the nature of the surface and bulk chemistry. The effect of calcite is observed to be associated with an enhancement in migration of the major cement components of calcium, silicate, sulfate and aluminate ions farther from the cement grain boundaries.

Large lead precipitates of about 200~500 μm are found in the cavity and broad inter-particle areas of lead-rich SWF. The elemental composition of the lead precipitates would consist of lead with high sulfur. However calcite addition leads to preferential deposition of lead at specific locations of higher intensity of calcium, silicon and sulfur in the inter-particle areas.

Key Words : Calcite, Lead, EPMA, Solidified Waste Forms (SWF)

INTRODUCTION

Cement-based solidification is a widely used technology for the disposal of hazardous and radioactive wastes. The U.S. Environmental Protection Agency also recognizes cementitious solidification as the 'best demonstrated available technology' (BDAT) for land disposal of most toxic elements.[1,2)]

Solidification processes convert liquid or semi-solid sludge wastes to solid forms encapsulating these wastes by cement through isolation, precipitation and/or adsorption. Stabilization is a process whereby chemical interactions between the waste and the binding agent convert a waste into a physically and chemically more stable form by chemical incorporation, ion exchange and/or chemisorption.[3)]

The mechanisms controlling the solidification/stabilization (S/S) of waste materials is very complex due to the mutual chemical and physical interactions between wastes and cement components as well as the aquatic, surface, molecular, and material chemistry of cement in its own right. Cocke[4)] has argued that the S/S systems require a large number of instruments to characterize the SWF with most solidified wastes forms (SWF) produced by the S/S of hazardous wastes still remaining in the "black box" category. Each characterization method however has its own set of limitations that restricts understanding of the complicated SWF.

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In particular, very little is known about the nature of chemical interactions of metal ions in these systems.[5] Recently, particular attention has been given to the direct investigation of the surface chemistry of metal ions in the cement-based systems since the waste materials reside principally on the surface of the cement particles.[4]

Electron probe microanalysis (EPMA) is a technique enabling quantitative and qualitative elemental analysis of solids through a focused beam of high energy electrons (5-30 KeV) that work to non-destructively ionize a solid specimen surface inducing emission of characteristic X-rays (0.1-15 KeV). Digital composition maps enable quantitative visualization of the spatial distribution of elemental constituents, which are displayed in gray scale or false color. Great flexibility and accuracy in analyzing unknown samples of arbitrary composition can be provided via quantitative matrix correction procedures. Typical applications of EPMA include metallurgical studies, failure analysis, thin film analysis, particulate analysis, mineral analysis, ceramic analysis, and many others. As a result, 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. Ziegler[6] illuminated the mechanism of zinc sorption to C-S-H by the EPMA investigation of Zn distributions in cross-sections of calcium silicate hydrate (C-S-H) powder samples.

The purposes of this study are (i) to investigate the effect of lead on the S/S of Pb wastes through the analysis of the migration of components away from the cement grain, (ii) to ascertain the location of Pb and other components in non-powdered samples by analysis of both inter-grain areas as well as the interior of grains, (iii) to investigate the effect of calcite on the S/S of Pb wastes by EPMA.

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_3SiO_5: C_3S), (ii) 27.9% of dicalcium silicate (Ca_2SiO_4: C_2S), (iii) 12.7% of tricalcium aluminate ($Ca_3Al_2O_6$: C_3A), (iv) 9.4% of calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$: C_4AF), and (v) 2.9% of calcium sulfate ($CaSO_4$ $2H_2O$).

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 8 μm, 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 [$Pb_6O_3(NO_3)_2(OH)_4$]. These XRD data were consistent with the results of Asavapisit et al.[8] and Gress et al..[9]

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 28 days. The samples are denoted KCiPbj where i is the calcite content,

and 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. 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_a), Ca (Ca-K_a), Si (Si-K_a), Al (Al-K_a), Fe (Fe-K_a) and S (S-K_a) were generated with a tightly focused electron beam (probe current; 100 nA) at an acceleration voltage of 15 keV. 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

Location and Fate of Pb on the S/S of Pb Wastes

The location of metals in cement-based solidification is complex and still the subject of debate with considerable uncertainty remaining with regard to the fixation mechanisms of the metals. The general nature of Portland cement has been proposed to explain the following phenomena: (i) the dissolution-precipitation (the so-called through-solution) reactions and (ii) the direct attack of water on grains of anhydrous cement.[6] The former reactions mainly occur in the cavities through the dissolution of the anhydrous cement components, whereby the dissolved phase becomes supersaturated and hydrated minerals precipitate from this solution. The latter reactions form a hydrated membrane of C-S-H gel around the cement grains during the first few minutes of reaction.[3,6,10] The membrane acts as a semi-protective film and slows reaction with the inward flow of water molecules and with the outward migration of mainly Ca^{2+} and silicate ions due to the difference of osmotic potential on both sides of the membrane.[3,11] The pressure differential causes the membrane to rupture periodically, and the breakdown of the membrane marks the onset of rapid hydration.

The former reactions between cement and wastes result in the formation of precipitates of the metals in the high alkaline environment of the pore-water solution. The location of the metal precipitates in SWF was investigated by the backscattered electrons (BSE) and electron dispersive spectroscopy (EDS) fitted in the EPMA. Because the intensity of the BSE signal mainly depends on the mean atomic number, brighter regions in the image correspond to sample areas consisting of heavier elements.[6]

In the BSE image of Pb-doped SWF(KP10), three bright large particles of about 200-500 μm of cross sectional length were found as shown in Figure 1(a). The three particles were identified by EDS (Figure 1(b)), as lead salts of sulfate

but possibly also containing carbonates and hydroxides. In our early study[12~14] lead precipitates were also identified as lead sulfate carbonate hydroxide ($Pb_4SO_4(CO_3)_2(OH)_2$: JCPDS file No. 38-354) by X-ray diffraction analysis. The results of EDS and XRD are consistent with the analysis of Thomas et al.[15] who carried out potentiometric titrations to ascertain the 'fate' of Pb in cement-water system. A saturated mixture of $Ca(OH)_2 + CaSO_4$ as an analogue of cement system was titrated against 0.05 M $Pb(NO_3)_2$ solution. They have argued that the first lead admixtures are converting into secondary precipitates through dissolution and precipitation at pH above 8.5 with fluctuation of the pH in the region pH 8.5-10, losing 15% SO_4^{-2} from the added alkali solution by subsequent analysis of the solution (after filtering the precipitation). It was concluded that the precipitates were mixed basic lead salts of variable stoichiometry involving nitrate, hydroxide and sulfate, probably with carbonate made by taking up CO_2 from air.

The latter reaction can explain reactions between C-S-H gel and hazardous substances. The location of other Pb-doped cementitious minerals in the areas among cement particles was investigated by EPMA micrographs. 'Area among cement particles' is denoted in our discussion here by 'inter-particle area'. The colored images represent the elemental distribution of Pb, Ca, Si, Al and S on the surface, but the colors provide qualitative descriptions and do not represent the absolute values of the element concentration within the sample. The concentrations of all measured elements increase in the following order: blue, green, yellow, red. A small portion of the Pb in KP10 is located on the surface of the cement particles as a result of adsorption to silicate surfaces, and most of the Pb is broadly spread throughout the matrix in inter-particle areas as shown (far from cement grains) in the Pb map of Figure 2.
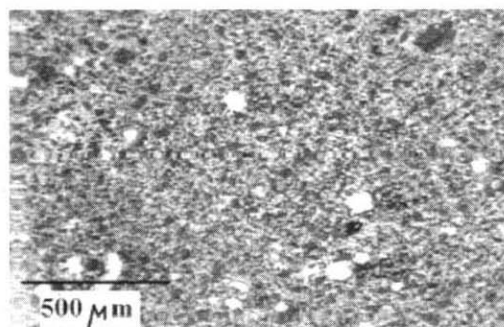
The observation that Pb accumulates in inter-particle areas is consistent with the argument of Cocke[7] that hydroxy-cations containing up to six
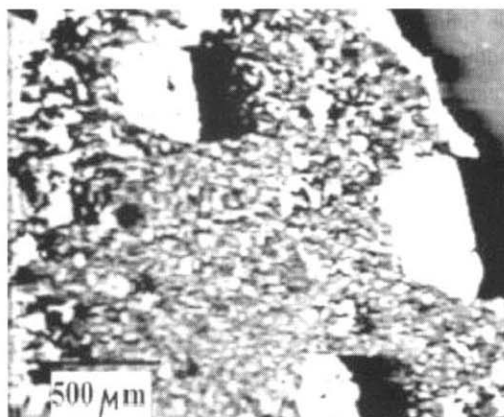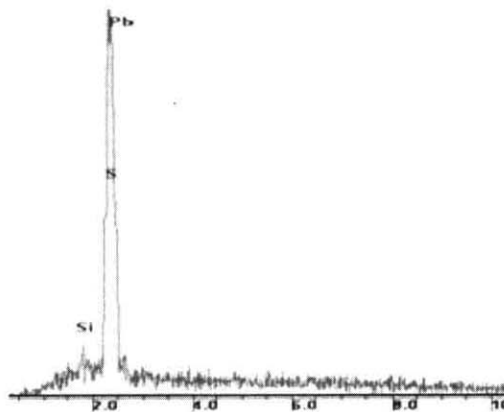
Figure 1. (a) Backscattered electron image (BSE) of KP10 in a large area of ×80 magnification, (b) electron analysis of brighter regions, (c) BSE of KC5P10 in a whole area of ×80 magnification.

Pb atoms such as $Pb_6O(OH)_6^{4+}$ formed at high pH can adsorb to silicate surfaces and/or precipitate as sulfates forming a membrane which
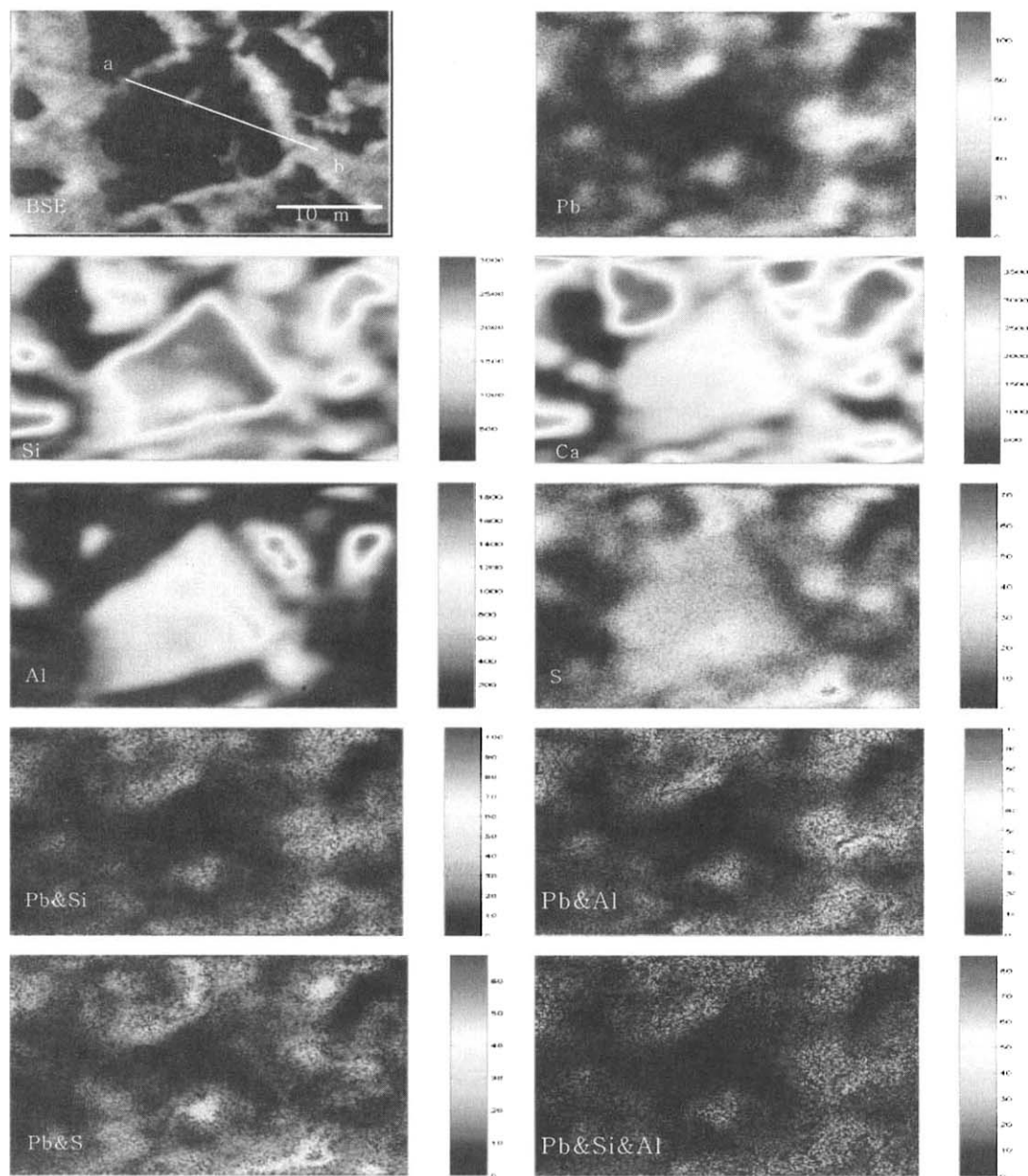
Figure 2. EPMA micrographs of ×3000 magnification from sample KP10 at 28 days: The gray-scale picture is the image from the backscattered electron (BSE), and the colored maps indicate the element distribution for Pb, Si, Ca, Al, S, Pb & Si, Pb & S, Pb & Al and Pb & Si & Al.

coats the clinker components. These include carbonates, sulfates, and other compounds that are extremely insoluble and have low surface energies.

By the simultaneous analysis of other elements in addition to lead (Pb & Si, Pb & Al, Pb & S and Pb & Si & Al), correlations between Pb and other components were investigated mainly in inter-particle areas. The locations of Pb & Si, Pb & Al and Pb & S are very similar to that of Pb ions. Location of Pb & Si & Al also looks like that of Pb & Si and Pb & Al.

The intensities of Pb & Si, Pb & Al and Pb & S are a little lower than that of Pb ions. As a result, the elemental composition of Pb-doped gel in the inter-particle areas may consist of Ca, Si, Al and S, etc. in accordance with the EPMA elemental maps.

It is apparent from these results that the lead is located in surface, near-surface, and inter-particle areas of cement grains. In the S/S of 10% Pb-doped waste, lead is located in the inter-particle areas in two different forms. One is commonly lead salts with sulfate, carbonate, and hydroxide, etc. Large accumulations of these translucent shapes were apparent on microscopic investigation (using a facility fitted to the EPMA). Another form occurs with calcium, silicate, low-aluminum, and low-sulfate, etc. Lead at the surface and near-surface exists at very low concentration

The Retardation Effect of Lead in the Hydration of Cement

The membrane of Pb species prevents cement hydration by coating some of the calcium silicate. The quantity of admixture required to form the membrane is affected by the surface area of the cement powder. As little as 0.15 weight% (*wt*.%) of the Pb admixture is sufficient to induce a retardation in the hydration of cement by the membrane.[15] As the hydration is not completely stopped by the membrane of Pb species, diffusional processes through the membrane coating are still active at a reduced rate, while the longer setting time promotes the development of polymerization.

EPMA mapping analysis indicated that the retardation effect of lead was subject to migration of cement components far from the cement grains. Since calcium and silicate ions are the main components of $Ca(OH)_2$ and C-S-H throughout most of hydrated cement matrix, the amount of outward migration of the two components is normally indication of the degree of hydration of cement. As can be seen from Figure 2-Ca and -Si, Ca^{2+} and silicate ions do not much migrate far from the cement grains

(only about 2 μm and 1~2 μm, respectively). A large amount of aluminate and sulfate ions still remaines in the cement grains even after the hydration of cement at a (presumably) reduced rate, and some sulfates are located in the inter-particle areas. The retardation effect of lead induces to make the marked leaching of lead associated with the weakened structure of Pb-doped SWF.[16,17] As examined by Lee[14] the strength of the weakened lead contaminated material(KP10) at 28-days curing was also below one-fourth (2,325 N/cm^2) of that (9,713 N/cm^2) of samples that did not contain lead.

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

Many researchers have argued that the presence of fine calcite particles in Portland cement accelerates the hydration of C_3S and C_2S and the formation of portlandite.[15,18] Ramachandran et al.[19] provided evidence that as much as 25% of the added $CaCO_3$ was incorporated into the C-S-H phase when C_3S was hydrated with 5% additional $CaCO_3$ for three days. Soroka et al.[18] also suggest that calcite filler acts as crystallization nuclei and thereby increases the crystallization rate of the portlandite, and consequently also the rate of the cement hydration. The broadening of the endotherm in the lower temperature range from 140-180°C indicates the presence of a higher amount of combined (rather than free) water associated with increased quality of calcium silicate hydrate and other hydrated minerals on addition of calcite.[20,21]

The Ca and Si maps in the presence of calcite (Figure 3) provide more evidence of rapid dissolution of C_3S and C_2S. Ca ions occupy a significant portion of the inter-particle areas and at considerable distance from cement grains and, as such, are well-situated to contribute to the formation of C-S-H. Si ions in KC5P10 migrate further to inter-particle areas than those in KP10. Nehdi[22] has argued that calcium ions start earlier to be removed from the cement-water solution in the presence of calcite, and enhance further dissolution of clin-
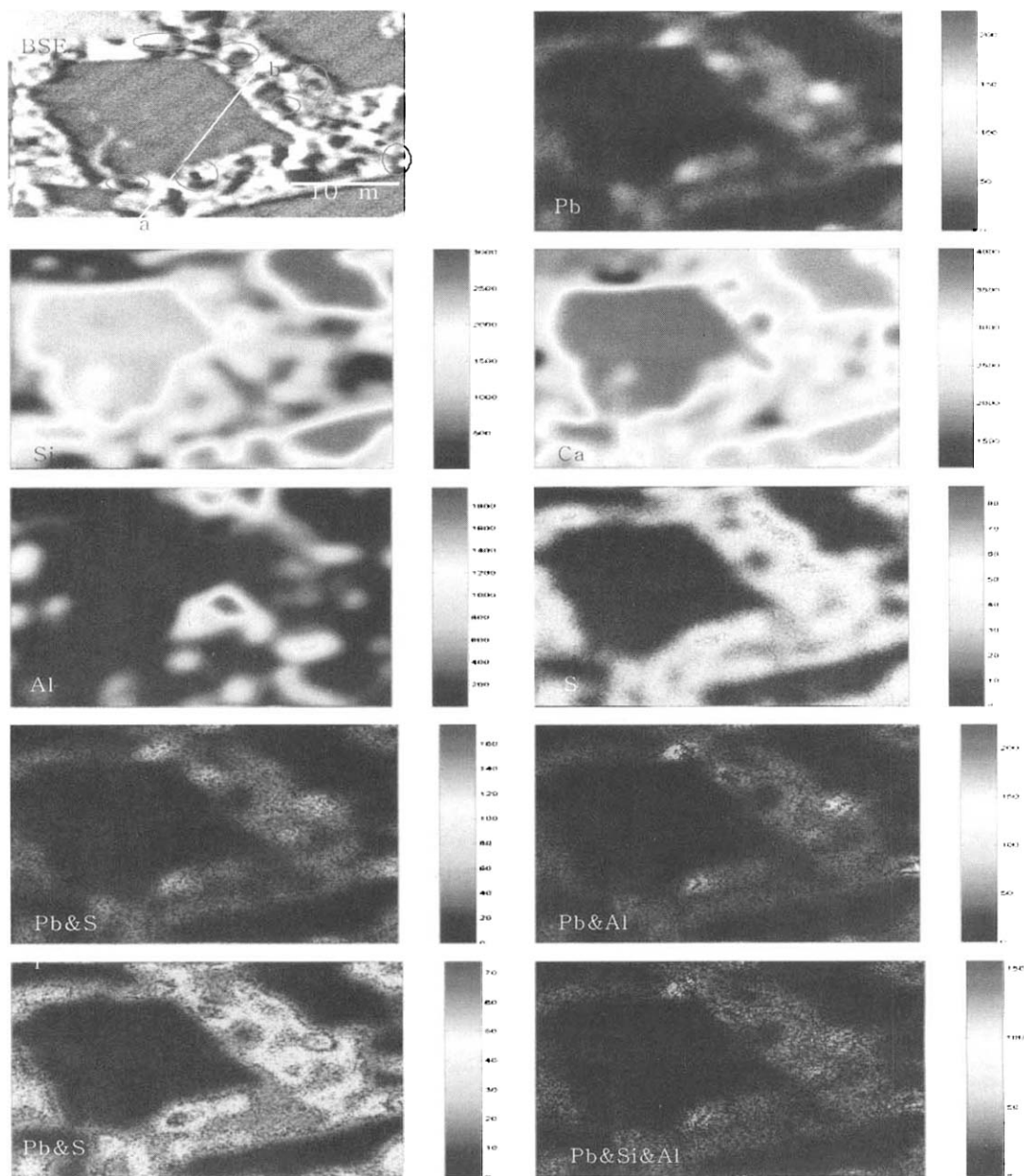
Figure 3. EPMA micrographs of × 3000 magnification from sample KC5P10 at 28 days: The gray-scale picture is the image from the backscattered electron (BSE), and the colored maps indicate the element distribution for Pb, Si, Ca, Al, S, Pb & Si, Pb & S, Pb & Al and Pb & Si & Al.

ker substances. The continued germination of $Ca(OH)_2$ by the earlier dissolution of calcium ions on addition of calcite also implies an increase in C_3S dissolution, and furthermore silicate ions are trapped inside the hydration shell.

In the membrane/osmosis model for Portland cement hydration, Birchall et al.[10] have demonstrated that the crystallization of calcium hydroxide is coincident with the onset of the second exotherm. They suggest that the removal of Ca^{+2} and OH^- from solution by calcium

hydroxide precipitation (reducing the ionic product) simply increases the osmostic driving force and hence promotes the rupture of the membrane formed by C-S-H gel on the cement particle's surface upon hydration.

Since calcite addition in SWF induces the rapid dissolution of C_3S and C_2S and, at the same time, allows formation of a supersaturated solution with the excess of Ca and Si ions and associated anions inside the membrane made from Pb precipitate, an excess of $Ca(OH)_2$ will accumulate on the fluid side of the membrane. An osmotic pressure differential on the membrane produced by an excess of silicate ions enhances earlier membrane rupture periodically in the presence of calcite.[10,20] The above model is able to explain the acceleration effect of calcite in the S/S of heavy metal wastes, which contributes to a reduction of the induction period by earlier membrane rupture. There is more proof of the ability of added calcite to induce early membrane rupture, by the observation of significant compressive strength in KC5P10 by around 7 days whereas KP10 has almost no compressive strength even at 14 days.[14] Sulfate ions in KC5P10 are relatively evenly dispersed throughout all inter-particle areas of cement (Figure 3). This map of 'S' indicates that calcite addition favorably enhances the dissolution of gypsum in the S/S of Pb wastes more than in samples to which calcite has not been added (cf. Figure 2). Aluminates are partially located in the cement grains and inter-particle areas.

As can be seen by comparing Figure 1a and c, the location of Pb in KC5P10 is markedly different to that in KP10. In the BSE image of KC5P10 there are no bright large areas that can be identified as lead precipitates with sulfates, carbonates and hydroxides as there are for KP10. The small bright particles that are evident in the back-scattered electron image of KC5P10 have been identified by EDS as resins used in sample preparation.

The disappearance of large lead precipitates in KC5P10 confirms that calcite additions induce a rapid dissolution of these precipitates in the S/S

process. The Pb in KP10 is mainly located in the broad inter-particle areas, but in KC5P10 Pb primarily exists in the specific locations marked with a circle in the BSE image of Figure 3. The location of Pb of higher intensity in the circles of Figure 3-Pb corresponds closely to the regions of higher intensity of Ca, Si and S in the inter-particle areas of Figure 3-Ca, Si, and S. In the analysis of Pb & Si, Pb & Al and Pb & Si & Al, the location and relative concentration of these components are very similar to those of Pb. Location of Pb & Si & Al is also similar to that of Pb & Si and Pb & Al. The Pb & S in KC5P10 is located more broadly than that in KP10.

CONCLUSION

The EPMA investigation in this study of cement-based S/S provides information to understand quantitative & qualitative insight into the nature of the surface and bulk chemistry. In the EPMA investigation, the accelerating effect of calcite on the S/S of Pb wastes is observed to migrate major cement components of calcium, silicate, sulfate and aluminate ions farther from the cement grain through the fast dissolution/ diffusion processes.

The location of Pb ions (also lead precipitates) and other components in non-crushed samples is easily ascertained by mapping analysis of elemental concentration and the investigation of BSE/EDS fitted in the EPMA. Pb ions in KP10 are found at the cavity (often including large lead precipitates of about 200~500 μm) 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.

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