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Effect of calcite on Pb-doped solidified waste forms in leaching

Dong-Jin Lee *

School of Environmental Engineering, Ajou University, San 5, Wonchun-dong, Youngtong-Gu,
Suwon, Kyunggi-do 443-749, South Korea

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Abstract

The alkalinity of cementitious materials rectifies a low pH of leachant to be over 12 in leaching. The rapid change of leachant pH produces the remarked variation of solubility of heavy metals in the toxicity characteristic leaching procedure. The release of lead on cementitious solid waste forms in leaching was observed in the pH range of particularly 12. The release of lead is significant dependant on the changed values of leachant pH. The pH static leaching procedure (PSLP) was implemented for assessing a quantitative measurement of total potential leachability with the continuing addition of acidic leachant up to the point of no change of leachant pH. The release of lead on Pb-doped solidified waste forms (SWF), in the PSLP, was 27.0% of initial concentration at the maximum meq CH_3COOH (about 24.0) added to g dry solidified wastes. In this study, the immobilization effect of calcite on SWF was investigated in the acidic condition by the PSLP. Calcite additions to SWF make a good fixation efficiency of about 92%. Calcite addition abundantly provides the acid neutralization capacity to protect SWF from the attack of acid, with the marked development of hydrated minerals (mainly portlandite and C–S–H) in accordance with the accelerating effect of cement hydration.

Keywords: Solidification; pH; Cement; Calcite; Lead

1. 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 (LaGrega et al., 2001; Cocke, 1990). The best system of cement-based S/S has the ultimate goal to be both physical and chemical immobilization (Parapar et al., 1998). Physical tests for evaluating solidified waste forms(SWF) using Portland cement 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 at the attack of acid (Van der Sloot, 1996).

It is widely acknowledged that the stability of SWF at the attack of acid is dependant on pH control for metal contaminants. Most metal ions normally make precipitates with hydroxides, and normally having minimum solubility in the pH range of 7.5–11. The high variation of solubility by the change of pH makes some limitations for measuring the precision of release of

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* Tel.: +82 31 219 2410; fax: +82 31 215 5145.
E-mail address: dongj7@ajou.ac.kr

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contaminants in many methodologies, even in the US-environmental protection agency (EPA) toxicity characteristic leaching procedure (TCLP) undoubtedly recognized as one of the most common leach tests. The precision of leachate concentration determined by the TCLP was found to be poor with five replicates. These results are entirely consistent with the work of Stegemann and Cote (1990). They investigated that sampling of a number of replicates (normally at least four replicates) was required to achieve a desired precision of ×/÷1.5 (i.e., 50%). The precision of each four replicates for different contaminants varied from ×/÷1.2 to 3.8 except lead. The precision of four replicate for lead was ×/÷19. They suggest that more replicates may be required to increase the precision for the regulatory purposes intended by the EPA.

In this study, the pH static leaching procedure (PSLP) has been performed for assessing a quantitative measurement of total potential leachability with preventing the remarked variations of solubility by the change of leachant pH. The PSLP was implemented in accordance with the continuing addition of acidic leachant up to the point of no change of the leachate pH produced at the maximum breakdown of the cement-based solidified form.

The presence of lead in wastes has been found to lower the rate of strength development in solidified waste forms using Portland cement in the previous investigation (Lee et al., 2005). Calcite addition is observed to markedly rectify this poor strength development behavior in Pb-doped SWF. 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 (Klieger and Hooton, 1990). 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 main objective of this study is to find out the immobilization effect of calcite on lead-rich cementitious waste forms in the acidic condition using the PSLP. In addition, the suitability of the PSLP has been examined for measurement of leachability of lead on SWF using Portland cement.

2. Materials and methods

2.1. Materials

Ordinary Portland cement (OPC) was purchased 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 ($Ca_3Al_2O_6$: 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 ($\geqslant$95.0% $CaCO_3$) with $\leqslant$4.0% $MgCO_3$ and $\leqslant$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 1.8 μm, maximum particle size of 8 μm, and residue on 20 μm screen of no more than 0.005%.

The wastes were prepared from lead nitrate which precipitated to form hydroxide sludge on adjusting the pH to 8.5 with 6.0 N sodium hydroxide and then dried at 104 °C for 24 h. 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 $[Pb_6O_3(NO_3)_2(OH)_4]$. The XRD data were consistent with the results of Asavapisit et al. (1997) and Gress and El-Korchi (1993).

2.2. Solidification procedure

Dry Pb waste and cement were mixed with water at a water to solid (cement, calcite and Pb wastes) ratio (W/S) of 0.3. After thorough mixing, the samples were introduced into polyethylene cylindrical moulds measuring 20 mm diameter × 40 mm height and were removed after 24 h. The curing was carried out in humid air at 20 °C for 28 days. The samples are denoted Cal*i*%Pb*j*%-K where *i* is the calcite content, *j* is the Pb-doped waste content. In this study, samples were prepared in triplicate and are denoted Pb10%-K (OPC + 10% lead wastes) and Cal5%Pb10%-K (OPC + 10% lead wastes + 5% calcite). The samples were cured for 28 days, and then dried at 104 °C for 24 h for leaching test.

2.3. Methods

The US EPA toxicity characteristic leaching procedure (TCLP) has basically been performed for investigation of the Pb releases and the change of pH on lead-rich cementitious solid waste forms. Samples were ground to particles of less than 9.5 mm in size, and then leached with acetic acid (pH 4.93 ± 0.05). Extraction fluid of the leachant was made with a addition of 5.7 ml glacial CH_3CH_2OOH to 500 ml of Micro-pore water, after then with a addition of 64.3 ml of 1 N NaOH to a volume of 1 l for dilution with Milli-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 h.

A separate experiment was carried out to monitor the change of pH and concentrations of lead and calcium during the 18 h 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