

LEACHABILITY OF PB-DOPED SOLIDIFIED WASTE FORMS USING PORTLAND CEMENT AND CALCITE: I. INVESTIGATION OF X-RAY DIFFRACTION

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Abstract : This study is investigated to assess leachability of Pb-doped solidified waste forms using Portland cement and calcite. X-ray diffraction was used for identification of mineral transformations occurring on the solidified waste materials formed during the leaching process. Particular attention is given to the leaching effects of calcite (CaCO_3) in the solidification/stabilization of lead. Rapid diffusion/dissolution of lead substances (KP10) at the attack of acid is mainly related to lead precipitates located in larger pores (capillary pores) and their openness in cavities. Calcite-added lead contaminated material (KC5P10) including almost no lead precipitates makes slow diffusion/dissolution of lead, which occurs in the structure of calcium lead silicate (sulfate) hydroxide (C-Pb-S-H). On the other hand, additional calcite on lead contaminated materials (KC10P10) including even a lot of lead precipitates in cavity areas such as KP10 are presumably very resistant to acid attack because enhanced calcium-silicate-hydrate (C-S-H) due to accelerating effect of calcite strongly encapsulates/protects even portlandite as well as lead precipitates, which not much dissolves even up to the 5th leach.

Key Words : Solidification/stabilization (S/S), Calcite; Lead, X-ray diffraction, Leachability

INTRODUCTION

Cement-based solidification/stabilization (S/S) is a widely used technology for disposal of hazardous wastes due to its relatively low cost and demonstrated effectiveness over many years.^{1,2)} The U.S. Environmental Protection Agency also recognizes cementitious solidification as the 'best demonstrated available technology' (BDAT) for land disposal of most toxic elements.^{3,4)}

Stabilization is a process of converting a

unstable toxic waste to a physically and chemically more stable form, involving a chemical interaction between wastes and the binding agent.⁵⁾ The purpose of the S/S process is to produce solids that are non-hazardous or less hazardous than the original waste, and to prevent pollutants from migrating into the environment.²⁾ The physicochemical process controlling the S/S of hazardous wastes is very complex and active since binders including cement contain a large number of components. The chemistry of hydraulic cement system especially with regard to the mechanism of S/S is still very active and controversial area. This is mainly due to the limitation of analytical tools

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but also due to the complexity of the system. Therefore most solidified waste forms (SWFs) still remain the unknown containment system even though the S/S technology has been considered very suitable to treat hazardous wastes, radioactive wastes, contaminated sites and mine tailings.

The assessment of hazard of the SWF is usually evaluated by leaching tests. In this work, we assess leachability of Pb-doped solidified waste forms using Portland cement and calcite. Particular attention is given to the leaching effects of calcite in the S/S of lead. Identification of mineral transformations occurring in the solidified waste materials formed during the leaching process was undertaken by XRD.

MATERIALS AND METALS

Cement was purchased as normal Portland cement from Sangyong Cement in Korea. 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 ($\text{Ca}_3\text{Al}_2\text{O}_6$: C_3A), (iv) 9.4% of calcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$: C_4AF) and (v) 2.9% of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Calcite was of high grade crystalline form ($\geq 95.0\%$ CaCO_3) with $\leq 4.0\%$ MgCO_3 and $\leq 1.5\%$ acid insolubles content. Its specific gravity was 2.7 and its BET specific surface area was $5.2 \text{ m}^2/\text{g}$. It was ground such that it exhibited an average diameter (D_{50}) of $1.8 \mu\text{m}$, maximum particle size of $8 \mu\text{m}$ and residue on a $20 \mu\text{m}$ screen of $< 0.005\%$.

The wastes were prepared from lead nitrate which precipitated to form hydroxide sludge by adjusting the pH to 8.5 with 6.0N sodium hydroxide and then dried at 104°C for 24 hours. The major crystalline phases present were identified by X-ray diffraction and found to principally be lead nitrate hydroxide [$\text{Pb}_2(\text{NO}_3)(\text{OH})_3$] and lead oxide nitrate hydroxide [$\text{Pb}_6\text{O}_3(\text{NO}_3)_2(\text{OH})_4$]. The formation of these minerals is consistent with the results of

Asavapisit *et al.*⁶⁾ and Gress *et al.*⁷⁾

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 20mm diameter \times 40mm height and removed after 24 hours. The curing was carried out in humid air at 20°C for 28days for each sample respectively. Samples were prepared in triplicate and are denoted KC_iP_j , where i is the calcite content and j is the Pb-doped waste content. In this study, samples were also prepared in triplicate. Samples used are 10% Pb-doped SWF with 0, 5 and 10% additional calcite, denoted KP10, KC5P10 and KC10P10, respectively.

Leaching tests were carried out on the 30-day-old hydrated pastes using 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 ($\text{pH } 4.93 \pm 0.05$). The solid phase was extracted with an amount of extraction fluid equal to 20 times 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, on the other hand, 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 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, at the same time, dried at 104°C for 24 hours for the investigation of XRD.

X-ray Diffraction (XRD)

XRD was used to identify and quantify the crystalline mineral phases present in the SWF. The mineralogical composition of the samples was analyzed using Cu K_α radiation at 35V and 25mA on a Philips 1830 XRD diffractometer. XRD scans were obtained using 0.04° steps with 2 second counting time. Diffact 5.0 software

and JCPDS diffraction files by JCPDS International Center for Diffraction Data were used for identifying mineral forms of SWF.

RESULT AND DISCUSSION

Fixation Mechanism of Lead in the Absence and Presence of Calcite

The X-ray diffraction pattern of Pb-doped solidified waste forms with cement paste after 28-days of curing time is shown in Figure 1. Most of the Pb, originally added as nitrate and hydroxide solids of $Pb_2(NO_3)(OH)_3$ and Pb_6O_3

$(NO_3)_2(OH)_4$, precipitates with sulfate and/or carbonate during the hydration of cement, eventually extremely insoluble lead precipitates formed such as lead carbonate sulfate hydroxide [$Pb_4SO_4(CO_3)_2(OH)_2$, JCPDS file No. 38-354] (P2) and lead carbonate hydroxide hydrate [$3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$, JCPDS file No. 9-356] (P3). From the diffraction studies there is no evidence of $Pb(OH)_2$, cerussite ($PbCO_3$), hydrocerussite ($Pb(CO_3)_2(OH)_2$) or anglesite ($PbSO_4$) in substantially crystalline form.

Lead species are preferentially deposited both as lead precipitates locating mainly in the cavity

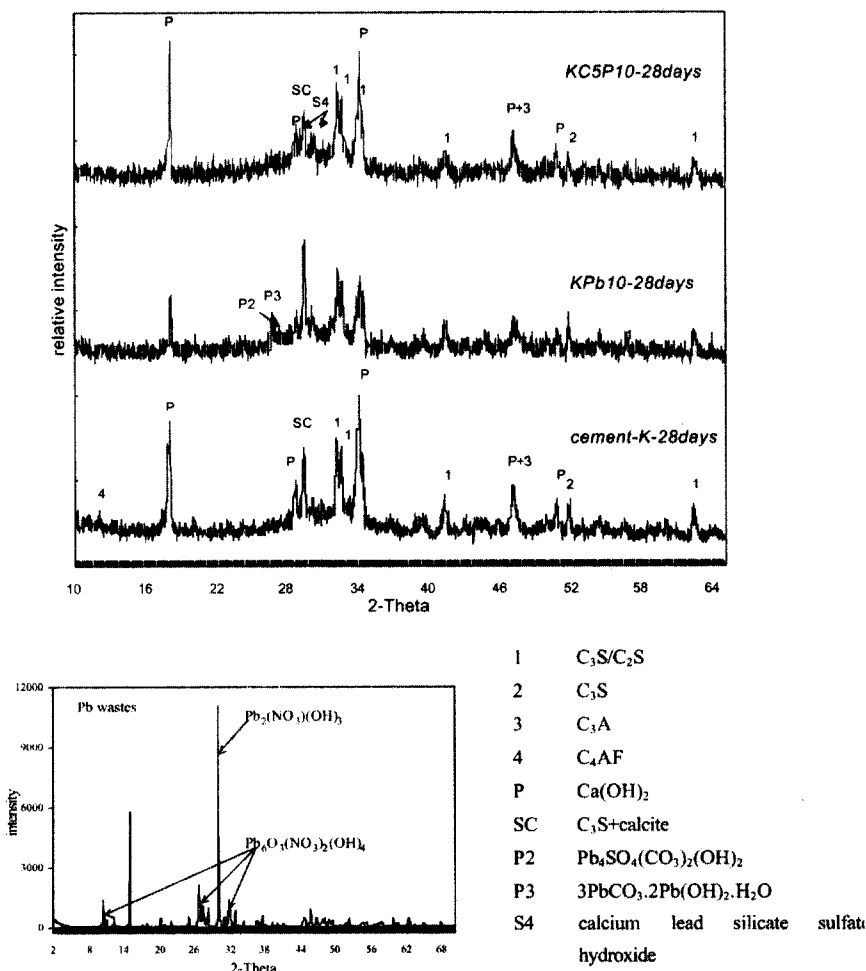
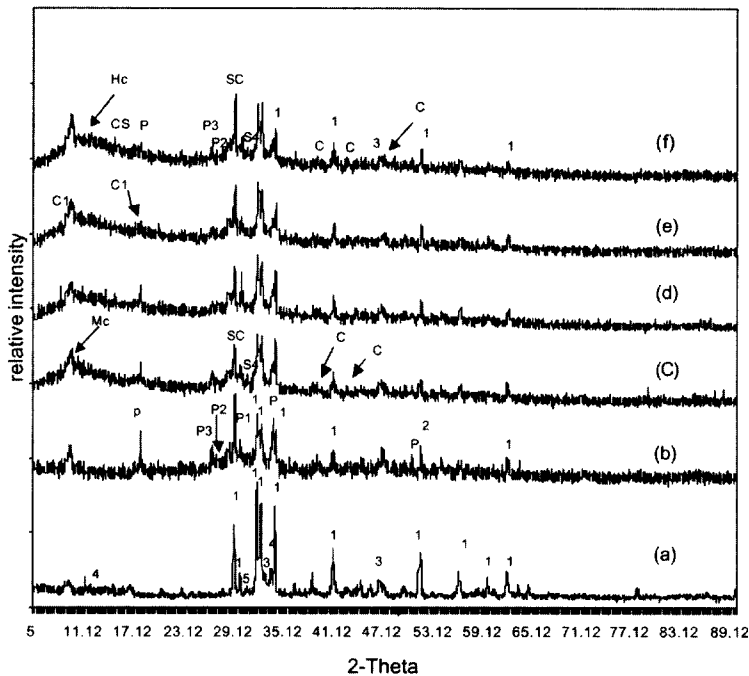


Figure 1. XRD patterns of the SWF at 28 days of curing time.

areas and as a impervious coating (membrane) of lead species around cement clinker grains in the early stages of curing.^{8,9)} In the latter stage of lead deposition, the membrane of lead species around the cement clinker grains prevents the hydration of cement by encapsulating some of the calcium silicate phases in the clinker. Thomas *et al.*¹⁰⁾ found that as little as 0.15 wt.% of the Pb admixture can induce a retardation effect in solidification due to the

slow process of cement hydration. The presence of the membrane formed by lead species significantly physically weakens the cement-solidified forms. There is clear evidence for the retarding effect of lead in that the intensities of the XRD peaks of the main clinker components C₃S, C₂S, C₃A, and C₄AF are not much reduced, and then portlandite is not much produced compared to hydrated materials of only cement clinker (cement-K) as shown in Figure 1



1	C ₃ S/C ₂ S	P1	Pb ₂ (NO ₃)(OH) ₃
2	C ₃ A	P2	Pb ₄ SO ₄ (CO ₃) ₂ (OH) ₂
3	C ₃ A	P3	3PbCO ₃ ·2Pb(OH) ₂ ·H ₂ O
4	C ₄ AF	P4	Pb wastes
5	C ₂ S	P5	lead carbonate hydroxide
P	Ca(OH) ₂	SC	C ₃ S+calcite(+C-S-H)
C1	3CaO· Al ₂ O ₃ · Ca(OH) ₂ · 18H ₂ O	CS	calcium carbo-silicate hydrate
T _c	3C ₃ A· 3CaCO ₃ · 32H ₂ O	S4	calcium lead silicate sulfate hydroxide
M _c	C ₃ A· CaCO ₃ · 11H ₂ O	H _c	Ca ₄ Al ₂ O ₆ (CO ₃) _{0.5} · (OH)· 11.5H ₂ O
C	CaCO ₃		

Figure 2. Leaching mechanism of solidified waste forms of KP10 in accordance to extraction number. (a) cement clinker (b) KP10 before leach at curing time of 28 days (c) KP10 after the 1st leach (d) KP10 after the 2nd leach (e) KP10 after the 3rd leach (f) KP10 after the 5th leach.

and there still remains in the intermediate lead precipitates (P2,P3).

Calcite addition in the S/S of Pb wastes (KC5P10) enhances the dissolution of lead precipitates of P2 and P3 as well as of C_3S/C_2S during the hydration of cement, due to an accelerating effect of calcite on the hydration of cement as shown in Figure 1. The presence of calcite results in the rapid crystallization of calcium hydroxide ($Ca(OH)_2$) coincident with the onset of C-S-H gel germination, which are main products of cement hydration, approximately 20% and 60% respectively.^{11,12} In calcite addition, it is observed to develop very insoluble products of silicate-rich crystal denoted as calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) (S4), which formed by chemical incorporation of re-dissolved Pb species into the silicate structure of the cement. The crystalline Forms of C-Pb-S-H like a "forest of coral" were investigated through the microscopy studies by SEM/ EDS in the earlier study.¹³

XRD Investigation on Leaching of 10% Pb-doped SWF

Results of X-ray diffraction analysis of the lead contaminated material (KP10) in accordance with extraction number by toxicity characterization leaching procedure (TCLP) are shown in Figure 2. A significant feature after leach is the marked decrease of calcium hydroxide (portlandite), which locates in (capillary) pores. The dissolution of portlandite induces the expansion of pores much more, particularly of capillary pore in cavities. The capillary pores of sizes from 10 nm to 10 μ m exist as the remainder of water-filled areas among the hydrated cement grains.¹⁴ Acid is likely to attack the SWF through these pores more than the gel pores which typically exhibit sizes below 10nm. Portlandite is an important contributor to the provision of acid neutralization capacity (ANC) of hydrated cement¹⁵ on leach.

The lead precipitates responsible for the P1~P3 peaks also underwent approximately a half removal on leaching mirroring the disso-

lution of portlandite as shown in Figure 2. Even though solids such as lead sulfate carbonate hydroxide (P2) and lead carbonate hydroxide hydrate (P3) have very low solubility, the release of lead in the initial stage of leaching might be consistent with the dissolution of these precipitates. This is attributable to the location of these solids within the capillary pores which acid can easily permeate.

A large quantity of calcium aluminate (C_3A) was removed on leaching as shown by the basis of $47.2^\circ 2\theta$ peak in Figure 2. At the same time calcium monocarboaluminate hydrate (M_c) and calcium hemicarboaluminate hydrate (H_c) were newly formed by the reactions between acid-degraded C_3A and carbonate taken up from air at the surface of cement clinker. Remineralization of calcium aluminum oxide hydroxide hydrate (C1) and calcium carbosilicate hydrate (CS) identified by Katali *et al.*¹⁶ were also investigated as shown in Figure 2.

Calcium within C_3S , C_2S and C-S-H phases was readily attacked by the acid leachant and this reaction led to polymerization of the silicate in the cement matrix.¹⁷ Cocke *et al.*¹⁸ have shown by XPS that acid attack is likely to link small units of polymerized silica at one or two corners of O-Si-O tetrahedral. The leached surfaces are negatively charged and very similar to silica gel which has its isoelectric point at pH 1.0 ~ 2.5. Cationic metals are thus liable to be adsorbed to the silica-rich surface of leached SWF since the bulk solution pH after leaching is around 5.0 to 6.0 during the first stage of leach but rises to about 12.0 after 2~6 hrs due to ANC produced mainly by portlandite during the leach.¹⁹

The remineralization of calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) of KP10 on leach is shown in Figure 3b. The amount of lead released from lead precipitates such as P1~P3 is determined by the rate of acid penetration into the pores at the leaching boundary. The dissolved lead ions can diffuse into the leachant solution, or migrate to the core of the SWF through the leached layer. The

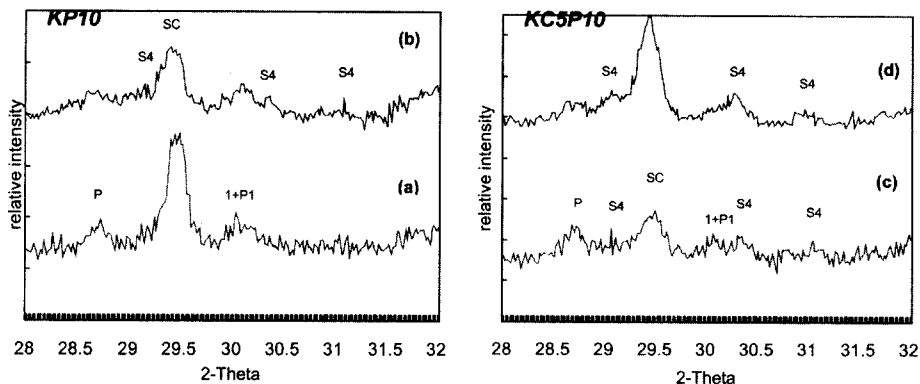


Figure 3. Comparison of XRD patterns of KP10 (a) before leaching and (b) after leaching and KC5P10 (c) before leaching and (d) after leaching in 28–32° θ .

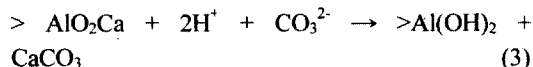
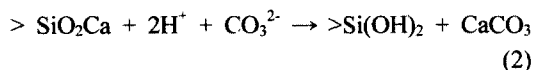
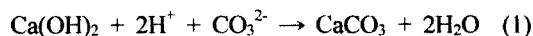
dissolved lead species may be incorporated as a minor component by adsorption/coprecipitation in the leached layer which becomes a silica-rich material due to the leaching of calcium. Cheng²⁰ has argued that adsorption of lead on amorphous polymerized silica as well as diffusion of lead into the bulk solution occurs simultaneously in the leached layer, significantly retarding the movement of lead on the solid surface of the leached material. The adsorption edge (the pH above which extensive adsorption to surfaces will occur) for Pb^{2+} is in the pH range of 5.0 to 6.0, while for Ca^{2+} it is in the pH range 9.0 to 12.0.¹⁹⁾

As a result, lead ions would be expected to diffuse initially into bulk solution at the attack of acid but, as the solution pH rises, undergo adsorption and/or surface chemisorption to the silica-rich surface of the leached SWF with the subsequent formation of mainly amorphous gel of C-Pb-S-H. The extent of formation of C-Pb-S-H will be determined both by the extent of degradation of C_3S and C_2S phases and the dissolution of lead precipitates. In KP10 before leaching, C-Pb-S-H crystal phases weren't particularly evident given the low extent of polymerization of cement components as a result of the retarding effect of Pb species as shown in Figure 3a. In leached KP10 however the C-Pb-S-H peak S4 [JCPDS file No. 18-292] with peaks 2θ values of 29.1, 30.3 and 31.1°

are very evident and are formed as a result of the marked reduction of approximately a half of calcium silicates and a half of lead precipitates in Figure 2c and 3b.

Calcite is an important provider of buffer capacity during acid attack as is an alkaline mineral such as portlandite. Portlandite can react directly with the CO_2 from ambient air to form calcite, and C-S-H can also be converted to calcite, water and a highly polymerized silica.²¹⁻²³⁾ Berner²⁴⁾ found that the degradation of calcite late started after the point of degradation of most of the portlandite. Calcite has been investigated to form an impermeable layer in cementitious SWFs by Van Dijk *et al.*²⁵⁾ as well as forming minerals that contribute to the acid neutralization capacity (ANC). Hinsenveld¹⁵⁾ and Bordersen and Nilsson²⁶⁾ indicated that artificially created cracks in cement specimens were healed by the precipitation of (mainly) calcite and magnesium hydroxide from the naturally present species when tap water was passed through the crack. The peaks of calcite at 39.4, 43.2, and especially 29.4 $2^\circ\theta$ were markedly increased and at 47.5 and 48.6 $2^\circ\theta$ newly appeared after leach as shown in Figure 2. The highest XRD peak of calcite is at 29.4 $2^\circ\theta$, but the peak is difficult to distinguish from that of unhydrated C_3S and C-S-H due to overlap. In KP10 after the 1st leach, calcite shown in the intensity of the 39.4, 43.2, 47.5, and 48.6 $2^\circ\theta$

may also be formed by the carbonation of portlandite, $> \text{SiO}_2\text{Ca}$ and $> \text{AlO}_2\text{Ca}$ during leaching as illustrated:



where, reactions of Equation (1), (2) and (3) will be determined by the total carbonate concentration in the leachate and the extent of Ca^{2+} ions released from $\text{Ca}(\text{OH})_2$, $> \text{SiO}_2\text{Ca}$ and $> \text{AlO}_2\text{Ca}$. Approximately a third of the calcite was removed in the 2nd leach. By the 3rd leach, portlandite was almost completely degraded, and

only a little calcite remained in the leached SWF. These results confirm the rapid degradation of KP10.

In KC5P10, the amount of portlandite markedly increased, with almost two times than that found in KP10 as shown in Figure 4. This was presumably influenced by the accelerating effect of calcite on the hydration of cement. The $\text{C}_3\text{S}/\text{C}_2\text{S}$ line at $29.4^\circ 2\theta$ was significantly decreased with the increased extent of hydration. At the same time the lead precipitates P1–P3 in the SWF almost disappeared after 28-days of curing in the hydration of cement, converting to C-Pb-S-H (S4) by the reprecipitation/incorporation of lead into C-S-H as shown in Figure 3c and 4b.

In the first leach of KC5P10, approximately above three-fourth of portlandite was degraded as shown in Figure 4. The degradation of

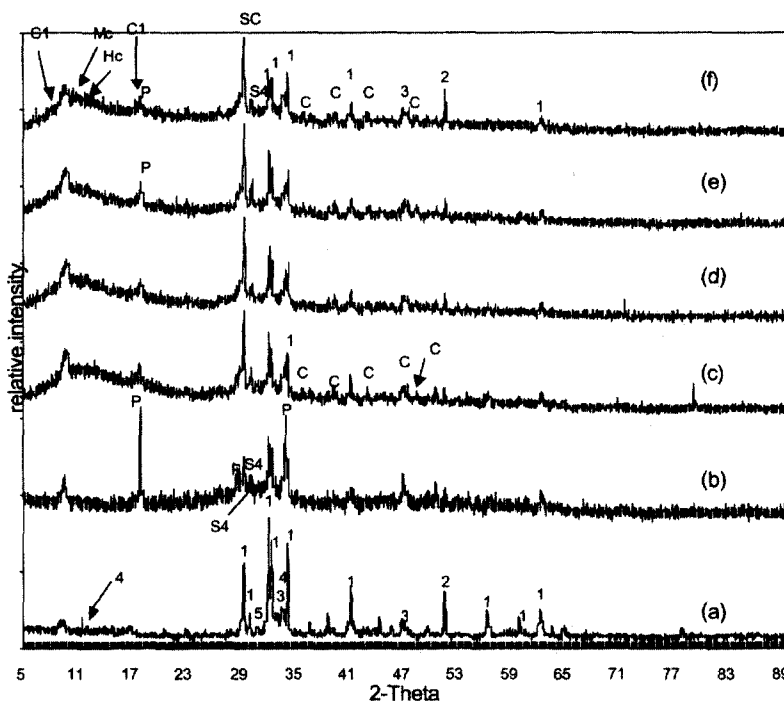


Figure 4. Leaching mechanism of solidified waste forms of KC5P10 in accordance to extraction number. (a) Cement clinker (b) KC5P10 before leach at curing time of 28 days (c) KC5P10 after the 1st leach (d) KC5P10 after the 2nd leach (e) KC5P10 after the 3rd leach (f) KC5P10 after the 5th leach.

portlandite normally determines the rate of reduction of the SWF with the enlargement of the pore structure due to the leaching of calcium. However, the release of calcium was two-thirds of that of KP10 yet the release of lead was below 1mg/L compared to that from KP10 of 219mg/L by toxicity characteristic leaching procedure (TCLP). The decrease in the release of lead in KC5P10 compared to that in KP10 may be caused by the absence of lead precipitates (P1–P5) in cavity areas in the 28-days sample and probably by the inaccessibility of lead incorporated within the C-S-H gel structure in non-cavity areas as shown in Figure 3c. In addition is the fact (or likely to be of greater significance) that the pH of the leach

solution/SWF mixture does not rise above 12 after leach. At this pH, any lead present will remain in precipitated form and not be solubilised (and therefore will not be leached). Interestingly, the peaks of calcite from the second to the fifth leach were essentially the same as those of the first leached SWF. The remineralization of Hc, Mc, and C1 also occurred with leaching. These results confirm the slow degradation of KC5P10.

In KC10P10, even portlandite, the major acid consuming mineral present, was not almost degraded to any great extent even after five extractions, and all other species as well as lead precipitates P2 and P3 were almost the same as those of the SWF before the leach (Figure 5).

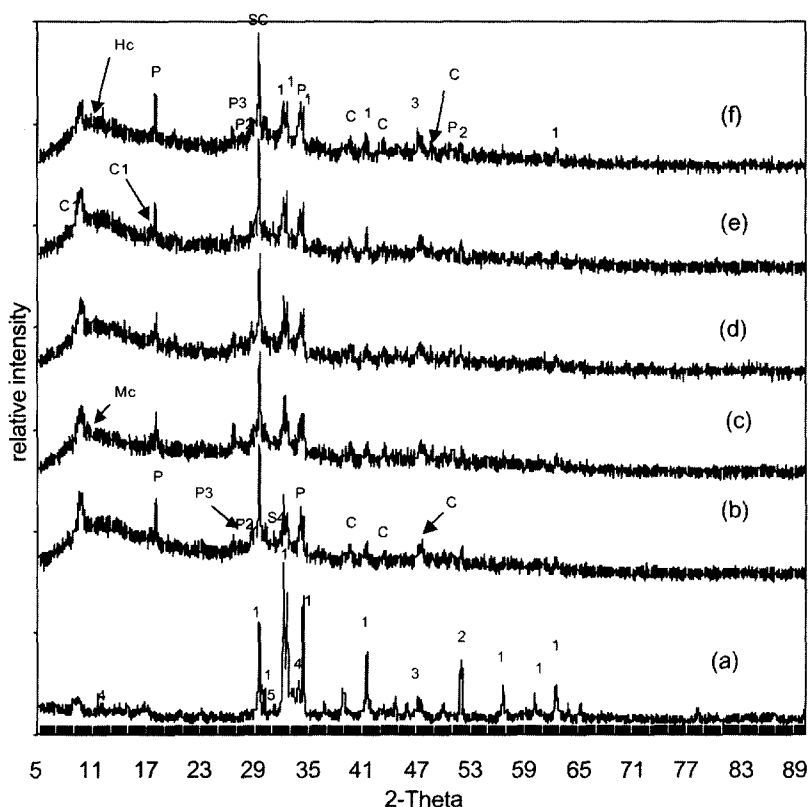


Figure 5. Leaching mechanism of solidified waste forms of KC10P10 in accordance to extraction number. (a) cement clinker (b) KC10P10 before leach at curing time of 28 days (c) KC10P10 after the 1st leach (d) KC10P10 after the 2nd leach (e) KC10P10 after the 3rd leach (f) KC10P10 after the 5th leach.

H_c, M_c, and C₁ were also remineralized as found for KP10 and KC5P10. It may be hypothesized that the addition of calcite encourages the development of cement hydration in the S/S of lead wastes, and the well-developed C-S-H with/without the lead species strongly encapsulates even portlandite as well as lead reprecipitates P1~P3. The well-hydrated C-S-H/C-Pb-S-H is liable to protect the SWF intensively against acid attack on hydrated cement, thereby reducing the leaching rate.

CONCLUSION

In this study, it is observed, in lead contaminated materials including lots of lead precipitates such as KP10, that the initial leaching rate of lead is principally compromised in the dissolution of lead salts (P1~P3) locating in capillary pores by XRD investigation in accordance with extraction time. Rapid diffusion/dissolution of hazardous substances at the attack of acid is mainly related to larger pores (capillary pores) and their openness in cavities, at the same time, with the rapid diffusion/dissolution of portlandite. Lead contaminated material including almost no lead precipitates such as KC5P10 makes slow diffusion/dissolution of lead, which mainly occurs in the structure of calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) compared to KP10.

On the other hand, although solidified waste form which 10% calcite has been added (KC10P10) includes a lot of lead precipitates in cavity areas, slower diffusion/dissolution of lead ions are observed, at the same time, with not much dissolution of even portlandite. It is reasonable that lead contaminated materials of KC10P10 are presumably very resistant to acid attack because enhanced C-S-H/C-Pb-S-H due to accelerating effect of calcite strongly encapsulates/protects even portlandite as well as lead precipitates locating in cavity areas.

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