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Corrosion of Cement-Based Solidified Wastes Due to Different Acid Attack

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Abstract

Durability of cement-based solidified wastes against different acid attack was investigated. The cement-based solidified wastes containing synthetic lead and chromium hydroxides at 0, 10, 20 and 30 wt.% were exposed to 0.5N acetic, nitric and sulfuric acid solutions. The percentage weight change of the cement-based solidified wastes after exposure to acids for different duration was determined and the physical appearance was inspected. Experimental results showed that sample weight loss increased with longer exposure durations in acetic and nitric acids, but at a descending rate. An increasing weight loss was also observed from samples with high concentration of lead and chromium hydroxides. Exposure to sulfuric acid resulted in the deposition of insoluble gypsum on the surface of the solidified wastes and as a result a gain in weight was found. In addition, resistance of the cement-based solidified waste matrices against acid attack was in the following order: sulfuric > acetic > nitric acid.

Keyworks: Stabilization/Solidification, lead hydroxide, chromium hydroxide, Portland cement, acid attack

1. Introduction

Landfills remain the major method used for the disposal of hazardous industrial wastes in Thailand. Despite continuing efforts to promote waste reduction, recycling, reuse and clean manufacturing technologies, some wastes will always require safe disposal to landfill. Pre-landfill treatment of hazardous industrial waste is therefore likely to be required in order to ensure its long-term safe disposal.

The relative simplicity of cement-based solidification processes and the ability of ordinary Portland cement (OPC) and other pozzolanic materials to treat a wide variety of wastes, particularly those containing heavy metals, has made this an attractive pre-landfill waste treatment technology for selected wastes. Environmentally acceptable cement-based solidified waste materials must retain waste components over very long time periods. This relies on both chemical and physical immobilization mechanisms produced by the cementitious binder materials. The long-term durability of the materials under the imposed disposal conditions is also a key factor controlling whether or not the waste has been successfully solidified.

Cement solidified waste materials are alkali in nature and therefore they are vulnerable to acid attack. The alkali materials in the pore water, and especially calcium hydroxide were consumed by the acid and rapidly depleted, resulting in the cement matrix being significantly decalcified [1-2]. The dissolution of calcium hydroxide crystal and the extensively decalcified calcium silicate hydrate (CSH) gels results in increased porosity and enlarged threshold capillary pores in the leached layers [3].This causes self-accelerating leaching and matrix deterioration [4]. These changes would cause progressive microstructural breakdown and loss of mechanical strength which eventually leads to complete disintegration of the solidified waste and greatly increases geometrical surface area for leaching.

The durability of hardened cement paste, mortar and concrete against different chemical degradation has been studied by several researchers [5-12]. Although extensively studied, the durability of the solidified waste materials is largely untested. In this work, the durability of cement-based solidified waste samples was investigated by determining weight loss from the samples after contact with acid solutions for varying durations. In addition, the physical appearance of the samples after exposure to different acid solutions was observed.

2. Materials and Methods

2.1 Synthetic Lead and Chromium Hydroxides

Two synthetic waste sludges were prepared by precipitating lead and chromium from 1M $Pb(NO_3)_2$ and $Cr(NO_3)_3$ solutions by adding 10M sodium hydroxide to pH 9.5 ± 0.1 and 7.5 ± 0.1, respectively. The sludges were vacuum filtered through Whatman No.1 filter paper and the filter cake was oven dried overnight at 105°C before being ground to a particle size of $< 500\,\mu m$ using mortar and pestle and stored in sealed glass bottles.

2.2 Sample Preparation

Solidified waste samples were prepared by mixing synthetic $Pb(OH)_2$ and $Cr(OH)_3$ with OPC at 0, 10, 20 and 30 wt.% (Table 1). A water to solid ratio of 0.45 was obtained by observation to maintain good workability during transferring the sample into a cylindrical plastic mould (25 mm high and 25 mm diameter). The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of metal waste before being transferred to the plastic mould. The cement solidified metal wastes were allowed to solidify in the sealed plastic moulds for 28 days to avoid carbonation prior to testing [13-14].

2.3 Corrosion Tests

Three acids were used to study the corrosion of the solidified waste samples. Acetic acid is a weak acid, which is generated during the decomposition of organic matter under anaerobic conditions. Nitric and sulfuric acid are strong mineral acids which were used to simulate acid rain. Each acid was used at a concentration of 0.5N. The initial pH of acetic, nitric and sulfuric acid solutions is 2.4, 0.5 and 0.8, respectively.

The weight and dimensions of the cylindrical samples were recorded prior to testing and a constant volume of acid solution to sample surface area of 20:1 was used to ensure that all surfaces of the samples were contacted with solution [3]. The solidified samples were suspended in the geometric center of the solution in a closed system under static conditions. Three sets of 5 samples with the same composition were suspended in five different bottles containing each acid solution. Each set of samples was exposed to acetic, nitric and sulfuric acid solutions, respectively for 1, 8, 15, 29 and 57 days. One bottle from each set was removed after each exposure time for analysis. The tests were completed in duplicate to confirm the reproducibility of the test results.

3. Results and Discussions

3.1 Corrosion due to Acetic Acid

Weight change data of cement-based solidified wastes exposed to 0.5 N acetic acid as a function of time is shown in Figures 1a and b. Results showed that the percentage weight loss from the samples gradually increased with increasing exposure duration, but at a decreasing rate.

A cement-based solidified waste consists of the hydration products of various constituents, mainly CSH gel and calcium hydroxide, waste components, unreacted cement clinker phases and the residue of the water-filled pores. These pores in the solidified waste formed the capillary porosity. The ingression of an aggressive acetic acid leachant into the pore water disturbs the chemical equilibrium formed with the surrounding solids and this may result in solubilization of insoluble components. $Ca(OH)_2$ is the most readily available alkali material in solidified waste and is solubilized when the pH drops below 12 [15]. The dissolution of $Ca(OH)_2$ results in an increased degree of capillary pore connectivity and leads to further ingression of the acid leachant. As a result, an extensive dissolution of $Ca(OH)_2$ and decalcification of CSH gels occurred. This led to the formation of macropores and macrocracking in the corroded layer.

It was observed that weight loss from the solidified wastes increased with rising concentrations of $Pb(OH)_2$ and $Cr(OH)_3$ in the mixes. The increased concentration of $Pb(OH)_2$ and $Cr(OH)_3$ resulted in a decreased cement content and therefore the ability of the solidified waste matrices to neutralize acid was reduced. In addition, the interfering effects of $Pb(OH)_2$ and $Cr(OH)_3$ on OPC hydration could induce a poor microstructure development of the solidified wastes.[16] As a result, the resistance of a cement matrix to acid corrosion was reduced.

3.2 Corrosion due to Nitric Acid

Similar effects on all cement-based solidified waste after exposure to 0.5 N nitric acid was observed, but at a greater rate of weight loss than acetic acid (Figures 2a and b). Nitric acid is a strong mineral acid, which dissociates completely, and form highly soluble calcium nitrate. According to the higher solubility of calcium nitrate (266.0 g/100g water at 0°C) compared to calcium acetate (43.6 g/100g water at 0°C), calcium nitrate was likely to precipitate in the porous corroded layer of the solidified waste less than calcium acetate [1]. This resulted in a lower diffusion resistance of the corroded layer and a greater rate of corrosion caused by nitric acid was observed.

3.3 Corrosion due to Sulfuric Acid

Figures 3a and b show weight change data of cement-based solidified waste at different exposure durations in 0.5 N sulfuric acid. A gain in weight of cement-based solidified wastes after exposure to sulfuric acid was observed. Similar observation was reported by several researchers that the weight gain was caused by the deposition of gypsum on the surface and in the porous corroded layer of the solidified wastes [5, 17, 18].

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

Gypsum, which is formed by the reaction between sulfate ion and calcium hydroxide, has very low solubility (0.22 g/100 g water, at 0°C) [1]. Formation of this insoluble gypsum layer can prevent the solidified waste matrices from further deterioration upon contact with sulfuric acid. However, this gypsum layer was loosely connected with the solidified waste and fell off spontaneously. This implies that the solidified waste was substantially deteriorated, although at a much slower rate compared to acetic and nitric acid.

3.4 The Physical Appearance of the Solidified Wastes after Exposure to Different Acids

There were cracks formed on the surface of the cement-based solidified wastes after exposure to acetic and nitric acids (Figure 4). The cracking surface was soft, porous and lighter in weight than the control. This cracking surface was reported to be composed mainly of silicon dioxide with only small percentages of other oxides [2]. After dehydrating the tested solidified waste in air for a period of time, the cracking surface was easily split into fragments. In the case of sulfuric acid exposure, the solidified waste was swelling due to the formation of a layer of gypsum on the surface. In addition, the physical appearance was consistent with the weight change results.

4. Conclusion

Durability of the cement-based solidified wastes against different acid corrosion was in the following order: sulfuric > acetic > nitric acid solution. The formation of the insoluble calcium sulfate on the surface of the samples can prevent the cement matrices from further corrosion when in contact with sulfuric acid solution compared to the formation of highly soluble calcium acetate and calcium nitrate during contact with acetic and nitric acid solutions. In addition, the solidified wastes were less durable to acid solutions when metal hydroxide concentration in the mixes was increased.

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6. References

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Table 1. Mixes of OPC with different synthetic metal hydroxides

OPC (% by wt.)	**$Cr(OH)_3$ (% by wt.)**	**$Pb(OH)_2$ (% by wt.)**	**w/s Ratio**
100	0	0	0.45
90	10	0	0.45
80	20	0	0.45
70	30	0	0.45
90	0	10	0.45
80	0	20	0.45
70	0	30	0.45

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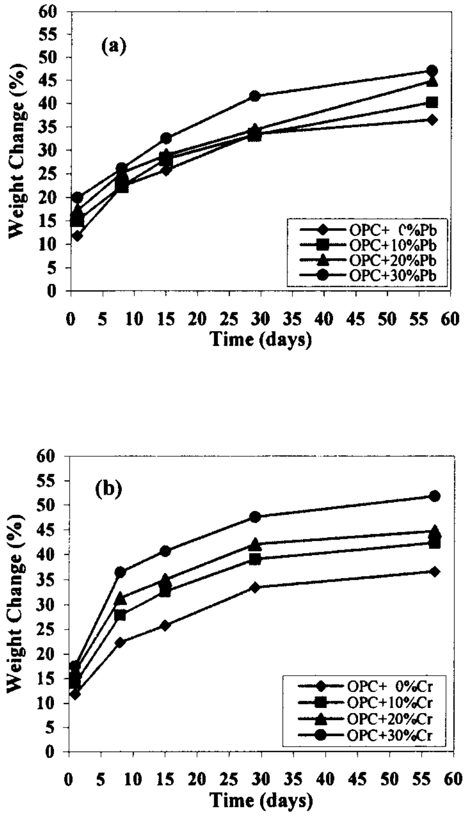

Figure 1 Effect of 0.5 N acetic acid on weight change of the solidified wastes in the presence of:

(a) $Pb(OH)_2$ and (b) $Cr(OH)_3$

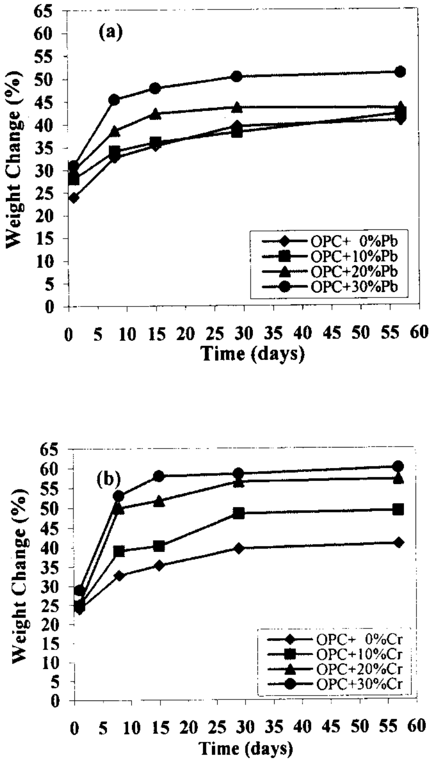

Figure 2 Effect of 0.5 N nitric acid on weight change of the solidified wastes in the presence of:

(a) $Pb(OH)_2$ and (b) $Cr(OH)_3$

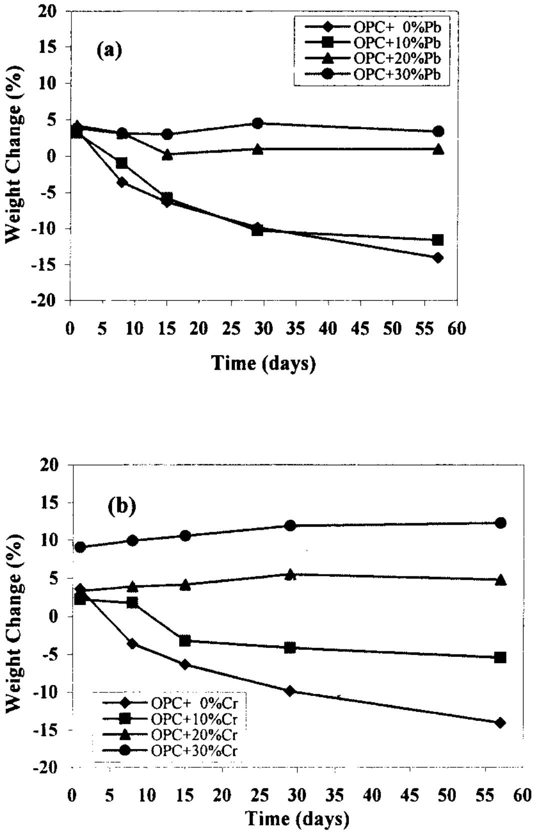

Figure 3 Effect of 0.5 N sulfuric acid on weight change of the solidified wastes in the presence of:

(a) $Pb(OH)_2$ and (b) $Cr(OH)_3$

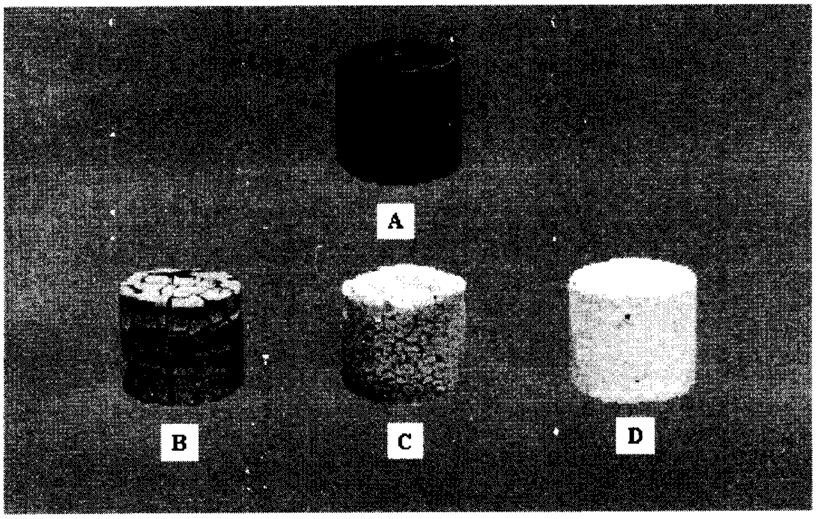

Figure 4 The physical appearance of the solidified wastes after exposure to different acids for 8 days : a) Control; b) acetic acid; c) nitric acid; and d) sulfuric acid