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Influence of condensed silica fume on the properties of cement-based solidified wastes

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Abstract

Influence of condensed silica fume (CSF) addition as cement replacement material on the properties of cement-based solidification products was investigated. Final setting, unconfined compressive strength, and leachability of the synthetic lead and chromium hydroxides were determined. CSF was used at 0, 5, 10, and 20 wt.%. substitution for Portland cement. A water-to-solid ratio (w/s) of 0.45 was used for all mixes. Experimental results showed that the severe retardation effect on ordinary Portland cement (OPC) hydration caused by lead hydroxide has been minimized due to the pozzolanic effect and, as a result, the time to final setting has been significantly reduced. In addition, compressive strength of the solidified wastes was increased to the highest with 10% cement replacement but decreased to lower than the one without CSF at 20% replacement. Leaching of the amphoteric lead and chromium hydroxides is primarily determined by leachate pH and therefore lead was found in the leachates at higher concentration than chromium. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Stabilization/solidification; Condensed silica fume; Portland cement; Strength; Leachability

1. Introduction

Cement-based stabilization/solidification (S/S) processes are potential treatment for hazardous wastes particularly those containing heavy metals. The technology aims to prevent the release of hazardous components from the solidified wastes after disposal in a landfill by limiting the solubility and mobility of the contaminants. The chemical changes that take place as a result of the interaction between waste components and Portland cement play an important role in controlling the quality of cement-based solidified waste products [1–6].

The most important factor in determining whether a particular cement-based S/S process is effective in treating a given waste is the reduction in the short- and long-term leaching of the waste. Leaching involves solubilization of species present in solid phases into the pore water and their transport through the network of connected pores within the solid into the bulk leachant by diffusion [7–9]. Porosity and pore size distribution have been reported to influence water permeability of cement pastes. Low permeability is associated with low porosity and pore size distributions that are fine enough to minimize the transport of fluids and ions into and from the material [10–13].

The chemistry of S/S waste also plays a key role in controlling leaching. The presence of calcium hydroxide maintains high pH conditions in the pore water and this ensures that waste components such as heavy metals present as hydroxides will remain insoluble [7]. The ingression of acidic leachant into the pore water disturbs the chemical equilibrium formed with the surrounding solids and this results in solubilization of insoluble metals. Calcium hydroxide, which is the most readily available alkali material in the solidified waste, is rapidly leached out [14]. This dissolution of calcium hydroxide into the pore water results in an increasing degree of capillary pore connectivity and leads to further ingress and exposure of CSH gel, calcium hydroxide, and encapsulated waste to the leachant.

The replacement of Portland cement by pozzolanic materials such as silica fume, fly ash, and blast furnace slag is known to result in the consumption of calcium hydroxide and alkali during pozzolanic reactions. This contributes to

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Table 1
Mix designs (wt.%)

OPC (g)	CSF (g)	$Pb(OH)_2$ (g)	$Cr(OH)_2$ (g)	w/s
100	0	0	0	0.45
95	5	0	0	0.45
90	10	0	0	0.45
80	20	0	0	0.45
90	0	10	0	0.45
85	5	10	0	0.45
80	10	10	0	0.45
70	20	10	0	0.45
90	0	0	10	0.45
85	5	0	10	0.45
80	10	0	10	0.45
70	20	0	10	0.45

the production of secondary CSH gel to fill the void space and causes further reduction of capillary pores [15–18]. It is expected that the addition of condensed silica fume (CSF) will modify the chemical composition of the solidified waste products by providing a neutral to mild alkaline environment for the encapsulated wastes. As a result, the concentration gradient between the pore water in the solidified wastes and the water quality of the surroundings is minimized and therefore leading to reduce leaching of the wastes [19]. In this work, the effects of CSF on final setting, unconfined compressive strength, and leaching characteristics of cement-based solidified wastes were investigated.

2. Experimental procedure

2.1. Materials

Ordinary Portland cement (OPC) Type 1 was supplied by The Siam Cement Public and the CSF is from the Microsilica JV in Australia.

Lead and chromium hydroxides were prepared by precipitation from 1 M lead nitrate and chromium nitrate solution by adding 10 M sodium hydroxide to control the pH of the solution. The slurries of lead and chromium hydroxides were thoroughly mixed to achieve pH values of 9.5 ± 0.1 and 7.5 ± 0.1. The slurry was vacuum filtered through Whatman No. 1 filter paper and the filter cake was dried overnight at 105°C before being ground to a particle size of < 500 μm.

2.2. Sample preparation

Solidified waste samples were prepared by mixing 5, 10, and 20 wt.% of CSF and 10 wt.% of synthetic lead and chromium hydroxides with OPC. A water-to-solid ratio (w/s) of 0.45 was used to maintain good workability during transferring the sample into a cylindrical plastic mould. The mix designs are summarized in Table 1. The slurry was mixed following the standard test method ASTM C 305-94 to achieve a uniform distribution of the solidification binders and the metal waste before being transferred to the plastic mould. The cement solidified metal wastes were allowed to solidify in the sealed plastic moulds to avoid carbonation prior to testing.

2.3. Time of setting of hydraulic cement by Vicat needle

The standard test method ASTM C 191-92 was modified to determine the time of setting of the cement metal waste mixes. The cement metal waste mixes were prepared at w/s ratio of 0.45. The mixture was then transferred into the ring and the excess mix was removed. The penetration of the needle into the samples was determined every 15 min. The final setting time was obtained when the needle did not sink visibly into the mix.

2.4. Unconfined compressive strength

The unconfined compressive strength of the solidified wastes was done following ASTM D 1633-96. A cylindrical sample with diameter of 50 mm and height of 100 mm was used. The compressive strength of the solidified waste samples was determined after curing for 1, 3, 8, 15, 29, 57, and 91 days. A set of five samples was used for compression test at each curing duration and the arithmetic average was made from five observations.

2.5. Dynamic leach test

Metal leaching from the solidified wastes was assessed using a modified ANSI/ANS 16.1 leach test on the samples cured for 28 days. Cylindrical samples (25 mm diameter and 25 mm height) were suspended in a plastic net in 0.2 N acetic acid solution, at a leachant volume-to-surface area ratio of 20:1. The leachates were removed to determine the pH and metal concentration was analyzed using atomic absorption spectrophotometry. Leachant was replaced periodically after intervals of static leaching. The leachants were renewed at 1, 8, 15, 29, and 57 days, in order to produce severe leaching conditions and allowing assessment of leaching performance over long time periods. Leach testing was done in duplicate to ensure the reproducibility of the data.

3. Results and discussion

3.1. Final setting of the solidified wastes

The effects of CSF on final setting of the cement metal waste mixes are shown in Fig. 1. The time to final set of control OPC was found to increase from 4 to 4.25 h when 5 wt.% of CSF was used, but it decreased to 4 and 3.75 h with 10 and 20 wt.%, respectively, substitution for Portland cement. A similar effect of CSF on the final setting time of OPC–Cr mixes was observed. It was noticed that the

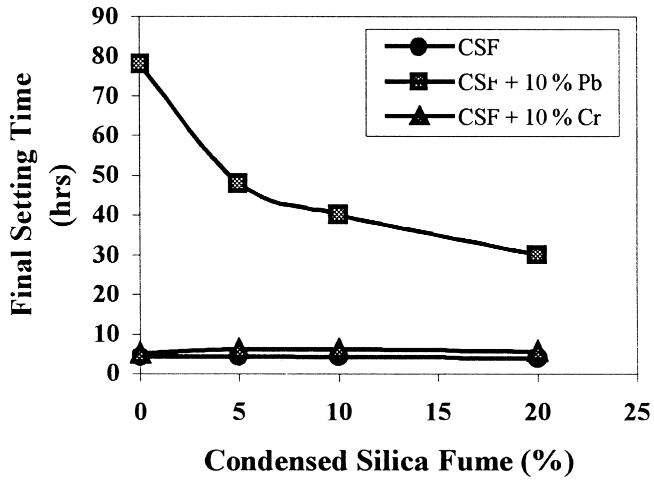

Fig. 1. Effect of CSF on final setting of cement-based solidified wastes.

CSF did not cause a significant effect on the final setting time of the control OPC and OPC–Cr mix when compared to those of the OPC–Pb mix.

Lead hydroxide has been reported to cause severe hydration retardation of OPC [1,4]. For a 10-wt.% addition of lead hydroxide to OPC, an increase in final setting time from 4 to 78 h has been observed. Lead, which is an amphoteric metal, is extensively resolubilized in a highly alkaline environment of cement and is adsorbed onto the hydrating surface of cement clinker particles and therefore limits the availability of water for hydration reactions [1]. It was observed that the time to final set of OPC–Pb mixes decreased from 78 to 48, 40 and 30 h when the CSF was used at 0, 5, 10, and 20 wt.% replacement for Portland cement, respectively. The consumption of calcium hydroxide and alkali by CSF during pozzolanic reactions reduced the alkalinity of the OPC–Pb system. It was possible that the reduction in alkalinity decreased the resolubilization of lead hydroxide and reduced the interfering effect on hydration retardation.

3.2. Unconfined compressive strength of solidified wastes

Fig. 2a–c show the effect of 0, 5, 10, and 20 wt.% replacement of CSF for Portland cement on the compressive strength of the solidified wastes during the 1- to 91-day curing periods. The results clearly show no significant effect of CSF on compressive strength during the 1 to 3 days of curing (Fig. 2a). The hardened cement incorporating 5- and 10-wt.% substitution during the 3 to 91 days of curing had higher strength than that of the control. From this investigation, the highest strength was obtained at the replacement level of 10% with an increased strength of about 33%, 25%, and 22% gained at the curing ages of 8, 29, and 91 days, respectively. This was considered to be the beneficial effects of pozzolanic reactions on strength, which occurred mostly during these curing durations [20].

In addition, a reduction in strength of the specimens with 20% cement replacement by CSF was observed. It was possible that the CSF, an extremely fine particle, acted as filler and occupied the pore space. The reduced pore space in the OPC/CSF systems probably affected both the OPC hydration and the pozzolanic reactions. This is because hydration products can only grow and occupy the space available to them. Hydration will cease

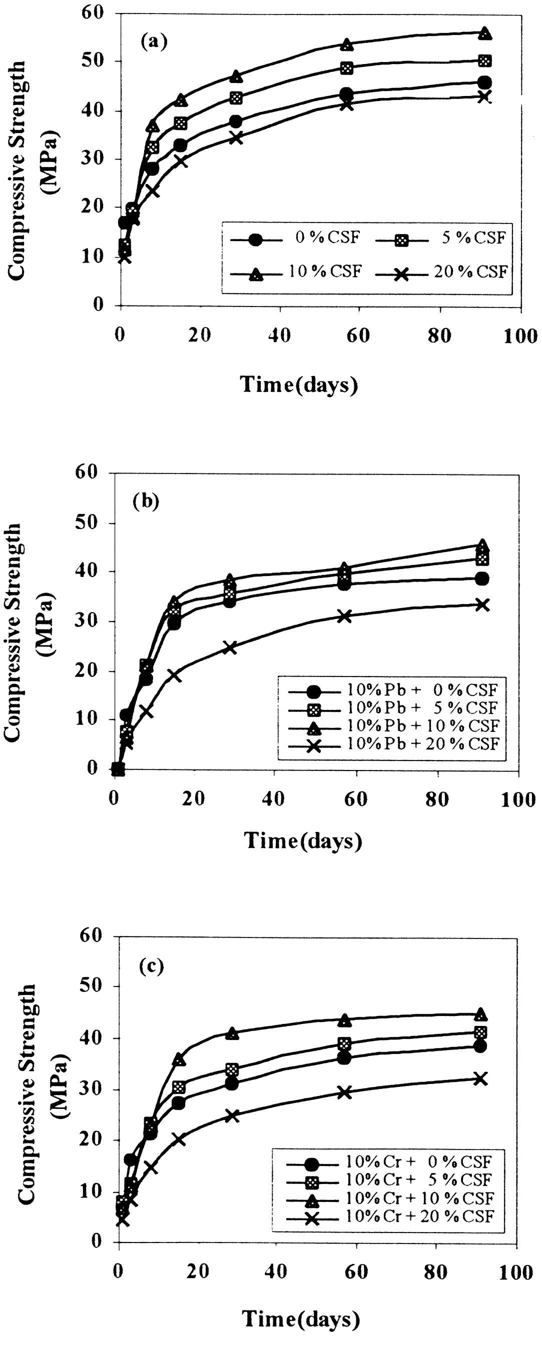

Fig. 2. Strength development of the solidified waste at different CSF content: (a) OPC/CSF mixes, (b) OPC/CSF/Pb mixes, and (c) OPC/CSF/Cr mixes.

if the pore space is filled [21]. This effect probably contributed to the lower degree of hydration and caused strength reduction.

Similar effects of CSF on strength were observed for both OPC/CSF/Pb and OPC/CSF/Cr systems, as shown in Fig. 2b and c. Compressive strengths of the specimens in the presence of Pb and Cr hydroxides were lower than those without waste at all levels of cement replacement by CSF. There are two possible explanations to this observation. The first is that interfering effects caused by Pb and Cr hydroxides via adsorption onto the hydrating surface of cement clinker particles incorporated into the CSH gels [1]. As a result, these CSH gels are different from those obtained from normal cement hydration. Another explanation is that the hydration of clinkers in the presence of lead nitrate induced an increase gel formation. This increased gel formation was associated with volume change in the specimens, leading to microcracking and therefore a decrease in compressive strength [22].

3.3. Leachability of metals from solidified wastes

Leachate pH of the solidified wastes after each interval of exposure to 0.2 N acetic acid is shown in Table 2. The cumulative amount of lead and chromium leached from the solidified wastes as a function of exposure duration is presented in Fig. 3a–b.

The pH of leachants from the control OPC/Pb systems changed from an initial pH of 2.9 to approximately between 4.4 and 4.8 after each interval of static leaching (Table 2). An increase of leachant pH was a result of dissolution of calcium hydroxide produced in large quantities during the hydration reactions of OPC. Calcium hydroxide and the high pH of the pore water provided a buffering capacity to the solidified waste forms against acid attack [9].

Similar variations in leachate pH were observed for the OPC/CSF/Pb and OPC/CSF/Cr systems except that leachate pH were lower than that without CSF. This is because calcium hydroxide, an OPC hydration product, was partly consumed by CSF during pozzolanic reactions and therefore the acid neutralization capacity of the systems with CSF was decreased. The development of secondary CSH during pozzolanic reactions between CSF and calcium hydroxide resulted in an increased amount of isolated pores and a shift to finer pores. This also affects acid neutralization capacity due to increased resistance to the diffusion of available alkalinity [23].

Table 2
Leachate pH of the solidified wastes at each interval of exposure

	Leachate pH					
Sample (% CSF)	Initial	Day 1	Day 8	Day 15	Day 29	Day 57
OPC/Pb system						
0	2.9	4.4	4.8	4.6	4.5	4.4
5	2.9	4.1	4.6	4.5	4.4	4.4
10	2.9	4.1	4.6	4.4	4.4	4.4
20	2.9	4.0	4.4	4.4	4.4	4.3
OPC/Cr system						
0	2.9	4.3	4.6	4.6	4.4	4.3
5	2.9	4.2	4.6	4.5	4.4	4.4
10	2.9	4.2	4.5	4.5	4.4	4.4
20	2.9	4.2	4.4	4.4	4.3	4.3

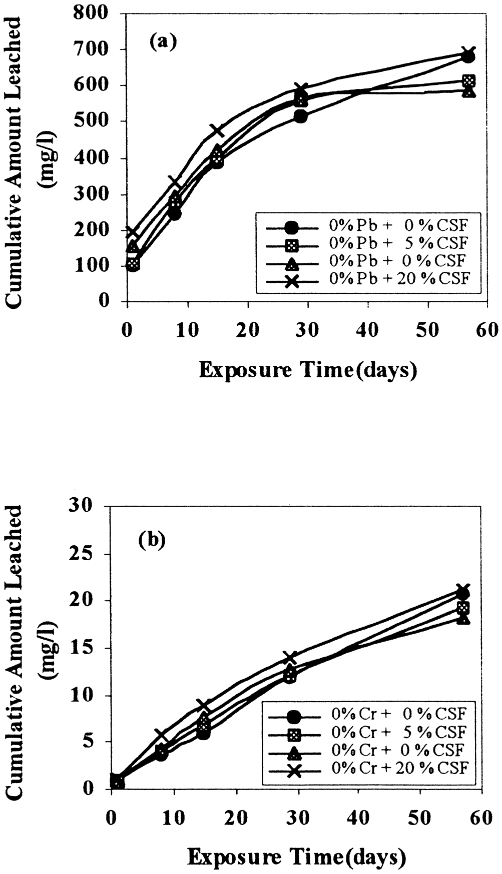

Fig. 3. Cumulative amount of heavy metals leached from the solidified wastes: (a) OPC/CSF/Pb and (b) OPC/CSF/Cr systems.

The cumulative amounts of Pb leached from the solidified waste after leaching for 57 days were 678, 610, 584, and 692 mg/l at 0%, 5%, 10%, and 20% cement replacement, respectively (Fig. 3a). During leaching tests of the monolithic samples, the ingress of the acetic acid leachant through the open and connected porosity led to a reduction in the pH of the internal pore water causing desorption and resolubilization of heavy metals.

Unlike lead hydroxide, the concentration of chromium cumulated in leachates during each interval of static leaching was much lower (Fig. 3b). This was because lead and chromium hydroxides are amphoteric metals and their solubilities are strongly dependent on leachate pH [7,8]. Lead and chromium hydroxides have minimum solubility around pH 9.5 and 7.5, respectively, whereas the leachate pH of the solidified wastes were between 4.0 and 4.8. The pH difference between the minimum solubility of lead hydroxide and the leachates was large compared to that of chromium hydroxide. As a result, lead was released from the solidified waste products at a higher rate than chromium.

The above data clearly indicated that there was no significant effect of CSF on leaching characteristics of lead and chromium when 5 and 10 wt.% of CSF were used. Metal release was determined by chemical interactions between the material and the leachant and by the microstructural properties of the material. The resistance of a cement matrix to acid attack depended on porosity, tortuosity, solubility, and acid neutralization capacity of the matrix components. In particular, acid neutralization capacity was reported to have a major influence on the rate of contaminant leaching [7,23].

4. Conclusions

The following conclusions can be drawn from this experimental study:

- CSF had a significant effect on final setting of the OPC/Pb samples. The final setting of OPC/Pb mixes decreased with increasing level of cement replacement from 0 to 20 wt.%. This is because the consumption of calcium hydroxide by CSF during pozzolanic reactions reduced the alkalinity of the OPC/Pb systems. As a result, the interfering effect on hydration retardation caused by lead hydroxide was reduced.
- The highest compressive strength was obtained at the 10% replacement of cement by CSF, but decreased at the 20% cement replacement. It was possible that the excess CSF occupied the pore spaces and reduced the available space for the hydration products and therefore limiting the extent of hydration.
- Leaching of the amphoteric lead and chromium hydroxides was strongly influenced by leachate pH.
- The replacement of cement by CSF resulted in reducing acid neutralization capacity of the solidified waste product. There are two possible explanations to this observation. The reduced calcium hydroxide, which was partly consumed by CSF during pozzolanic reactions, resulted in decreasing acid neutralization capacity of the systems with CSF. Another explanation is that the development of the secondary CSH during pozzolanic reactions resulted in an increased amount of isolated pores and finer pores in the solidified product. This affects acid neutralization capacity due to increased resistance to the diffusion of available alkalinity.
- Leachability of lead hydroxide was 30 times higher than that of chromium hydroxide, despite a similar variation in leachate pH for both OPC/CSF/Pb and OPC/CSF/Cr systems. This was because leachate pH of the OPC/CSF/Pb samples were much lower than the minimum solubility pH of lead hydroxide itself and therefore lead hydroxide was likely to be resolubilized more into the leachates.

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