

LEACHABILITY OF Pb-DOPED SOLIDIFIED WASTE FORMS USING PORTLAND CEMENT AND CALCITE :

II. INVESTIGATION OF SEM/EDS

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Abstract : This study was examined to assess leachability of Pb of solidified waste forms (SWF), which are prepared from lead nitrate, in conjunction with Portland cement and calcite. The effect of calcite in the solidification/stabilization of lead was particularly assessed. Compressive strength and leach were basically examined to investigate effects of lead and calcite on SWFs. SEM (scanning electron microscopy) was used for identifying mineral transformations and microstructure changes of the SWF during leaching processes. It was found that lead contaminated materials (KP5, KP10 and KP20) were highly leached. SEM showed that rapid release of lead at the attack of acid is mainly related to larger pores and their openness in cavities. The leached SWFs showed flaky substances of "honey-comb" microstructure after initially leached. The flask substances were then disappeared after the fifth leach. It is noted, however that the SWFs containing calcite before leaching showed dense microstructure with portlandite appearing as "needle-shaped" silicate crystals. The surface of SWFs was initially covered with the "jungle-shaped" silicate crystals, and in the fifth leaching it was then covered with the thick "lumpy-shaped" crystals. These results as above confirm the slow diffusion of lead in the presence of calcite.

Key Words : Solidification/stabilization (S/S), Calcite, Lead, SEM, Leachability

INTRODUCTION

Cement has been widely used for the solidification and stabilization (S/S) of hazardous and radioactive wastes. Portland cement is one of most common S/S agents due partly to its ability to set and harden under water.^{1,2)} Solidification based on cement produces solidified waste forms (SWF), which have forms of the physical and chemical fixation/binding of wastes in the structure of the hydrated cementitious materials through the cement hydration.³⁾ 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 physically immobilization of the toxic contaminants and chemically bound to the encapsulating solid.⁴⁻⁶⁾

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⁾ It is well known that the mechanism of hydration is still a very controversial area with the lack of understanding of hardening processes.

Nevertheless, understanding of the immobilization mechanisms and the structure of pores in the hydrate structure are important to predict lea-

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chability of the SWF and to develop stability of SWFs. Electron microscopy is valuable at least to visualize the microstructural role of pores. Quantification of the pore structure by SEM is developing in conjunction with an effort of sophisticated image analysis technology.^{8,9)} A study to assess leachability of Pb on SWF using Portland cement and calcite is presented in this paper. Attention is particularly given to the effects of calcite in the S/S of lead. SEM was used for identifying mineral transformations and microstructure changes during leaching processes.

EXPERIMENTS

Materials

Cement used was a normal Portland cement supplied from Sangyong Cement in Korea. Its chemical and mineralogical composition is shown in Table 1.

Table 1. The chemical and mineralogical composition of cement used

Chemical composition (wt.%)						Mineralogical composition (wt.%)					
CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaSO ₄	
62.4	20.7	6.8	3.1	1.7	3.3	41.7	27.5	12.7	9.4	2.9	

Calcite used was high-grade crystalline form ($\geq 95.0\%$ CaCO₃) with $\leq 4.0\%$ MgCO₃ and $\leq 1.5\%$ acid insolubles content. Its specific gravity was 2.7 and its BET specific surface area was 5.2 m²/g. It was ground such that it exhibited an average diameter (D₅₀) of 1.8 μ m, maximum particle size of 8 μ m and residue on a 20 μ m screen of $< 0.005\%$.

The wastes were prepared from lead nitrate, which precipitated to form hydroxide sludge on adjusting the pH to 8.5 with 6.0N sodium hydroxide. It was then dried at 104°C for 24 hours. X-ray diffraction (XRD) showed that the major crystalline phases present were found to be lead nitrate hydroxide [Pb₂(NO₃)(OH)₃] and lead oxide nitrate hydroxide [Pb₆O₃(NO₃)₂(OH)₄]. The formation of these minerals is consistent with the results of previous authors.¹⁰⁾

The various proportion of Pb waste and cement were mixed with water which was added to mix at a water/solid (cement, calcite and Pb wastes) ratio (W/S) of 0.3. The mixtures were cast into polyethylene cylindrical moulds (20mm diameter (40mm height) and then demoulded after 24 hours. The specimens were cured in humid air at 20°C for 28days for each sample respectively. Samples were prepared in triplicate; as designated with KC*i*P*j*, where *i* is the calcite content and *j* is the Pb-doped waste content. Samples used are 10% Pb-doped SWF with 0, 5 and 10% additional calcite; as designated with KP10, KC5P10 and KC10P10 respectively. 20% Pb-doped SWF with 0, 5 and 10% additional calcite; as designated with KP20, KC5P20 and KC10P20, respectively.

Methods

Unconfined Compressive Strength (UCS)

UCS was tested on the samples using an Instron testing machine. The samples was capped with Masonite[®] to limit the effect of cracking. Loading was increased until maximum load was achieved to show visible cracks appeared.

Toxicity Characteristic Leaching Procedure (TCLP)

Leaching tests were carried out on the hydrated pastes cured for 30 days, by means of the US EPA Toxicity Characteristic Leaching Procedure (TCLP). Samples were ground to particles of less than 9.5mm in size, and leached with acetic acid (pH 4.93). The solid phase was extracted with an amount of extraction fluid equal to 20 times of the weight of the solid phase. The samples were agitated in a rotary tumbler at 30 rpm for 18 hours. After the first extraction residues of all samples were weighed, collected at the same weight respectively, and returned to the extraction bottles to repeat the extraction. The amount of new leachant equal to 20 times of the weight of the solid phase was refilled for each extraction. Each extraction was carried out at room temperature for 18 hrs. This

procedure was repeated up to the fifth extraction. The residues of samples after the first to fifth extraction were collected, and then dried at 104°C for 24 hours for the investigation of SEM.

Scanning Electron Microscope (SEM)

SEM images were obtained using a Hitachi 4500 SEM fitted with electron dispersive spectroscopy (EDS). Samples for SEM analysis were cured for 28 days and then dried at 104°C for 24 hours. The dried solid samples were carefully fractured and coated with carbon to prevent electronic charging effects during the analysis.

RESULTS AND DISCUSSION

Preliminary Investigation on Effects of Pb-doped SWFs

Figure 1 shows the effect of Pb on change of the UCS in cement hydration. It was found that lead-contaminated (i.e., KP5, KP10, KP20) materials produced less UCS, compared to high UCS of the pure cement. This may be due to retardation effect of lead in the hydration of cement. All 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.

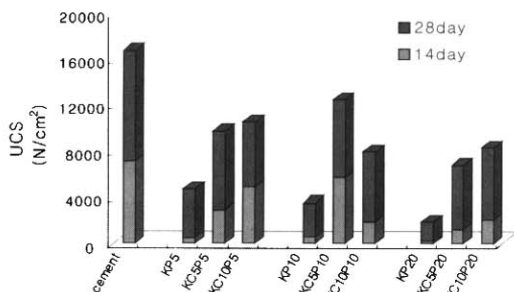


Figure 1. Unconfined compressive strength (UCS) of Pb-doped solidified waste forms in the absence and presence of calcite at 14 days and 28 days of curing time.

The UCS of Pb-doped SWF with the presence of calcite is shown in Figure 1. It is of interest to note that the UCS of the samples were partially rectified by addition of calcite; that is, approximately 3000 N/cm² at 14 days and about 6000 N/cm² at 28 days in case of KP10. Pb-doped SWF with addition of 5% calcite resulted in 2-3 times increase of the UCS, as compared to samples without calcite (i.e., KP5, KP10, KP20). The UCS of samples containing 5% calcite is always observed to be slightly superior to that of 10% calcite addition. 20% lead-doped samples containing 10% calcite yields a slightly stronger than those with only 5% calcite on UCS. Strength development of KC10P20 is observed to be more than twice that of KP20 at 60 days.

The leachability of lead on the SWFs was measured through TCLP. The leaching results on the release of lead are plotted in Figure 2. The total raw concentrations of lead present in the SWFs containing 5%, 10% and 20% Pb-doped wastes are 1,925, 3,930, and 7,860 mg/l, respectively. Lead concentrations in the extraction fluid for 5%, 10% and 20% lead-doped materials solidified by cement are 79.2 mg/l, 388.0 mg/l, and 1,020 mg/l, respectively. These are equivalent to approximately 4%, 10% and 13% respectively, in comparison with of total lead initially present. Calcite addition results in remarkable reduction (approximately below 0.1 % of total lead) of lead release ranging from KC5P5, KC5P10, KC10P10 and KC10P20.

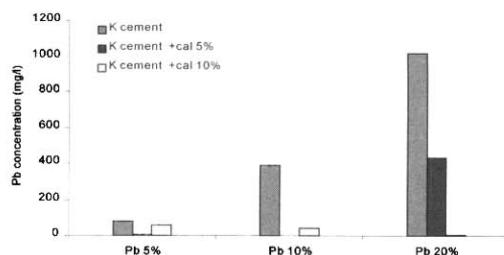


Figure 2. Variation in leachability with calcite addition.

SEM/EDS Investigation on Leaching

Electron microscopic analyses and energy dispersive analyses on leached SWF can provide very valuable insight into the physical/chemical characteristics of the microstructure and morphology of these solids, which may be able to interpret leaching effects of SWF. SEM image of KP10, before leaching (Figure 3a), shows no portlandite and no needle-shaped silicate crystal, which are main crystalline products in the hydration of cement, because lead ions in the cement-based S/S make an effect of retardation in the hydration of cement.

After the initial leaching, the micrographs shown in Figure 3b show loosely bound flaky substances with very poorly crystalline structure. The result is consistent with the observations of Cocke et al.¹¹⁾ who described the morphologies as a "honey-comb" structure. After the fifth leaching, even the flaky substances as well as C-S-H gel almost disappear, and only large cement grains without any crystalline minerals remain in the cavity regions. It is envisaged by this stage that most of hydrated substances are leached due to the permeable structure of the poorly bound materials. It is evident that a

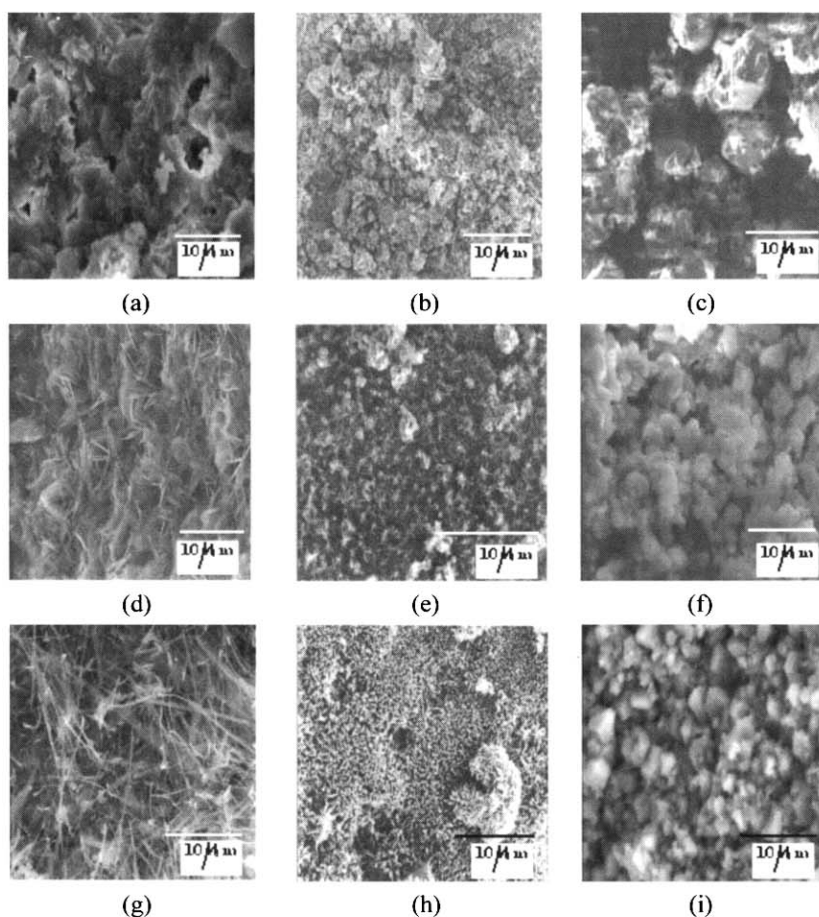


Figure 3. Comparison among SEM images of 10% Pb-doped SWFs in the cavity before/after leach. (a) KP10 before the leach (b) KP10 after the 1st leach (c) KP10 after the 5th leach (d) KC5P10 before the leach (e) KC5P10 after the 1st leach (f) KC5P10 after the 5th leach (g) KC10P10 before the leach (h) KC10P10 after the 1st leach (i) KC10P10 after the 5th leach. Only (b), (e) and (h) are investigated in the area of non-cavity.

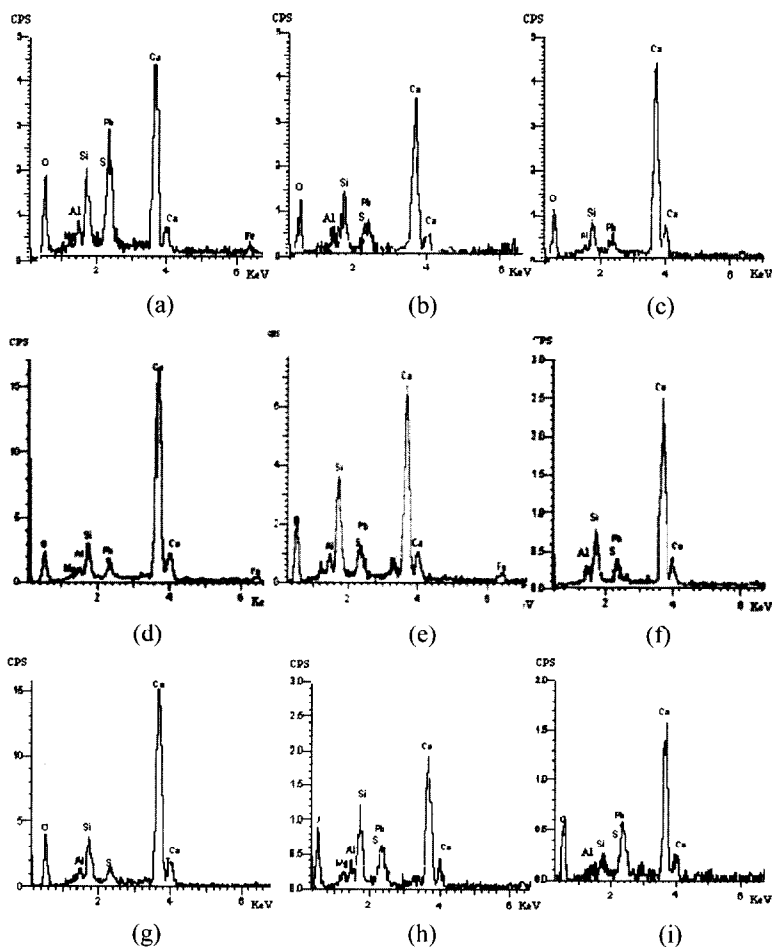


Figure 4. Comparison among EDS images of 10% Pb-doped SWFs in the cavity before/after leach. (a) KP10 before the leach (b) KP10 after the 1st leach (c) KP10 after the 5th leach (d) KC5P10 before the leach (e) KC5P10 after the 1st leach (f) KC5P10 after the 5th leach (g) KC10P10 before the leach (h) KC10P10 after the 1st leach (i) KC10P10 after the 5th leach.

couple of large pores or macrovoids after leaching make the structure prone to acid attack. Higher release of lead on the attack of acid is mainly related to the presence of larger pores and their openness within cavities.

The corresponding EDS spectra of SEM micrographs (see Figure 3) are shown in Figure 4. It can be seen that the percentage of lead in KP10 has been markedly decreased due to leaching as shown in Figure 4a, b, and c from 33.0 wt.% before leaching to 18.7 wt.% after the initial leaching and only 6.3 wt.% after the fifth leaching.

On the other hand, the SWF containing

calcite is densely covered with portlandite or needle-shaped silicate crystals containing a little lead in the hydration of cement as shown in Figure 3d and g. These two hydrate products strongly protect the solidified forms or provide acid neutralization capacity (ANC) against from acid attack at the surface of the SWF. In the initial leaching of KC5P10 and KC10P10, these “jungle-shaped” crystals were found throughout the cavity and non-cavity regions (Figure 3e and h). The presence of these crystals suggests a possible mechanism for the minimization of leaching of the SWF. To initiate the growth of “jungle-shaped” crystals, remineralization on the

surface of the SWF must be occurred. The elemental composition of the crystals in KC5P10 consists of Ca, Si, Pb, Fe, Al, K, and S, and the elements were Ca: 54.2, Si: 18.8, Pb: 12.0, Fe: 4.9, Al: 2.0, K: 5.8, and S: 2.3 % on the basis of elemental weight. The crystals are consistent with calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) with high Ca, Si, and Pb, and Fe and Al substituted for Si at a relatively high level in the structure. The potassium acts on a charge compensation cation on the surface of set cement.¹²⁾

It is reasonable to assume that the “jungle-

shaped” crystals of C-Pb-S-H without any pore can preserve the SWF from acid attack on the surface of leached samples. Even though the jungle-shaped crystals disappeared after the fifth leaching, the surface of SWF was covered by the thick “lumpy” crystals produced most likely as a result of re-precipitation as shown in Figure 6f and i. It is assumed, therefore, that the crystals can strongly protect solidified forms from the attack of acid, as compared to the fifth-leached forms of KP10 (Figure 3c). The crystals consist of high Ca and Si with a little Pb, S, and Al in KC5P10, and of high Ca and

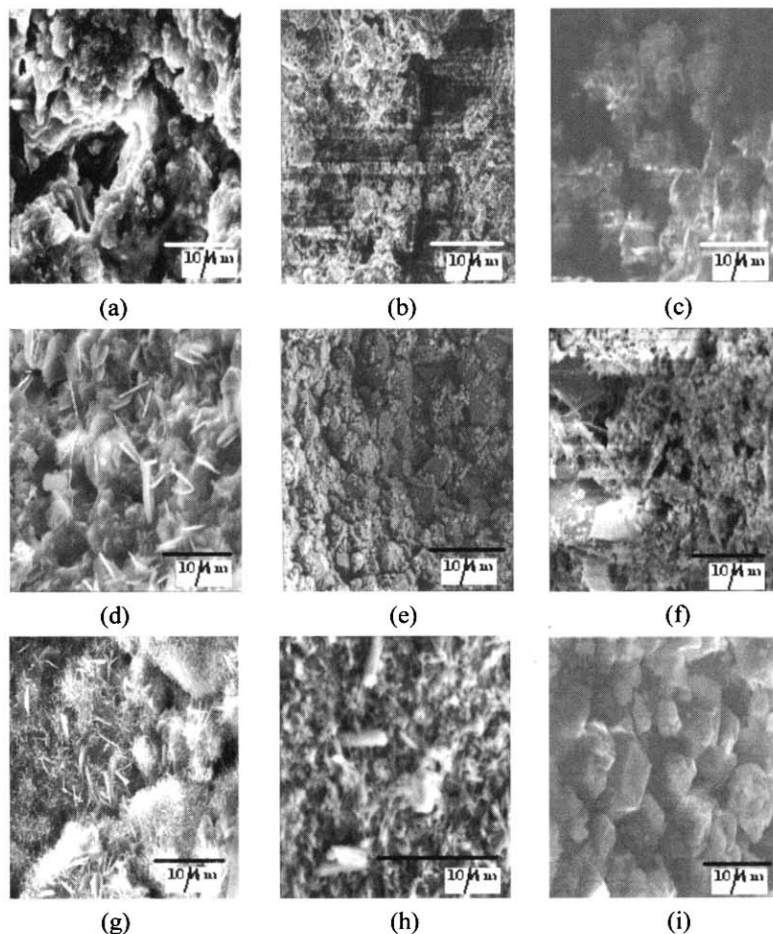


Figure 5. Comparison among SEM images of 20% Pb-doped SWFs in the cavity before/after leach. (a) KP20 before the leach (b) KP20 after the 1st leach (c) KP20 after the 5th leach (d) KC5P20 before the leach (e) KC5P20 after the 1st leach (f) KC5P20 after the 5th leach (g) KC10P20 before the leach (h) KC10P20 after the 1st leach (i) KC10P20 after the 5th leach.

Pb with a little Si, S, K and Al in KC10P10 (Figure 4f and i).

SEM and EDS Investigation on the Leaching of High Pb-doped SWF

The SEM/EDS results for the 20% Pb-doped SWFs, shown in Figure 5 and 6, confirm the effectiveness of calcite in minimizing the effect of acid attack. As seen in the 10% Pb-doped SWF, the KP20 image, before leaching (Figure 5a), shows no portlandite and no “needle-shaped” silicate crystals, with showing significant cavities that acid may permeate and attack the matrix through. The leached KP20 micrographs after the initial leaching indicate the “honey-comb” structure similar to those observed for leached KP10. The EDS results show that leaching induces a marked decrease in lead content up to less than half of that originally present (Figure 6a, b and c).

On the other hand, the 20% Pb-doped SWF containing also consists of densely covered portlandite or needle-shaped silicate crystals similar to the “coral-shaped” structure. The coral-shaped silicate crystals with portlandite certainly provide strong protection of the SWF from acid attack.

Even though portlandite or silicate crystals were not observed after the initial leaching of KC5P20, the surface of the leached SWF looks presumably very resistant to acid attack. After the fifth leaching, the “jungle-like” silicate crystals, as shown in the leached samples of 10% Pb-doped SWF on the addition of calcite (KC5P10, KC10P10), were observed throughout all cavity regions. In the initial leaching of KC10P20, the “jungle-like” crystals were also appeared. In the fifth leaching, the surface of the leached SWF was covered by the thick and lumpy crystals previously as observed in KC5P10 and KC10P10 after the fifth leach. These “jungle-like” and “lumpy” deposits should be quite resistant for protecting the SWF at the attack of acid.

CONCLUSIONS

Conclusions are as follow:

- 1) It is observed that lead contaminated materials (i.e., KP5, KP10, KP20) were highly leached (equivalent to approximately 4~13% of the total lead concentration) by TCLP as well as a weak compressive strength (only 20~40% of UCS of pure cement at 28-days curing time). SEM confirms that rapid release of lead at the attack of acid is mainly related to larger pores (capillary pores) and their openness in cavity areas of lead contaminated materials (Figure 3a and 5a). The SWF on leaching makes it a “honey-comb” microstructure of loosely bound flaky substances after the initial leaching. Most C-S-H gel as well as the flask substances, after the fifth leaching (Figure 3c and 5c), disappears from the surface of SWF. These microstructural findings by SEM give evidence of rapid release of lead at the attack of acid on lead contaminated materials. The investigation of EDS also shows marked decrease of lead from the surface of SWFs from 33.0 wt.% before leach to 18.7 wt.% after the initial leaching and only 6.3 wt.% after the fifth leach.
- 2) Additions of calcite are observed to rectify the poor strength development of lead contaminated materials with a UCS of approximately 2~3 times compared to the absence of calcite. Calcite addition results in marked decrease of lead release (below 0.1% of total lead concentration) on leaching. The SWFs containing calcite have denser microstructure with portlandite and “needle-shaped” silicate crystals (Figure 3d, 3g, 5d and 5g) compared to SWFs in the absence of calcite. In the initial leaching, “jungle-shaped” silicate crystals were found to be consistent with chemical composition of calcium lead silicate hydroxide (C-Pb-S-H) with high

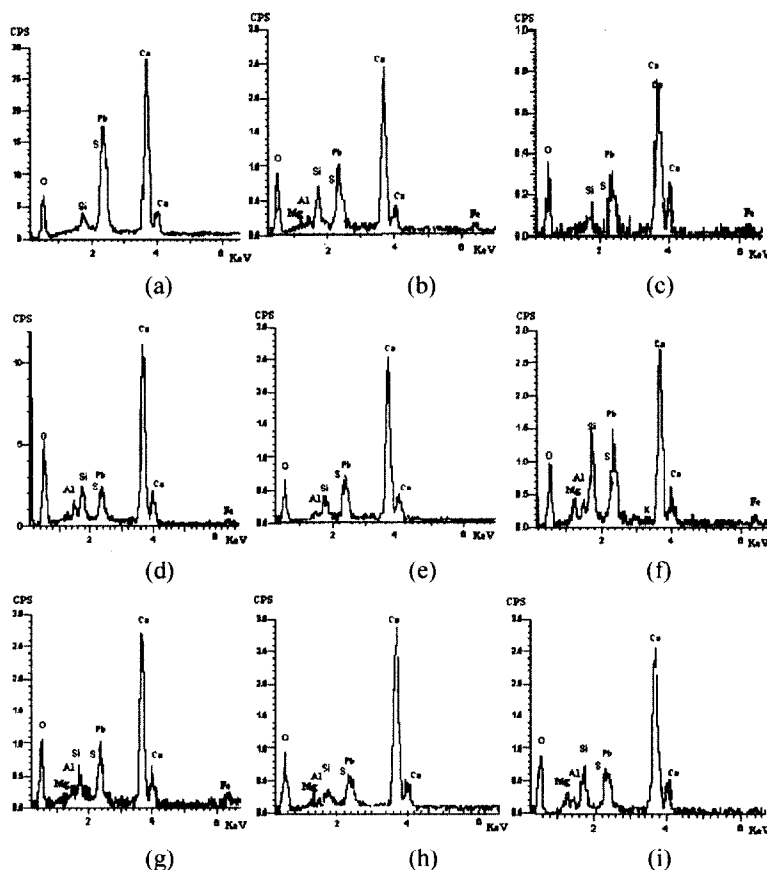


Figure 6. Comparison among EDS images of 20% Pb-doped SWFs in the cavity before/after leach. (a) KP20 before the leach (b) KP20 after the 1st leach (c) KP20 after the 5th leach (d) KC5P20 before the leach (e) KC5P20 after the 1st leach (f) KC5P20 after the 5th leach (g) KC10P20 before the leach (h) KC10P20 after the 1st leach (i) KC10P20 after the 5th leach.

Ca, Si and Pb and Fe and Al substitute for Si (Figure 3e, 3h and 5h). After the fifth leaching, the “jungle-shaped” crystals disappeared, however the surface of SWFs was covered with the thick “lumpy-shaped” crystals produced most likely through re-precipitation during continuing leach (Figure 3f, 3i and 5i). It is evident by these SEM/EDS that calcite additions make a slow release of lead from the SWF on leaching.

- 3) It is found by SEM/EDS investigation that rapid release of lead from the SWF is mainly associated with the presence of larger pores (mainly capillary pores) and their openness within cavities. On the other

hand, micropores (gel pores) produced within well-hydrated cement (such as C-S-H gel) affect slow release of lead. For this reason, investigation of the large and meso-pores including the extrinsic open porosity by SEM/EDS provides a quantitative measurement of leachability of SWF at the attack of acid.

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