

FIXATION OF LEAD CONTAMINANTS IN Pb-DOPED SOLIDIFIED WASTE FORMS

Dongjin Lee[†], David Chung, Jongyeon Hwang, Hyunjin Choi

National Institute of Environmental Research, Environmental Research Complex,
Kyungseo-dong, Seo-gu, Incheon, 404-708, South Korea
(received September 2006, accepted June 2007)

Abstract : Fixation of lead contaminants in the solidification/stabilization using Portland cement has been investigated by X-ray diffraction, scanning electron microscopy and compressive strength. The presence of lead was observed to produce lead carbonate sulfate hydroxide ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$), lead carbonate hydroxide hydrate ($3\text{PbCO}_3 \cdot 2\text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$) and two other unidentified lead salts in cavity areas and was observed to significantly retard the hydration of cement. By 28 days, however, the XRD peaks of most of the lead precipitates have essentially disappeared with only residual traces of lead carbonate sulfate hydroxide and lead carbonate hydroxide hydrate evident. After 28 days of curing, hydration appears well advanced with a strong portlandite peak present though C-S-H gel peaks are not particularly evident. Lead species produced with the dissolution of lead precipitates are fixed into the cement matrix to be calcium lead silicate hydrate (C-Pb-S-H) during cement-based solidification.

Key Words : Cement, Solidification/Stabilization(S/S), Lead, X-Ray Diffraction, SEM

INTRODUCTION

Heavy metals and hazardous organic substances can cause significant damages to the environment and human health as a result of the mobilities or solubilities of these substances.¹⁾ Hazardous and radioactive wastes, contaminated sites and mine tailings typically require a treatment to prevent the release of toxic substances into the environment but the increase in quantity of these wastes is of concern.

Solidification/stabilization (S/S) has been considered to be a suitable process for managing such wastes because it is a relatively cheap and effective technology. The U.S. Environmental Protection Agency (U.S.-EPA) recognizes cement-based solidification as the 'best demonstrated

available technology' (BDAT) for land disposal of most toxic elements.^{2,3)}

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.⁴⁾ The reduction of hazardous effect of S/S for hazardous substances is achieved by making the toxic contaminants physically immobile and/or chemically bound to the binders.⁵⁾ The degree of hazard of the solidified waste forms (SWF) is usually evaluated by leaching tests.

The presence of lead in wastes has been found to lower the rate of strength development in solid waste forms when cement is used for S/S purposes. The major objective of the present study is to find the mechanism of the effect of Pb contaminants in the presence of Portland cement. The 'fate' of Pb contaminants is investigated by SEM and X-ray diffraction for the identification

[†] Corresponding author
E-mail: dongj7@me.go.kr
Tel: +82-32-560-7289; Fax: +82-32-568-2041

of mineral transformations occurring during the setting process.

EXPERIMENTS

Materials

Cement used was purchased as ordinary Portland cement (OPC) from Ssangyong Cement in Korea. The cement has the following mineralogical composition: (i) 41.7% of tricalcium silicate (Ca_3SiO_5 : C₃S), (ii) 27.9% of dicalcium silicate (Ca_2SiO_4 : C₂S), (iii) 12.7% of tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$: C₃A), (iv) 9.4% of calcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$: C₄AF) and (v) 2.9% of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The wastes were prepared from lead nitrate which precipitated to form hydroxide sludge on adjusting the pH to 8.5 by adding 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 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 and Pb wastes) ratio (W/S) of 0.3. After complete mixing the samples were introduced into polyethylene cylindrical moulds measuring 20 mm diameter \times 40 mm height and removed after 24 hours. The curing was carried out in humid air at 20°C for 2, 7, 14, and 28 days for each sample respectively. Samples were prepared in triplicate and are denoted KPi, where *i* is the Pb-doped waste content.

Methods

Unconfined compressive strength (UCS) was tested on the samples using an Instron testing machine. The top and bottom of the samples were capped with masonite to limit the effect of cracking. Load was increased until cracks began to appear. The compressive strength was calculated as the applied load divided by the cross-

sectional area.

X-ray Diffraction (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. Difftect 5.0 software and JCPDS diffraction files by JCPDS International Center for Diffraction Data were used for identifying mineral forms of SWF.

Scanning electron microscope (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 SEM analysis. Chemical elements of Ca, Si, Pb, Al, K, Mg and S were identified by EDS investigation.

EXPERIMENTAL RESULTS

Effect of Lead on the UCS and Leaching Test of SWF

The results of UCS measurements on solidified waste forms (SWF) in the absence and presence of lead over 2 months of curing time are shown in Figure 1. Normal OPC develops a strength of around 7000 N/cm² for 14 days' curing and only 9500 N/cm² after 28 days. The effect of Pb in inducing poor strength development in cement-K is obviously shown with the retardation effect. The strengths in all samples containing Pb are essentially zero up to 14 days, but increase to 20% (40% in Pb5-K) of that for pure cement paste (K0) at 28 days. Pb10-K and Pb20-K achieve a UCS of 40% of regular OPC after 60 days and appear to continue to gain some strength thereafter.

In the earlier studies,⁸⁾ 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 from SWF are

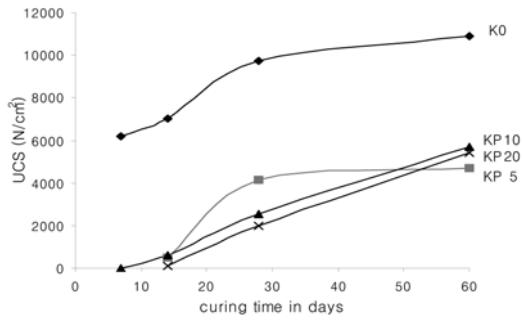


Figure 1. Effect of lead on unconfined compressive strength in the cementitious solidification up to 2 months of curing.

equivalent to approximately 4%, 10% and 13%

respectively. In KP10, the maximum concentration of lead extracted by the pH static leaching procedure is about 27% of total amount of SWF.⁹⁾

X-ray Diffraction Analysis of Pb-doped SWF

In the absence of any significant proportions of added lead, it is clear from Figure 2 that OPC rapidly hydrates with clear evidence of the diminution of OPC constituents (C_3S , C_2S , C_3A and C_4AF) and of the high formation of portlandite ($Ca(OH)_2$) and probably C-S-H gel after only two days of curing. Unidentified hydrated products are observed at 2θ values of 44.6, 65.0 and 78.1° after 7 to 14 days of curing.

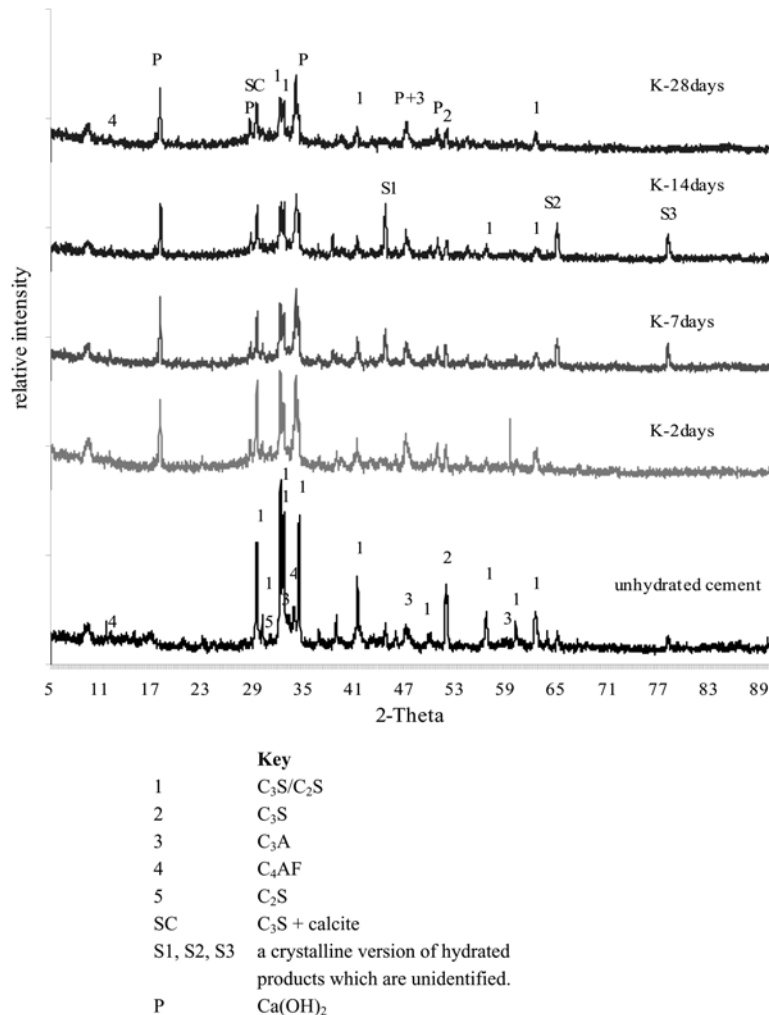


Figure 2. X-ray diffraction patterns of K0 samples at 2, 7, 14 and 28 days of curing.

The presence of lead appears to induce considerable retardation in the curing process with C_3S , C_2S , C_3A , and C_4AF little changed, even after 14 days, from that present in the unhydrated cement (Figure 3). There is very little evidence of the presence of hydration products other than a little portlandite at 14 days curing time. The XRD signature of the precipitated lead salt present in the initial synthetic waste (P1 : $Pb_2(NO_3)(OH)_3$) is evident in the cemented solid as are a number of secondary precipitates presumably as a

result of interaction of solubilised lead with sulfate derived from the OPC and carbonate anions from the atmosphere. In particular, there is evidence for the presence of lead carbonate sulfate hydroxide [P2 : $Pb_4SO_4(CO_3)_2(OH)_2$, JCPDS file No. 38-354], lead carbonate hydroxide hydrate [P3 : $3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$, JCPDS file No. 9-356] and two other unidentified lead salts (P4 and P5) (Figure 3). From the diffraction studies there is no evidence of $Pb(OH)_2$, cerussite ($PbCO_3$), hydrocerussite ($Pb(CO_3)_2(OH)_2$) or anglesite ($PbSO_4$)

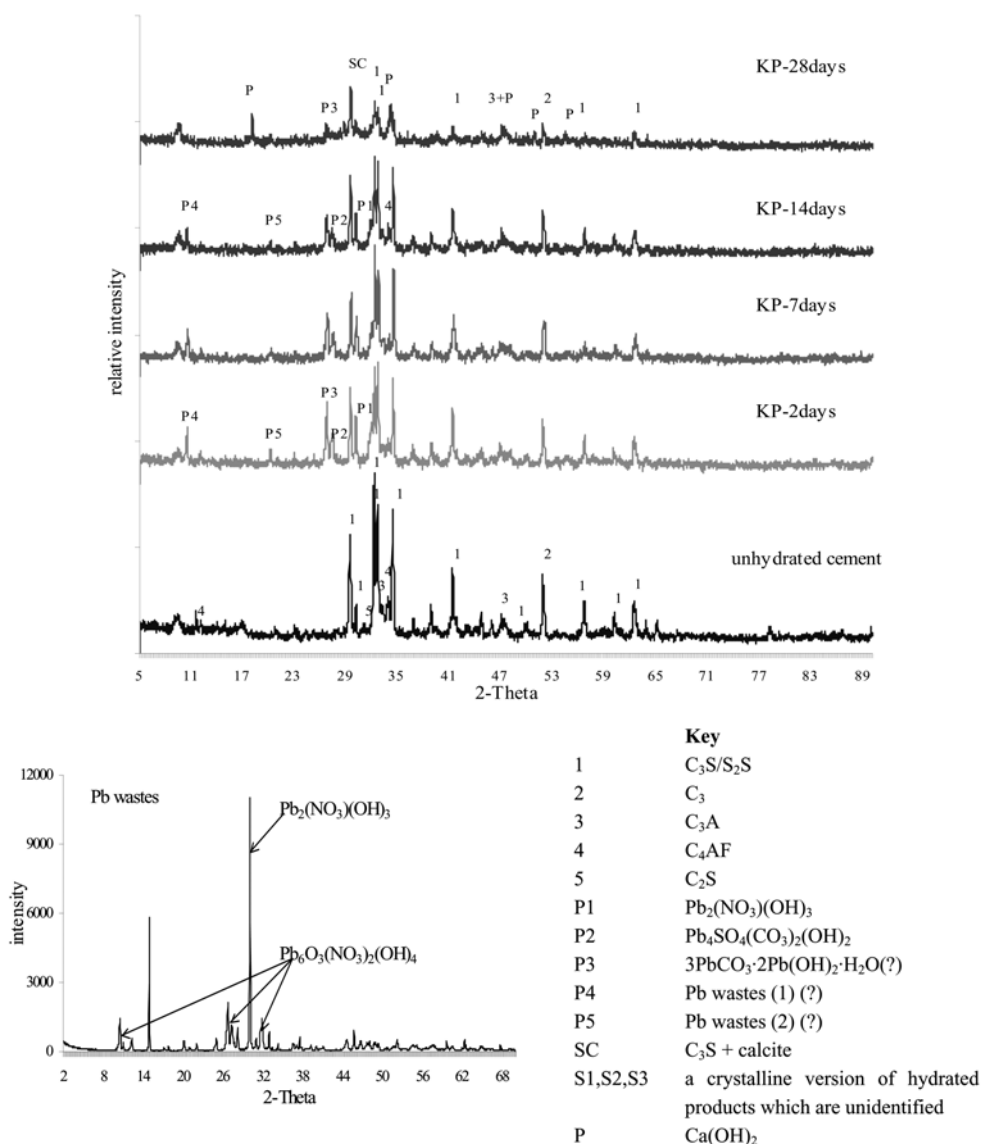


Figure 3. X-ray diffraction patterns of KP10 samples at 28 days of curing.

in substantially crystalline forms. In our early study,¹⁰⁾ the lead precipitates including sulfate were also found by electron probe microanalysis (EPMA).

The peaks of the five precipitated lead salts (P1 - P5) in KP10 maintain a reasonably high albeit diminishing intensity over the first 14 days of curing. By 28 days however, the XRD peaks of P2, P4 and P5 lead compounds have essentially disappeared with only residual traces of P1 and P3 evident. After 28 days of curing, hydration appears well advanced with C_3S , C_2S and C_3A peaks markedly decreased and a strong portlandite peak present though C-S-H gel peaks are not particularly evident.

DISCUSSION

Solidification/stabilization processes are able to produce solids that are non-hazardous or less hazardous than the original waste, and to prevent pollutants from migrating into the environment.⁴⁾ The non- or less hazardous effect of S/S for hazardous substances is achieved by making the toxic contaminants physically immobile and/or chemically bound to the binding agents present.⁵⁾ However heavy metals in the cement-based S/S process (which has generally been considered to be a suitable process for managing such wastes) may, at times, exhibit (or induce) specific interactions between the waste and the binding agent which limit the fixation process. In addition the effect of additional binding agents, which may be added in order to rectify specific limitations in the fixation of heavy metals, is an area of research in which many challenges remain not least because of the extreme complexity of the heterogeneous systems of interest.

'Fate' of Lead Wastes on the Cement-based S/S

Lead, one of the priority metallic pollutants, has been found to hinder the S/S process due to the retarding effect it induces.^{4,11-13)} Lead ions (Pb^{2+}) released from lead precipitates such as $Pb_2(NO_3)(OH)_3$ and $Pb_6O_3(NO_3)_2(OH)_4$, may form

polynuclear species such as $Pb_6O(OH)_6^{4+}$ at the high pH (of 12-13) approached in cement-water solution.¹¹⁾ The pH is especially important for the behavior of lead as it exhibits amphoteric properties and is highly soluble both at low and high pH with maximum insolubility shown in the pH range of 7.5-10.⁴⁾ In view of this, the solubility of lead in the early cement hydration period may actually be higher than that in the original Pb wastes and the possibility exists that a portion of the Pb wastes may rapidly dissolve in the initial stages of cement hydration.

The lead hydroxy-cations derived from the original Pb solids can adsorb to silicate surfaces and/or precipitate as sulfate or carbonate compounds. Results of the present study indicate that the Pb concentration in the cement solution sharply decreases to approximately 600 mg/L within 2 minutes. A likely explanation for this effect may be that the original Pb wastes rapidly convert to secondary precipitates through dissolution and re-precipitation processes in the early hydration of cement.

Lead Precipitates in the Cavity Areas

Based upon the XRD investigation of lead enriched solidified samples, precipitates of lead carbonate sulfate hydroxide ($Pb_4SO_4(CO_3)_2(OH)_2$), lead carbonate hydroxide hydrate ($3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$) and two other unidentified lead salts (P4 and P5) are found in cavity areas (Figure 3).

Large accumulations of lead precipitates rich in sulfate are found in the large cavity area ($120 \mu m \times 120 \mu m$) by electron microscopy and Energy Dispersive X-ray analysis (Figure 4(a) and (b)). These precipitates are encapsulated in the cavity by the cement-solidified materials. However, as pH in the cement pore waters undergoes fluctuations during the progress of hydration, the Pb salts undergo solubilization and reprecipitation periodically.^{12,13)} Pb salts (P1~P5) undergo a very slow dissolution over 14 days of curing but have essentially disappeared after 28 days. These Pb solids located in the cavity areas are readily accessible to leach water and would be expected to dissolve under both strongly acidic conditions as well as under strongly basic conditions.¹³⁾

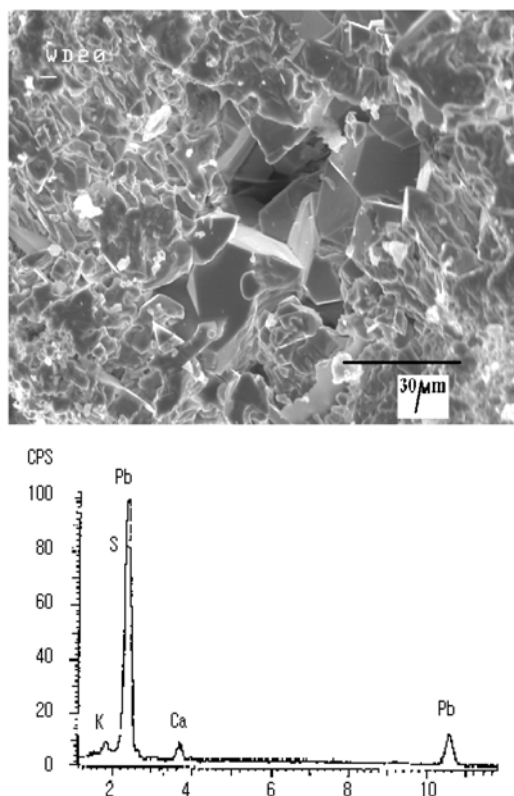


Figure 4. (a) Microscopic image and (b) elemental analysis of lead precipitates in the cavities of KP20.

Membrane Formation and Retarding Effect of Lead Species

A significant finding of this study is the preferential deposition of lead both as lead precipitates in the cavity areas and as a membrane of impervious coating of lead species around cement clinker grains in the early stages of curing. These are consistent with argument of Cote¹⁴⁾ and Parapar et al.¹⁵⁾ respectively. In the latter stage of lead deposition, the membrane of lead species around the cement clinker grains prevents the hydration by encapsulating some of the calcium silicate phases in the clinker. Thomas *et al.*¹²⁾ found that as little as 0.15 wt.% of the Pb admixture can induce a retardation effect in solidification by slowing the hydration process. The presence of the membrane formed by lead species significantly weakens the cement-solidified forms physically as shown by the UCS (Figure

1). There is clear evidence for the retarding effect of lead in that the intensities of the XRD peaks of the main clinker components C_3S , C_2S , C_3A , and C_4AF are not reduced, portlandite is not produced and there is little reduction in the intermediate lead precipitates (P1~P5) till 14 days of curing.

Cement-water solution concentrations of calcium and sulfate in samples without Pb (K0) suddenly decrease in the first few minutes as a result of formation of calcium sulfoaluminate (ettringite).¹²⁾ The rapid decrease in concentration of these ions is not apparent however in samples containing Pb (KP10) due presumably to the retardation in clinker dissolution by the Pb-rich membranes that form around clinker components.

At 28 days, most XRD peaks of lead secondary precipitates (P1-P5) almost disappear with only minor peaks of P1 and P3 evident. There is evidence for the development of hydration at 28 days with C_3S , C_2S and C_3A peaks markedly decreased though any specific peaks of C-S-H are not apparent (possibly because of its XRD amorphous nature). It is argued that the coating around clinker components (C_3S , C_2S , C_3A , ...) by lead compounds retards the dissolution/hydration of clinker cement. C_4AF is generally considered most resistant to hydration and peaks still remain at 14 days though its dissolution is essentially complete by 28 days.

Fixation Model on the Cement-based S/S of Lead Wastes

From the findings of these studies, the following model for the fixation mechanism of lead in the cement-based S/S appears reasonable. The original Pb wastes dissolve very rapidly in the highly alkaline environment of cement and produces extremely insoluble precipitates such as lead carbonate hydroxide and lead sulfate carbonate hydroxide (P1~P5). Lead species also coat the clinker components, preventing their hydration for long periods. At the same time, as hydration is not completely prevented by the coating of Pb species, diffusion processes through the coating are still active at a reduced rate.^{5,11)} As a result,

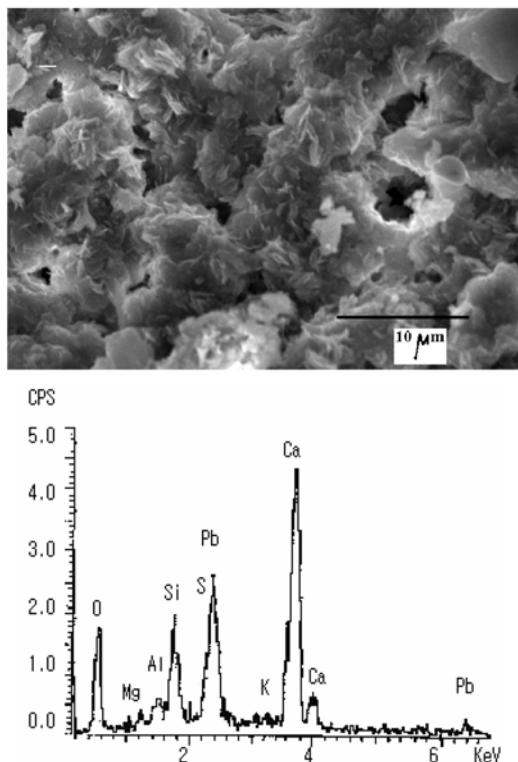


Figure 5. (a) Microscopic image and (b) elemental analysis of KP10 at 28 days of curing.

an excess of portlandite will accumulate on the fluid side of the membrane particularly after 14 days as shown in the XRD investigation on Pb enriched solidified material. Precipitation of portlandite will induce a marked differential in ionic strength on either side of the membrane with a resultant buildup in osmotic pressure. This pressure will induce rupture of the membrane with a subsequent normalization in ionic composition.^{5,16} The membrane will then reform and the process of osmotic pressure buildup begin again.

The time of periodical rupture of the membrane depends on the properties of the cement components. Precipitation processes to fix lead compounds occurs within a narrow zone between the solutions at high degrees of supersaturation.¹³ It is also likely that the silicate-rich pore water within the membrane will induce the formation of fresh Pb precipitates from Pb acquired from the transient P1-P5 species. It is expected that solids of the general form calcium lead silicate hydrate

(C-Pb-S-H) will accumulate.

The micrographs and chemical composition of the C-Pb-S-H gel both was identified by SEM/EDS as shown in Figure 5. Bhatt¹⁷) has argued that the lead is fixed into the cement matrix, forming a metallic calcium silicate hydrate during cement-based solidification. Some investigators found the metal hydroxide simply encapsulated in a silica matrix that prevents its removal except by destroying the matrix.^{4,18} Lead solidified in this way is leached at rates that are much below those that would be predicted based on the solubility of lead hydroxides. Conner⁴) has argued that lead is strongly bound in the hydrated product matrix, at least in cement-based systems. Cocke¹¹) gave evidence that binding energies of lead ions are consistence with silicate, carbonate, or hydroxide compounds by XPS.

CONCLUSIONS

This study has examined the effect of lead contaminants in the presence of Portland cement. The reduced rate of strength development arises because lead species coat the surface of cement components in the clinker and, in so doing, hinder the hydration of these entities. In cavity areas, a large quantity of lead precipitates which, based upon the results of SEM/EDS and XRD investigations, have been shown to be principally lead carbonate sulfate hydroxide ($\text{Pb}_4\text{SO}_4(\text{CO}_3)_2(\text{OH})_2$), lead carbonate hydroxide hydrate ($3\text{PbCO}_3 \cdot 2\text{Pb}(\text{OH})_2 \cdot \text{H}_2\text{O}$) and two other unidentified lead salts.

Most XRD peaks of five lead secondary precipitates at 28 days, almost disappear with only minor peaks of principally lead carbonate sulfate hydroxide and lead carbonate hydroxide hydrate evident. There is evidence for the development of hydration with C_3S , C_2S and C_3A peaks markedly decreased though any specific peaks of C-S-H are not apparent possibly because of its XRD amorphous nature. The lead contaminants are fixed into the cement matrix, forming a lead calcium silicate hydrate (C-Pb-S-H) during cement-based solidification.

REFERENCES

1. Mulligan, C. N., Yong, R. N., and Gibbs, B. F., "Remediation technologies for metal-contaminated soil and groundwater," *Engineering Geology*, **60**(1-4) 193-207 (2001).
2. 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*, **16**(4): 295-303 (1996).
3. Landreth, R. E., Guide to the disposal of chemically stabilized and solidified waste, EPA SW-872, U. S. Environmental Protection Agency, Cincinnati, OH (1986).
4. Conner, J. R., Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, New York (1990).
5. Yousuf, M., Mollah, A., Vempati, T. C. L., and Cocke, D. L., "The Interfacial chemistry of solidification/stabilization of metals in cement and pozzolanic material systems," *Waste Management*, **15**(2) 137-148 (1995).
6. Asavapisit, S., Fowler, G., and Cheeseman, C. R., "Solution chemistry during cement hydration in the presence of metal hydroxide wastes," *Cem. Concr. Res.*, **27**(8) 1249-1260 (1997).
7. 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).
8. 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).
9. Lee, D., "Performance of pH Static Leaching Test for evaluating Leachability of Solidified Waste Forms," *Environ. Eng. Res.*, **9**(5), 231-237 (2004).
10. Lee, D., "Electron Probe Microanalysis (EPMA) Investigation of Lead Location on the Solidification/Stabilization of Pb Wastes," *Environ. Eng. Res.*, **9**(6), 299-307.
11. Cocke, D. L., "The binding chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilization systems," *J. Hazardous materials*, **24**, 231-253 (1990).
12. Thomas, N. L., Jameson, D. A., and Double, D. D., "The effect of lead nitrate on the early hydration of Portland cement," *Cem. Concr. Res.*, **11**, 143-153 (1981).
13. Cartledge, F. K., Butler, L. G., Chalasani, D., Eaton, H. C., Frey, F. P., Herrera, E., Tittlebaum, M. E., and Yang, S. L., "Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using Portland cement fixing agents," *Environ. Sci. Technol.*, **24**(6) 867-873 (1990).
14. Cote, P., Contaminant Leaching from Cement-based Waste Forms under Acidic Conditions, Ph.D thesis, McMaster University, Canada (1986).
15. Parapar, J. F. V., Francoy, C. R., Rodriguez-Pinero, P., Martinez, L. S., and Pereira, C. F., "Stabilization/solidification of hazardous metallic wastes: prediction of leach test performance to optimize S/S mixtures," *Waste Management*, **16**(2) 175-182 (1998).
16. Tashiro, C., Takahashi, H., Kanaya, M., Hirakida, I., and Yoshida, R., "Hardening property of cement mortar adding heavy metal compound and solubility of heavy metal from hardened mortar," *Cem. Concr. Res.*, **7**, 283-290 (1977).
17. Bhatti, M. S. Y., "Fixation of metallic ions in Portland cement," *Superfund '87* 140-147 (1987).
18. Bishop, P. L., "Leaching of inorganic hazardous constituents from stabilized/solidified hazardous wastes," *Hazard. Wastes Hazard. Mater.*, **5**(2) 129-143 (1988).