pH EFFECTS ON LEACHABILITY OF PB-DOPED SOLIDIFIED WASTE FORMS USING PORTLAND CEMENT AND CALCITE

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Abstract : This study shows an effect of the pH on leachability of Pb-doped solidified waste forms(SWF) in the Toxicity Characteristic Leaching procedure (TCLP). Since the SWF using Portland cement has sufficient acid neutralization capacity (ANC), the pH of the leachate will be high up to 12 during the early extraction time. The leaching of lead is observed to be occurred initially only in the early and last extraction time because lead species markedly makes insoluble re-precipitates in the pH range of approximately 6~12 during the middle extraction time. In sequential (modified) TCLP, lead was released from Pb-doped SWF(KP10) in only the 1st and 2nd extraction whilst the pH was greater than 12.0. In all extractions of calcite-additional SWF(KC5P10), insignificant amounts of lead were released because the reaction pH was such that the lead solids present were in their domain of maximum insolubility.

INTRODUCTION

Solidification/stabilization (S/S) is a widely used technology for disposal of hazardous and radioactive wastes. Cement-based S/S technology has been considered highly suitable for the treatment of hazardous wastes due to its relatively low cost and demonstrated effectiveness over many years.[1,2] The best system of cement-based S/S has the ultimate goal of to be both physical and chemical immobilization.[3] Physical tests for evaluating solidified waste forms (SWF) include the measurement of compressive strength, setting time, bulk density, porosity, permeability, and durability. Chemical aspects are delineated by the implementation of different leaching tests and the chemical analysis of leachates.[4]

Many different leaching tests have been used to evaluate the likely release of contaminants from SWF under various environmental conditions.[4,5] The US EPA Toxicity Characteristic Leaching procedure (TCLP) is undoubtedly one of the most common leach tests. The TCLP test is designed to assess the leaching behavior of organic and inorganic contaminants in liquid, solid, and multiphasic wastes. For solid wastes, the test involves an extraction of crushed sample in a buffered acetic acid solution for 18 hours, at a 20:1 liquid-solid ratio and analysis of the leachate. Liquid wastes, which contain less than 0.5% dry solid material, is defined as the TCLP extract after filtration through a 0.6 to 0.8 (m glass fiber filter. For wastes containing greater than 0.5% solids, the test involves separating the

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liquid from the solid phase, and the liquid stored for later analysis.

Since cement-water solution will be high alkaline environment within a few minutes, interactions between the cement components and heavy metals must be considered carefully in aqueous chemistry of the solution. In particular, it is widely acknowledged that the stability of SWF is dependant on pH control for metal containment. The control of pH has also been shown to affect the leachability of some other inorganic and organic species. Most metal ions normally make precipitates with hydroxides in the pH range of 7.5-11 and having minimum solubility.

The purpose of this study is to investigate an effect of pH on leachability of Pb-doped SWF in the TCLP. Attention is particularly given to the effects of calcite in the S/S of lead. A sequential TCLP with successive aliquots of acetic acid has been examined for evaluating a stability of the contaminant solid and the change of pH in a long-term extraction.

EXPERIMENTS

Materials

Ordinary Portland cement was purchased from S Cement in Korea and used in all studies. The cement has the following mineralogical composition: (i) 41.7% of tricalcium silicate (Ca_3SiO_5: C_3S), (ii) 27.9% of dicalcium silicate (Ca_2SiO_4: C_2S), (iii) 12.7% of tricalcium aluminate ($Ca_3Al_2O_6$: C_3A), (iv) 9.4% of calcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$: C_4AF), and (v) 2.9% of calcium sulfate ($CaSO_4 \cdot 2H_2O$).

Calcite used was of high grade crystalline form ($\geq 95.0\%$ $CaCO_3$) with $\leq 4.0\%$ $MgCO_3$ and $\leq 1.5\%$ acid insolubles. Its specific gravity was 2.7 and its BET specific surface area was 5.2 m^2/g. It was ground such that it exhibited an average diameter (D_{50}) of 1.8μm, maximum particle size of 8μm, and residue on 20 μm screen of no more than 0.005%. The addition of up to 5% calcite to cement clinker has been recommended by the American Society for

Testing and Materials (ASTM), the Canadian Standards, and many countries in Europe.[7] Calcite addition to cement (i) acts as a partial substitute for gypsum as a set controller, (ii) results in some reduction in the energy costs for grinding clinker, and (iii) results in improvements in some characteristics of the hardened concrete.

The wastes were prepared from lead nitrate which precipitated to form hydroxide sludge on adjusting the pH to 8.5 with 6.0N sodium hydroxide and then dried at 104°C for 24 hours. The major crystalline phases present were identified by X-ray diffraction to be lead nitrate hydroxide, [$Pb_2(NO_3)(OH)_3$] and lead oxide nitrate hydroxide [$Pb_6O_3(NO_3)_2(OH)_4$]. These XRD data were consistent with the results of Asavapisit et al.[8] and Gress et al.[9]

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. The samples are denoted KCiPbj where i is the calcite content, j is the Pb-doped waste content. In this study, samples were prepared in triplicate and are denoted K0 (regular OPC), KP10 (OPC + 10% lead wastes) and KC5P10 (OPC + 10% lead wastes + 5% calcite). The samples were cured for 28 days, and then dried at 104°C for 24 hours for leaching test.

Methods

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 $\pm$ 0.05). Extraction fluid of the leachant was made with a addition of 5.7 ml glacial CH_3CH_2OOH to 500ml of Micro-pore water, after then with a addition of 64.3 ml of 1 N NaOH to a volume of 1 liter for dilution

with Mili-pore water. 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. A separate experiment was carried out to monitor the change of pH and concentrations of lead and calcium during the 18 hrs period. The pH of the leachate was measured by dipping a glass electrode into the extraction bottle. After allowing the leachate to settle for about 1 min, a small quantity (10 ml) of total 1.2 liter leachate were withdrawn at 12 intervals, and leachant of same amount with-drown was refilled into the extraction bottle. Meanwhile the extraction bottle was returned to the rotary extractor to continue the extraction. The extract was separated from the solid phase by 0.6-0.8μm glass fiber filter filtration. A Perkin-Elmer 4000 Inductively Coupled Plasma (ICP) was used to determine metal concentrations in the leachate extracted.

In sequential leaching test as a modified TCLP, particle size of samples and pH of leachant were used with the same as TCLP test. After grinding, 60 grams of each sample were collected for extraction. After the first extraction residues of all samples, on the other hand, were weighed, collected at the same weight respec-tively, 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 tem-perature for 18 hrs. This procedure was repeated up to the seventh extraction.

The chemical equilibrium modeling program MINEQL+ was used for speciation solubility calculation of lead precipitates dependant on leachate pH. Limitation in thermodynamic data and interferences from rate dependent reactions certainly restrict MINEQL+ from applying chemical equilibrium models in the cement-water system including heavy metal species.

RESULTS AND DISCUSSION

The Effect of pH in the TCLP

The change in leachate pH and the concentration of Pb release as a function of extraction time in the TCLP are shown in Figure 1. The leachate pH is observed to increase sharply on interaction of the leachant (of pH 4.93) with considerable acid neutralizing capacity (ANC), presumably as a result of dissolution of minerals, and then to plateau at values in the pH 11-12 range. The pH of KP10 leachate is observed to increase more rapidly and to reach a slightly higher final pH than that of KP0 and KC5P10. The time taken for the leachate to reach pH 11 is 2, 4 and 8 hours for KP0, KP10 and KC5P10, respectively and the pH at which the leachate plateaus is in the order KP10 > KP0 > KC5P10.
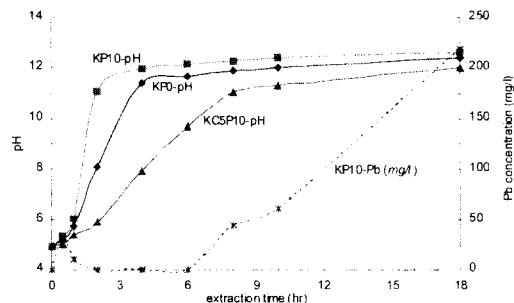

Figure 1. Leachate pH and lead concentration by the toxicity characteristic leaching pro-cedure.

The rise in pH of the leachate is due to the dissolution of the cement matrix which consists mainly of $Ca(OH)_2$ and C-S-H.[10~12] Shrinking core model by Hinsenveld[10] suggests that $Ca(OH)_2$ dissolves more rapidly than the C-S-H gel with the dissolution of $Ca(OH)_2$ largely determining the rate of reduction in mass of the SWF. It was consistent with the observation of X-ray diffraction[13,14] and scanning electron microscopy (SEM)[15] that the quantity of Ca $(OH)_2$ in KP0 markedly decreased more than that in KC5P10 on leaching. The reduction in mass markedly varys in accordance with the solid waste forms. It is observed that the a decrease in mass after 18-hours leaching is to
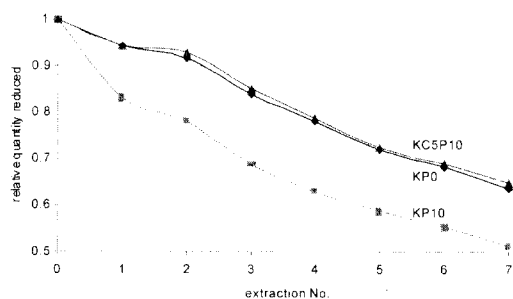
Figure 2. The inclination of reduced quantity of SWF samples by sequence toxicity characteristic leaching procedure.

Figure 3. Relationship between the leaching concentration of Pb and solubility of Pb solids.

be 16.9% for KP10 compared to 5.7% for KP0 and only 5.6% for KC5P10 as shown in the first extraction of Figure 2. Not surprisingly, the order of reduction in mass is the same as the order of leachate pH increase; that is, the SWF exhibiting the greatest decrease in mass on leaching also exhibits the greatest increase in leachate pH.

The extent of release of lead from KP10 is shown in Figure 1 and observed to occur both in the first 1-2 hours and after 6 hours of leaching. However, in KC5P10, no detectable release of lead occurred. The lead was released at pH below 6 and above 12 with no measureable release of lead in the range of pH 6 to12. Similar results have been reported previously by Parapar et al.[3]

As also shown in Figure 3, these leach results are generally consistent with the expected solubility of a range of simple lead precipitates $(PbCO_3(s)$, $Pb(OH)_2(s)$ and $Pb(CO_3)_2(OH)_2(s))$ with the low pH dissolution arising because of the acid dissolution of lead solids and the high pH dissolution arising from the stability of soluble lead carbonate complexes (particularly $Pb(CO_3)_2^{2-}$). It is noticeable however that the lead concentrations observed in the leachates are significantly lower than the lead concentrations expected to be in equilibrium with any one of these simple solid phases.

The discrepancy may be accounted for either by the slow dissolution kinetics of these phases (if present), or (more likely) by the existence of lead solids that are considerably more insoluble
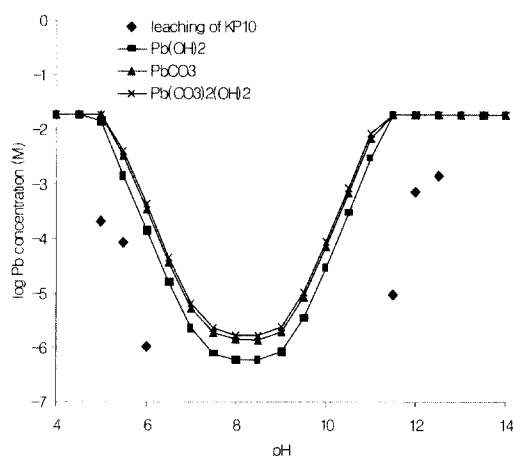
than $PbCO_3(s)$, $Pb(OH)_2(s)$ or $Pb(CO_3)_2(OH)_2(s)$. Indeed, results reported elsewhere of XRD[13,14] and SEM[15] analyses of these cement-solidified wastes reveal the presence of lead precipitates involving (sulfate), carbonate and hydroxide anions as $Pb_4SO_4(CO_3)_2(OH)_2$ and $3PbCO_3 \cdot 2Pb(OH)_2 \cdot H_2O$. Unfortunately a lack of thermodynamic data excludes analysis of the pH dependent solubility of such phases.

Interestingly, lead was not released from calcite-additional SWF(KC5P10) during the TCLP in Figure 1. This presumably occurs because of higher stability of the SWF and thus its slower rate of dissolution. For this SWF, the leachate pH did not exceed 12.0 - a pH insufficiently basic to induce any significant degree of dissolution.

The relationships between leachate pH and calcium concentration generated on applying the TCLP to KP0, KP10 and KC5P10 are shown in Figure 4. As indicated above, the calcium in the leachate is likely to be released mainly from $Ca(OH)_2$ rather than the more stable C-S-H gel.[11] He has argued that $Ca(OH)_2$ does not exert a large effect on the strength of the cement products but contributes significantly to ANC of hydrated cement. Because the leachant acid decomposes the SWF by the dissolution of $Ca(OH)_2$ 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.[12] Thus, the more calcium that is leached, the greater the expected release of other metals (such as lead) given the greater accessibility of the leachant to the solid matrix. In this case, the higher the pH (at least above some critical pH), the greater the release of Pb (because its solubility increases dramatically at high pH) is produced.

Additionally, as it was suggested in our previous works[13,14] that the amount of $Ca(OH)_2$ and "coral-like" crystals of C-S-H including a lead content in KC5P10 was higher than that in KP10 as a result of the accelerating effect of calcite on cement hydration. These enhanced hydrated materials may be more resistant to acid leaching - an effect consistent with the observed lower rate of reduction in mass on leaching of KC5P10 compared to KP10 as well as the lower concentrations of calcium in the leachate from KC5P10 compared to KP10 (Figure 4).

As shown in Figure 1, the pH of the leachate increases sharply in the early stages of the extraction such that, over the majority of the 18-hour test period, negligible leaching is occurring because the pH of the reaction mixture lies in the region of maximum stability for most lead precipitates. Lead is only leached when the pH of the reaction mixture falls into high or low pH regimes where the lead precipitates are more soluble. While it could be argued that
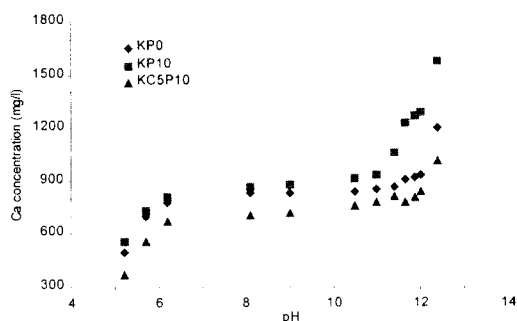

Figure 4. Relationship between leachate pH and Ca concentration by TCLP.

neutralization of a potential leachant and the resultant increased stability of a contaminant solid represents the stability of the waste to attack under possible environmental conditions, the temporal evolution of the leachate composition in TCLP does not provide insight to the more likely scenario of the solid waste form being attacked by a continually refreshed acid stream (as may occur for example in leaching of a solid waste by a flowing acid mine drainage stream).
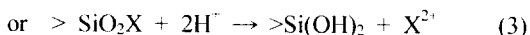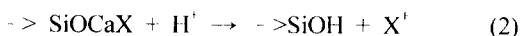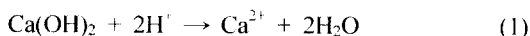
pH in the Sequential Leaching Test

The cementitious waste possesses an acid neutralizing capacity (ANC) that is high enough to continue to produce a highly alkaline reaction mixture with decompose of SWF at the attack of acid. A highly alkalinity continually produced makes limitations to measuring a potential of stability of the contaminant solid with the change of pH. One approach to overcoming some of limitations may be to use a sequential procedure in a long-term extraction in which the solid waste is leached with successive aliquots of acetic acid.

As shown in Figure 2, the mass of SWFs in KP0 and KC5P10 were reduced by approximately 28% after five extractions however, for KP10 up to 41.2%. The breakdown of Pb-doped SWF(KP10) in mass is also observed to be markedly occurred in our early study of microscopic study (SEM).[15] After the initial leaching, the micrographs of KP10 show loosely bound flaky substances with very poorly crystalline structure after then the fifth leaching, even the flaky substances as well as C-S-H gel almost disappear. Only large cement grains without any crystalline minerals remain in the cavity regions. 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. 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, these "jungle-shaped" crystals were found in the cavity and non-cavity regions through remineralization on the surface of the SWF must be occurred. 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.

The decrease of calcium is to be expected given both the decreasing mass of SWF remained after leaching and the (presumably) decreased proportion of readily leachable calcium to calcium in more refractory forms. The highly breakdown of SWF including $Ca(OH)_2$ and C-S-H on KP10 markedly enhances the release of calcium through the dissolution of $Ca(OH)_2$ and C-S-H compared to KC5P10 as shown in Figure 5. The following equations for the release of calcium are proposed as below:

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O \qquad (1)$$

$$- > SiOCaX + H^+ \rightarrow ->SiOH + X^+ \qquad (2)$$

$$or > SiO_2X + 2H^+ \rightarrow >Si(OH)_2 + X^{2+} \qquad (3)$$

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

As shown in Figure 5, lead was released from KP10 in only the 1st and 2nd extraction whilst calcium was markedly released with the highly breakdown of SWF. The pH on only the
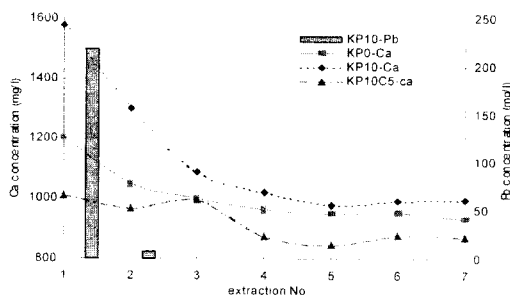
1st and 2nd extraction of KP10 is observed to be greater than 12.0. In all extractions of calcite-additional SWF(KC5P10), insignificant amounts of lead were released because the reaction pH(9 < pH < 12) was such that the lead solids present were in their domain of maximum insolubility.

CONCLUSIONS

This study shows an effect of the pH on leachability of Pb-doped solidified waste forms (SWF) in the Toxicity Characteristic Leaching Procedure (TCLP). The rise in pH of the leachate is due to the dissolution of the cement matrix which consists mainly of $Ca(OH)_2$ and C-S-H. The leachate pH is observed to increase sharply on interaction of the leachant (of pH 4.93) with considerable acid neutralizing capacity (ANC), and then to plateau at values in the pH 11-12 range. The pH of leachate on Pb-doped solidified waste forms(KP10) is observed to increase more rapidly and to reach a slightly higher final pH ($\geq$12.0) than that of a hydrated cement(KP0) and a calcite-additional Pb-doped SWF(KC5P10). The leaching of lead is observed to be occurred initially only in the early and last extraction time because lead species markedly makes insoluble re-precipitates in the pH range of approximately 6~12 during the middle extraction time in KP10. However, in KC5P10, no detectable release of lead occurred. The lead was released at pH only below 6 and above 12 with no measurable release of lead in the range of pH 6 to12.

In a sequential(modified) TCLP, lead was released in only the 1st and 2nd extraction of KP10 whilst calcium was markedly released with the highly breakdown of SWF. However, in all extractions of calcite-additional SWF, insignificant amounts of lead were released.

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Figure 5. Calcium and lead concentration of lea-chate by sequence toxicity characteristic leaching procedure.

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