

LEACHABILITY OF Pb-DOPED SOLIDIFIED WASTE FORMS USING PORTLAND CEMENT AND CALCITE: III. INSIGHT OF LEACHING MECHANISM

Dongjin Lee[†]

School of Civil and Environmental Engineering, The University of New South Wales,
Sydney, NSW 2052, Australia

(received November 2003, accepted August 2004)

Abstract : This study is examined 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 of lead substances (KP20) at the attack of acid is mainly related to dissolution rate of lead precipitates located in larger pores (capillary pores) and their openness in cavities. On the other hand, additional calcite on lead contaminated materials (KC5P20, KC10P20) including even a lot of lead precipitates in cavity areas such as KP20 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

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)}

The best system of cement-based S/S has the ultimate goal of fixing hazardous substances in a matrix of hydrated products. Fixation mecha-

nisms in S/S are 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. Identification of hazardous substances in the cement matrix and the location of these has not been adequately addressed with significant limitations of available characterization tools for investigation of S/S.⁵⁾

Immobilization mechanisms were illustrated in Figure 1 that possible interactions between cement particles and hazardous substances include mechanisms as below: A: adsorption, C: chemisorption, D: diadochy, Ic: incorporation, Is: intrusion, P: precipitation, R: reprecipitation, S: substitution. Immobilization mechanism of hazar-

[†]Corresponding author

E-mail: dongj7@empal.com

Tel: +61-2-9385-5562, Fax: +61-2-9385-6139

Figure 1. Illustration of possible interactions between cement particles and hazardous Substances. A: adsorption, C: chemisorption, D: diodochy, Ic: incorporation, Is: intrusion, P: precipitation, R: reprecipitation, S: substitution.

dous wastes on the cement-based solidification especially with regard to the chemistry of cement and wastes is still active and controversial area. This is in part due to the complexity of the system and the inadequacy of our analytical tools. It was found with regard to the immobilization mechanisms of heavy metals that precipitation reactions appeared to be formation of relatively more insoluble species of normally hydroxides (carbonate) salts in the pore area in the initial stage of the S/S due to the increase of pH up to 13 for the hydration of cement.

C-S-H, which has a high specific surface area with its high density of irregular hydrogen bonding, creates a strong potential for sorption. After cement-based systems generates significant quantities of C-S-H in at least a few days of hydration, the first-formed C-S-H dose has an especially high chemical reactivity with resulting sorption and physical inclusion of toxics to/into the cement grains. In areas external to the C-S-H gel and in the cavities, there are chemical reactions such as chemisorption and precipitation/reprecipitation of hydroxides, carbonates, silicates, sulfates, and other more complex species with hazardous substances, substitution,

ion exchange and adsorption with the extent of the particular reaction dependent particularly on the pH of the system.⁵⁾ Chromium may be substituted for the silicon in the C-S-H gel^{6,7)}, and nickel and cobalt have been found to substitute for calcium.⁴⁾ Cadmium as $\text{Cd}(\text{OH})_2$ can be incorporated on a microscopic scale with C-S-H and/or portlandite.⁸⁾ In the S/S of radioactive wastes iodine is partly incorporated into C-S-H and uranium is sorbed and co-precipitated onto C-S-H.⁹⁾

More crystalline phases may form which are particularly amenable to substitution reactions. For example, ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), a product formed in the early stages of Portland cement hydration, possesses a structure which is relatively tolerant to modest deviations in composition.⁴⁾ Calcium can be replaced by other divalent metal cations such as zinc, lead, cadmium and nickel and aluminum can be replaced by trivalent cations of chromium, manganese, titanium, etc. Sulfate and hydroxide can be replaced by CrO_4^{2-} , AsO_4^{2-} , ZnO_4^{2-} , $\text{B}(\text{OH})_4^-$, CO_3^{2-} , etc.^{4,10)}

Understanding of the above immobilization mechanisms and the location of hazardous substances in the hydrate structure is most important in predicting leachability of the solidified waste forms (SWF) and in developing more stable SWFs. In this work, we assess leaching mechanisms operating under various conditions based on the likely immobilization mechanisms and the location of lead in the cement matrix. Particular attention is given to the leaching effects of calcite in the S/S of lead. Physical characterization on the SWF after leach was undertaken by X-ray diffraction was used for identification of mineral transformations occurring during the leaching process.

MATERIALS AND METHODS

Cement used was purchased as normal Portland cement from Sangyong Cement in Korea. The cement has the following mineralogical composition: (i) 41.7% of tricalcium silicate

(Ca₃SiO₅: C₃S), (ii) 27.9% of dicalcium silicate (Ca₂SiO₄: C₂S), (iii) 12.7% of tricalcium aluminate (Ca₃Al₂O₆: C₃A), (iv) 9.4% of calcium aluminoferrite (Ca₄Al₂Fe₂O₁₀: C₄AF) and (v) 2.9% of calcium sulfate (CaSO₄ 2H₂O).

Calcite used was of 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 μm, maximum particle size of 8 μm and residue on a 20 μm 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 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 [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 Asavapisit and Cheeseman¹¹⁾ and Gress and El-korchi.¹²⁾

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±0.01. After thorough mixing the samples were introduced into polyethylene cylindrical moulds measuring 20mm diameter × 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*i*Pb*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 20% Pb-doped SWF with 0, 5 and 10% additional calcite, denoted KP20, KC5P20 and KC10P20, 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 (pH 4.93±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 25 mA 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.

RESULTS

Insight of Fixation Mechanism and the Location of Lead in Unleached SWF

Understanding of the location of hazardous substances in the hydrate structure is most important in predicting leachability of the solidified waste forms (SWF) as well as in illuminating fixation mechanism of lead. Lead, initially present as Pb₂(NO₃)(OH)₃ (S) and Pb₆O₃(NO₃)₂(OH)₄ (S) as shown in Figure 2, will dissolve on mixing with cement and water. The solubilised lead ions will undergo a variety of rapid reactions including initial adsorption to the surface of the clinker materials and, as these clinker materials dissolve causing an increase in alkalinity and resultant pH increase, will begin

into the C-S-H gel that forms from dissolving clinker components.¹³⁾ The resultant gel, which we will denote as C-Pb-S-H (a non-stoichiometric representation of a gel containing incorporated or substituted gel, is apparently exceedingly more impermeable than lead precipitates.

On the other hand, the accelerating effect of calcite enhances the polymerization of the silicate at the surface of cement components, advancing in the dissolution of the initial lead salts in the hydration of cement in the earlier study.¹⁴⁾ Hydration of the clinker components will occur at a greater rate with the faster breakage of Pb-impregnated coating periodically compared to that observed in the absence of calcite. The rapid dissolution of lead salts with the development of C-S-H, at the same time, makes faster diffusion of dissolved lead ions into C-S-H gel to be calcium lead silicate (sulfate) hydroxide (C-Pb-S-H: S4), and then partially enhancing crystal forms of the C-Pb-S-H such as "coral-reef" silicate structure.¹³⁾ Through the development of cement hydration by the addition of calcite, the well-developed crystalline C-Pb-S-H as well as C-S-H is likely to encapsulate portlandite as well as the un-dissolved lead precipitates in the silica matrix in the earlier microscopy studies.¹³⁾

XRD Investigation on the Leaching of 20% Pb-doped SWF

In the S/S of 20% Pb waste (KP20), lead precipitates (P1~P5) were markedly produced from initial lead wastes in the cavity regions at 28-days of curing time as shown in Figure 2b. Less portlandite ($\text{Ca}(\text{OH})_2$) was produced than in 10% Pb-doped SWFs due to the more retarding effect of Pb in the hydration of cement,¹⁴⁾ $\text{Ca}(\text{OH})_2$ does not exert a large effect on the strength of the cement products but contributes significantly to ANC of hydrated cement. Calcite (CaCO_3) also appeared, presumably as a result of reaction of carbon dioxide from the air with products arising from the hydration of cement.

By leaching on KP20, portlandite and calcite were extensively removed and the lead precipitates

were also substantially degraded. These results confirm the rapid diffusion/dissolution of lead on leaching. Carboaluminate hydrates ($3\text{C}_3\text{A} \cdot 3\text{CaCO}_3 \cdot 32\text{H}_2\text{O}$: Hc, $\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)_{0.5} \cdot (\text{OH}) \cdot 11.5\text{H}_2\text{O}$: Tc and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{OH})_2 \cdot 18\text{H}_2\text{O}$: C1) were freshly produced with the release of aluminum from the cement grains of C_3A and C_4AF , and calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) crystals (S4) were produced increasingly as lead ions released from lead salts were adsorbed to silicate matrix.

Interestingly, on calcite-additional SWFs as KC5P20 and KC10P20, portlandite and calcite were not decreased substantially by acid attack, even up to the fifth leach as shown in Figure 3 and 4. Even lead precipitates P2 and P3 as well as most portlandite were similar to those of SWF before the leach. Only P5 in KC5P20 and P4/P5 in KC10P20 after the fifth leach were reduced to approximately three-fourth of that originally present. These observations result in the slow diffusion/dissolution of lead on leach. The remineralization of carboaluminate hydrates (Hc,C1) was made with the dissolution of C_3A and C_4AF . As a result of increased adsorption of Pb species to the larger numbers of well-developed silicate surfaces, C-Pb-S-H crystals (S4), produced around the surface of SWFs, were increasingly produced as shown in the earlier microscopy study.¹³⁾

DISCUSSION

In general, the leachability of SWFs is governed by a number of factors including: (i) the location of hazardous substances in the SWF, (ii) the production of crystalline minerals adsorbed/chemisorbed/incorporated on/into the surface of SWF during the hydration of cement, and (iii) the remineralization with the leached constituents on/into the surface of the leached SWF. The SWF has the structure of a porous solid at least partially saturated with water.²⁾ Rapid diffusion/dissolution of hazardous substances on the attack of acid is mainly related to the presence of larger pores (capillary pores)

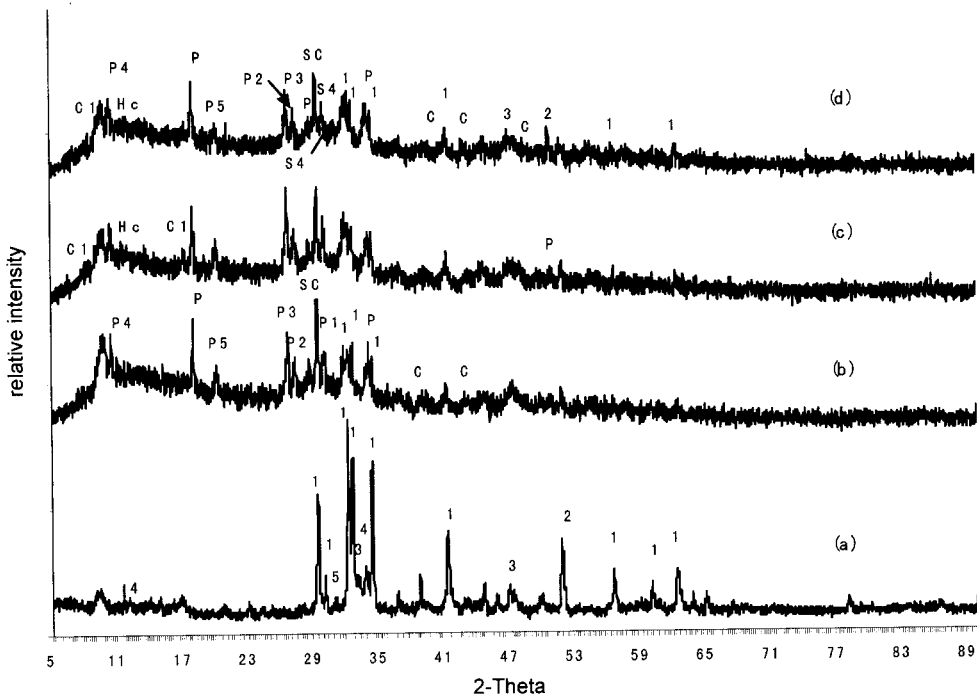


Figure 3. Leaching mechanism of solidified waste forms of KC5P20 in accordance to extraction number. (a) cement clinker (b) KC5P20 before leach at curing time of 28 days (c) KC5P20 after the 1st leach (d) KC5P20 after the 5th leach.

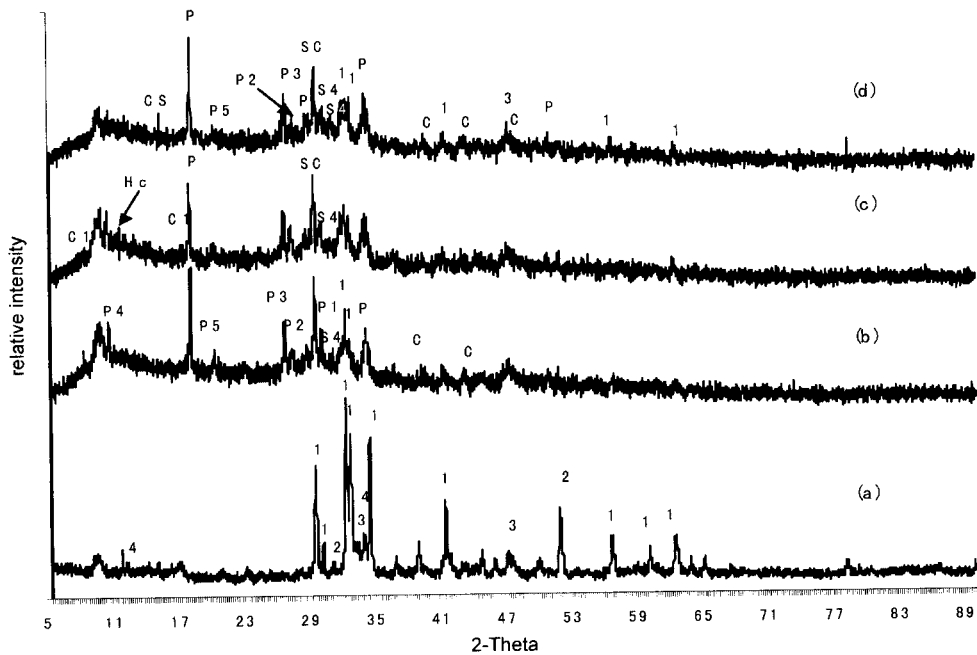
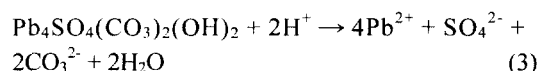
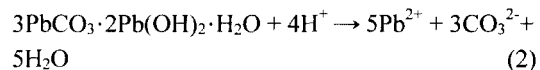
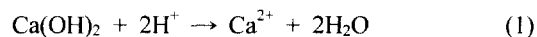


Figure 4. Leaching mechanism of solidified waste forms of KC10P20 in accordance to extraction number. (a) cement clinker (b) KC10P20 before leach at curing time of 28 days (c) KC10P20 after the 1st leach (d) KC10P20 after the 5th leach.

and their openness within cavities.¹⁵⁾ On the other hand, micropores (gel pores) occur within the C-S-H gel which is essentially a coherent assemblage of colloidal particles through which diffusion is expected to be slow.

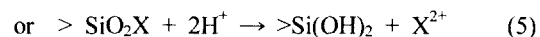
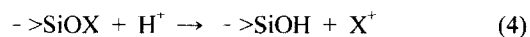
In the Pb-doped SWFs, the degree of lead leaching also depends on the number and size of larger pores, which lead precipitates will be mainly located in. The initial leaching rate of lead will be dominated by the dissolution of these lead precipitates, and the release of calcium will be dominated by the dissolution of portlandite. Shrinking core modeling by Hinzenfeld¹⁶⁾ suggests that $\text{Ca}(\text{OH})_2$ dissolves more rapidly than the C-S-H gel with the dissolution of $\text{Ca}(\text{OH})_2$ largely determining the rate of reduction in mass of the SWF. The following equations for the dissolution of lead precipitates and portlandite in cavities are proposed:



The rate of reactions Equation (1)-(3) will be governed initially by the solubility of these products in the acidic leach media. If the pH of the system is maintained in the acidic region (pH<5-6) by continual supply of acidic leachant, then dissolution will continue as long as readily accessible lead precipitates are available. Alkalinity will be released however as the SWF dissolves and, if the supply of leachant is insufficient to neutralize this alkalinity, the pH of the system undergoing leaching will rise. Precipitates of lead carbonate (sulfate) hydroxide or mixed forms of these solids however are highly insoluble in the pH 6-12 region and little solubilisation of lead will occur. Only if the pH rises above 12 will high concentrations of lead again be released because lead is amphoteric substance on pH.

On the S/S of lead (in the sample of KP20), the above mechanisms on the dissolution of lead precipitates located in the capillary pores (see Figure 1) significantly affect the higher leaching of lead with the higher dissolution of $\text{Ca}(\text{OH})_2$. While the leachant acid decomposes the SWF by the dissolution of $\text{Ca}(\text{OH})_2$ and other alkaline materials, the pore structure of the leached SWF becomes enlarged with the release of calcium. The porosity of cementitious SWFs have been found to increase from 0.3~0.5 before leach to 0.8 after leach.²⁾ Thus, the more calcium that is leached from portlandite, the greater the expected release of other metals (such as lead) given the greater accessibility of the leachant to the solid matrix. The microscopy studies of Pb-contaminated SWF (KP20) in the earlier work¹³⁾ gave clear evidence on the higher leaching of lead in the accordance with the increase of porosity with the higher dissolution (or breakdown) of lead precipitates as well as hydrated products ($\text{Ca}(\text{OH})_2$ and C-S-H).

The slower leaching of lead will be determined primarily through the displacement/dissolution of lead ions forming coordinate covalent bonds with silicate oxygens. Ortego *et al.*¹⁷⁾ have proposed the following generalized mechanism of polymerization with the release of toxic metals ions:

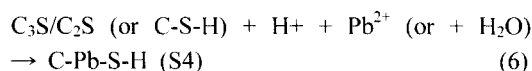


where X = calcium, potassium, sodium or toxic metal ions, $\text{Si}(\text{OH})_x \rightarrow$ branched and cross-linked silicates condensed.

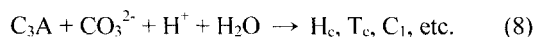
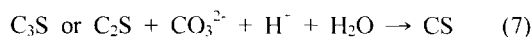
The attack of acid decomposes the SWF by the dissolution of portlandite and other alkaline materials, leaving the silica-rich minerals. The adsorption of lead ions on the silica-rich surface is expected to be significant since the isoelectric point of SiO_2 gel is at pH 1.0~2.5 so the surface sites will be negatively charged at the pH of the leach solution (pH 5.0~6.0) observed.¹⁶⁾

The lead ions derived from dissolution of lead

precipitates and / or desorbed from silica surfaces can diffuse toward the kernel of the SWF as well as toward the acetic acid solution since free lead ions as with other free cations are expected to be quite low within the kernel. Since the adsorption edge of lead (pH 5~6) is lower than that of calcium (pH 9~12) on the surface of SiO₂ gel, the extent of adsorption of lead is expected to be very much higher than that of calcium. The migration of lead ions on the silica-rich surface and toward the kernel of the SWF has been seen to result in formation of a variety of Pb-rich gelatinous products:



It is also recognized that carbon dioxide from the air will diffuse into the system, especially at high pH where the aqueous concentration of carbonate in equilibrium with the atmosphere is high. Carbonation of C₃S and C₃A can result in formation of carbo-silicate hydrates and carboaluminate hydrates, respectively as follows:



The remineralization is shown in Equation (6) to (8) are likely to reduce the leaching rate of lead through the reduction in porosity of the SWF and as a result of increased adsorption of Pb ions to the larger numbers of surfaces sides.

On the calcite additions, significantly slower leaching of the lead is expected to occur from the SWF (KC5P20, KC10P20) because of the accelerating effects of calcite on the hydration of cement. The significantly higher proportion of Pb bound in impermeable C-Pb-S-H phases induced the slow leaching of Pb. In addition, higher development of well-hydrated C-S-H strongly encapsulated even portlandite as well as lead precipitates in capillary pores against the attack of acid.

CONCLUSION

In this study, it is observed, in lead contaminated materials including lots of lead precipitates such as KP20, that the initial leaching rate of lead is principally compromised in the dissolution of lead salts locating in cavity areas by XRD investigation. Rapid diffusion/dissolution of lead at the attack of acid is mainly related to the location (capillary pores) of lead salts and their openness in pores, at the same time, with the rapid diffusion/dissolution of portlandite. At the attack of acid, carboaluminate hydrates (H_c, T_c, C₁) were freshly produced with dissolution of C₃A and C₄AF, and calcium lead silicate (sulfate) hydroxide (C-Pb-S-H) crystals (S4) were produced increasingly as lead ions released from lead salts were adsorbed to silicate matrix.

On the other hand, although lead contaminated materials that calcite has been added such as KC5P20 and KC10P20 include 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 KC5P20 and KC10P20 are presumably very resistant to acid attack because enhanced C-S-H due to accelerating effect of calcite strongly encapsulates/protects even portlandite as well as lead precipitates locating in cavity areas. This investigation results in the slow diffusion/dissolution of lead on leach in calcite-additional SWFs. The remineralization of C-Pb-S-H (S4), H_c, C₁ and CS on the surface of SWFs during leaching is likely to reduce the leaching rate of lead through the reduction in porosity of the SWF and as a result of increased adsorption of pb ions to the silicate surfaces. Significantly slower leaching of the lead is expected to occur from the calcite-doped samples because of the significantly higher proportion of Pb bound in impermeable C-Pb-S-H phases as well as higher development of well-hydrated C-S-H strongly encapsulating even portlandite as well as lead precipitates against the attack of acid.

REFERENCE

1. LaGrega, M. D., Buckingham, P. L., and Eavns, J. C., *Hazardous Waste Management*, McGraw-Hill, Inc., New York, pp. 641-704 (1994).
2. Conner, J. R., *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York (1990).
3. Landreth, R. E., *Guide to the disposal of chemically stabilized and solidified waste*, EPA SW-872, U. S. Environmental Protection Agency, Cincinnati, Ohio (1986).
4. Gougar, M. L. D., Scheetz, B. E., and Roy, D. M., "Ettringite and C-S-H Portland cement phases for waste ion immobilization: a review," *Waste Management*, **14**(4), 295-303 (1996).
5. Cocke, D. L., "The binding chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilization systems," *J. Hazard. Mater.*, **24**, 231- 253 (1990).
6. Yousuf, M., Mollah, A., Parga, J. R., and Cocke, D. L., "An infrared spectroscopic examination of cement-based solidification/stabilization systems- Portland cement types V and IP with zinc," *J. Environ. Sci. Health*, **A27**(6), 1503-1519 (1992).
7. Kindness, A., Macias, A., and Glasser, F. P., "Immobilization of chromium in cement matrices," *Waste Management*, **14**(1), 3-11 (1994).
8. Cartledge, F. K., Butler, L. G., Chalasani, D., Eaton, H. C., Frey, F. P., Herrera, E., Tittlebaum, M. E., and Yang, S., "Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using Portland cement fixing agent," *Environ. Sci. Technol.*, **24**(6), 867-873 (1990).
9. Atkins, M. and Glasser, F. P., "Application of Portland cement-based materials to radioactive waste immobilization," *Waste Management*, **12**, 105-131 (1992).
10. Vempati, R. K., Mollah, M. Y. A., Chinthala, A. K., and Cocke, D. L., "Solidification/stabilization of toxic metal wastes using coke and coal combustion by-products," *Waste Management*, **15**(5/6), 433-440 (1995).
11. Cheeseman, C. R., Asavapisit, S., and Fowler, G., "Solution chemistry during cement hydration in the presence of metal hydroxide wastes," *Cem. Concr. Res.*, **27**(8), 1249-1260 (1997).
12. Gress, D. L. and El-Korchi, T., "Microstructural Characterization of Cement-solidified Heavy metal Wastes," *Chemistry and Microstructure of Solidified Waste Forms*, Spence, R. D. (Eds.), Lewis Publishers, Tennessee, pp. 169-185 (1993).
13. Lee, D., "Leachability of Pb-doped solidified waste forms using Portland cement and calcite: II. Investigation of SEM/EDS," *Environ. Eng. Res.*, **9**(2), 66-74 (2004).
14. Lee, D., "Leachability of Pb-doped solidified waste forms using Portland cement and calcite: I. Investigation of X-ray diffraction," *Environ. Eng. Res.*, **9**(3), 49-58 (2004).
15. Glasser, F. P., "Chemistry and Microstructure of Solidified Waste Forms," *Chemistry and Microstructure of Solidified Waste Forms*, Spence, R. D. (Eds.), Lewis Publishers, Tennessee, pp. 1-40 (1993).
16. Hinsenveld, M., *A Shrinking Core Model as a Fundamental Representation of Leaching Mechanisms in Cement Stabilized*, Ph.D Thesis, University of Cincinnati, Ohio (1992). Ortego, J. D. and Barroeta, Y., "Leaching effects on silicate polymerization- An FTIR and ²⁹Si NMR study of lead and zinc in Portland cement," *Environ. Sci. Technol.*, **25**, 1171-1174 (1991).
17. Ortego, J. D. and Barroeta, Y., "Leaching effects on silicate polymerization- An FTIR and ²⁹Si NMR study of lead and zinc in Portland cement," *Environ. Sci. Technol.*, **25**, 1171-1174 (1991).