Effects of sucrose and sorbitol on cement-based stabilization/solidification of toxic metal waste

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Abstract

The effects of sucrose or sorbitol addition on the hydration, unconfined compressive strength and leachability of Portland cement pastes containing 1% Pb and 1% Zn were studied as a function of time. Whereas Pb and Zn were found to shorten the time to achieve maximum hydration of Portland cement, the combination of these metals with 0.15 wt% sucrose or 0.40 wt% sorbitol retarded the setting of cement by at least 7 and 28 days, respectively, without affecting the strength at 56 days. The leachability of Pb and Zn evaluated by the TCLP 1311 protocol at 56 and 71 days was slightly reduced or unchanged by the addition of sucrose or sorbitol. SEM-EDS and XRD analyses revealed that ettringite precipitation was favored whereas the formation of CSH gel, which accounts for most of the strength of hydrated cement, was delayed in cement pastes containing both metals and sucrose or sorbitol. These results indicate that controlled additions of sucrose or sorbitol can add flexibility to the handling of cement-treated metal waste, particularly when it needs to be transported by truck or pipeline between the treatment plant and the disposal site, without affecting its long-term performance.
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1. Introduction

Stabilization/solidification (S/S) is a widely used technique for immobilizing toxic metal ions in industrial waste prior to landfilling. The binder of choice is most often Portland cement, owing to its ready availability, high strength and amply documented performance [1]. The main components of Portland cement are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and calcium sulfate (gypsum or anhydrite, 10% max). During cement hydration, C_3A reacts with sulfate ions coming from the dissolution of calcium sulfate to form crystals of ettringite (AFt) and monosulfate (AFm), thus preventing the flash set of Portland cement. C_3S and C_2S undergo hydration to form calcium hydroxide (CH) and calcium silicate hydrate (CSH), which is the principal contributor to cement strength [2]. The CSH plays a key role in immobilizing adventitious metal ions by means of physical adsorption [3], coprecipitation [4] and formation of metallosilicates [5–7]. Further metal uptake is provided via ion substitution in ettringite crystals [3].

Sugars and their derivatives are found in many industrial wastes and byproducts, either as individual molecules or as the repeating units in long-chain compounds. For example, wood sugars and oligosaccharides mixed with lignosulfonates are byproducts from the manufacture of pulp and paper. They are widely used as retarders to control the setting of cement [8–13]. There has been no study published, however, on the effects of sugars as additives in cement-based S/S processes. The retarding influence of sugars could be advantageous when the waste-cement mixture needs to be transported for some distance between the S/S treatment plant and the disposal site. In these situations, early hardening of the cement in the truck box or pipeline could result in severe operational difficulties and limited flexibility. In the present research, a sugar (sucrose) and a sugar alcohol (sorbitol) were investigated. Both additives are highly resistant to alkali attack but differ in their affinity toward silicon: sorbitol is a silicon binder [14], whereas sucrose is not [8,12]. As a result, these two additives are expected to interfere differently

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with the cement hydration reactions. Sucrose is one of the most effective and commonly used retarders for cement setting. The addition of 0.075 wt% sucrose increases the induction period of the hydration process from 2.5 to 31 h [11]. Moreover, sucrose has been shown to enhance the specific surface area of hydrated cement pastes by increasing the number of small (1–2 nm) pores at the expense of medium-sized (4–20 nm) pores [15]. Sorbitol is often employed as a water-reducing plasticizer (superplasticizer) in cement admixtures, that is, it decreases the water needed to make the cement workable which, in turn, enhances its strength [16,17].

The objective of this study was to explore the effects of small additions of sucrose or sorbitol on metal leachability and strength development for specimens of metal waste treated by cement-based stabilization/solidification. Synthetic Pb and Zn waste solutions were used because both metals are common to industrial waste streams and have been identified as priority metallic pollutants by the US Environmental Protection Agency [18]. To aid in the interpretation of the results, the degree of cement hydration and the microstructure of the treated waste matrix were also assessed as a function of time.

2. Materials and methods

2.1. Sample preparation

Synthetic waste solutions containing 25.0 g/L of each Pb and Zn were prepared by dissolving 40.0 g $Pb(NO_3)_2$ and 114 g $Zn(NO_3)_2 \cdot 6H_2O$ per litre of distilled-deionized water. Sucrose and sorbitol were dissolved in these solutions at concentrations ranging between 0 and 10 g/L; equivalent metal-free solutions were also prepared. The solutions were pre-cooled to 10 °C and then mixed with normal Portland cement Type 10 (ASTM Type I) at a liquid-to-cement ratio of 0.40:1 in a plastic bowl over an ice-water bath. (Temperature control was necessary because certain mixtures – most notably those containing sorbitol – released more heat than others.) The mixtures were stirred with a plastic spoon until they were homogeneous, i.e., for about 7 min or, in the case of those which contained synthetic waste, about 12 min because of their higher viscosity. They were then poured into cylindrical PVC molds measuring 2 inches in diameter and 4 inches in height. To minimize the entrapment of air bubbles, the cylinders were filled in two successive layers and each layer tamped 50 times. Cylinders were placed in triple-sealed, air-tight polyethylene bags and immersed in a room temperature (20–22 °C) water bath to cure.

Table 1 provides the compositions of all sample mixtures. The Pb and Zn concentrations were each either 0 or 1.00 wt% of cement (i.e., 0.01 g of metal per gram of cement). Sucrose and sorbitol ranged from 0 to 0.40 wt%. Two types of control sample were prepared. The first ("Control") consisted only of hydrated Portland cement; the second ("Control M") additionally contained Pb and Zn but no sorbitol or sucrose. At least 12 test cylinders were prepared of each mixture, which allowed the strength, leachability and loss on ignition to be determined in triplicate after four different curing periods: 7, 14, 28, and 56

Table 1
Sample compositions

Batch name	Pb content (wt% of cement)	Zn content (wt% of cement)	Sorbitol/sucrose content (wt% of cement)
Control	0	0	0
Sorbitol	0	0	0.40
Sucrose-low	0	0	0.15
Control M	1.00	1.00	0
Sorbitol M	1.00	1.00	0.40
Sucrose-low M	1.00	1.00	0.15
Sucrose-high M	1.00	1.00	0.38

days. Additional tests were performed for the metal-free mixtures after curing 1 day (loss on ignition) and 3 days (loss on ignition and strength), and for the waste-containing mixtures after 71 days (leachability).

2.2. Strength testing

Immediately after they were removed from the molds, sample cylinders were capped top and bottom with sulfur according to ASTM C617-98 [19] and the unconfined compressive strength was measured according to ASTM C109 [20].

2.3. Loss on ignition testing

A small portion of each sample was crushed and ca. 1.5 g of the 850–2000 μm fraction oven-heated for 24 h at 105 °C to find the evaporable water-free weight, W_{105}, and again for 2 h at 1005 °C to determine the fully dehydrated weight, W_{1005}. The degree of hydration α_{LI} is given by the equation

$$\alpha_{LI} = \frac{W_{105} - W_{1005}}{0.24 W_{1005}} \tag{1}$$

in which 0.24 is the reported fraction of non-evaporable water in fully hydrated Portland cement [2,21].

2.4. Standard leaching procedure

The mobility of Pb and Zn in treated waste samples was determined using the regulatory Toxicity Characteristic Leaching Procedure (TCLP) [22]. 20.0 g of sample with particle size 425–850 μm was combined with 400 mL 0.100 M acetic acid (pH 2.88) in a 500 mL polypropylene bottle and rotated end-over-end at 30 rpm for 18 h at room temperature. The extract was passed through a 0.7 μm borosilicate microfiber filter, and its pH measured using a Metrohm 6.0233.100 combination glass electrode. It was then acidified to pH 2 with concentrated nitric acid and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Varian Vista Pro ICAP Radial spectrometer. The detection limits for Pb and Zn were 0.025 and 0.05 mg/L, respectively.

Although the TCLP is a static batch test and does not simulate actual field conditions, it remains the standard regulatory method for monitoring the performance of full-scale cement-based stabilization/solidification operations in North America and for

laboratory studies of the leaching behavior of cement-stabilized waste.

2.5. Microstructure analyses

After reaching the desired curing time, a small slice (*ca.* 0.5 g) was removed from the inner part of the sample cylinder, immersed for 24 h in acetone to halt hydration [23], dried at 105 °C for 15 min, and then imbedded in epoxy resin. An oriented thin-section was cut, lapped and polished using oil-based media so as not to alter the water-soluble minerals. After carbon-coating, it was analyzed with a JEOL JSM 5900 scanning electron microscope in backscattered electron (BSE) mode to improve contrast between different mineral phases [24,25]. The elemental composition of mineral phases was determined by X-ray energy dispersive spectrometry (EDS) using an Oxford Link ISIS system (120 s live-time) calibrated with corundum for Al, barium sulfate for S and O, orthoclase for Si and K, periclase for Mg, wollastonite for Ca, and jadeite for Na. Pure metal standards were used to calibrate Fe, Pb and Zn. SEM-EDS analyses were carried out on days 7, 28, and 56 for the samples containing Pb and Zn. The metal-free samples were analyzed on days 1, 7, and 56.

2.6. Grey level analyses

Each BSE image consists of 1280×960 pixels having grey levels ranging from 0 (black) to 256 (white). The grey levels are directly related to the atomic number of the material, and thus can be used to distinguish between mineralogical phases: unhydrated cement grains are the brightest features, CH and other hydration products (abbreviated OHP, mainly composed of CSH) appear as two shades of grey, whereas pore space is black. These phases also appear as separate peaks in grey-scale histograms (Fig. 1), and the areas under these peaks can be used to calculate the percentage of individual phases [25,26]. For each sample, calculations were carried out on 15 adjacent BSE images and the results were averaged to obtain a representative phase distribution. Each image measured 254×190 μm, yield-

ing a resolution of 0.198 μm/pixel. The degree of hydration of a sample can also be calculated from the results of grey level analyses [27]:

$$\alpha_{GL} = 1 - \frac{UC_i}{UC_0} \tag{2}$$

in which UC_i and UC_0 are the area fractions of unhydrated cement particles at time t_i and the start of the hydration process, respectively. The value of UC_0 can be evaluated from the densities of Portland cement ($d_c = 3.14$ g/cm³) and water ($d_w = 1.00$ g/cm³) and the water-to-cement mass ratio ($R = 0.40$).

$$UC_0 = \frac{1/d_c}{(1/d_c) + (R/d_w)} \tag{3}$$

2.7. XRD analyses

The mineralogy of the metal-containing samples at day 7 was characterized by X-ray diffractometry using a Philips PW 1050-3710 diffractometer with Cu-Kα radiation. Scans were carried out in the range $5° < 2\theta < 75°$ with a 0.04° step interval and a counting time of 2 s per step.

3. Results and discussion

3.1. Degree of hydration

Fig. 2 depicts degree of hydration as a function of time for pure cement (Control) and cement containing 1% Pb and 1% Zn (Control M). The curing of metal-free cement proceeded in two stages – a period of rapid hydration lasting about 3 days, followed by a slower reaction period exhibiting zeroth-order kinetics – and required 56 days to reach the maximum hydration level of 80%. The addition of Pb and Zn greatly accelerated the overall curing process, with maximum hydration being achieved in only 7 days. It would appear that added metal ions somehow interfere with the mechanistic step(s) responsible for terminating stage-1 of the hydration process.
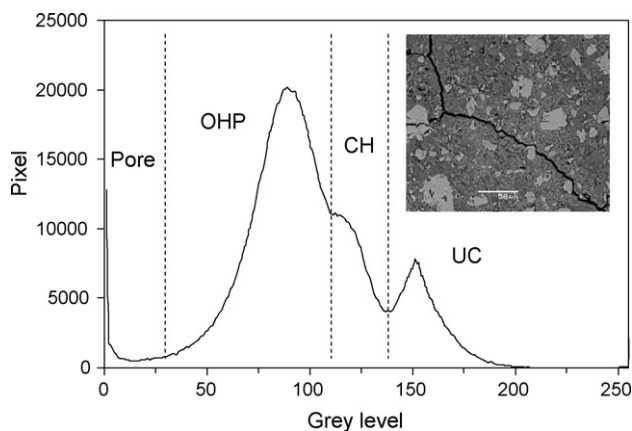

Fig. 1. BSE image of Control sample at day 7 and its grey level histogram obtained with the Image-Pro Plus 5.0 software (UC: unhydrated cement grains, OHP: other hydration products).
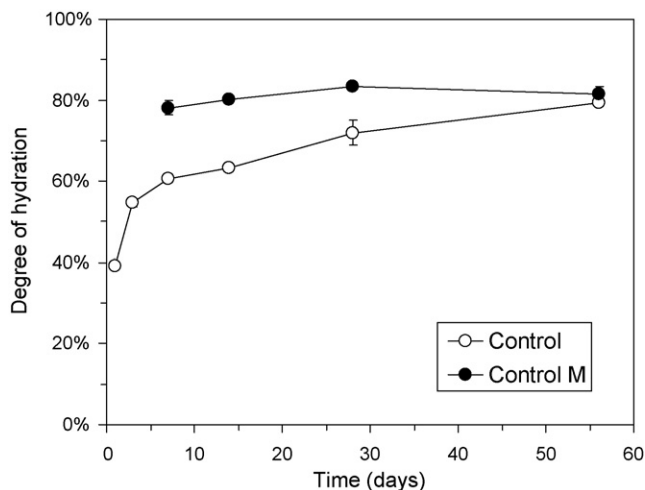

Fig. 2. Effect of 1% Pb + 1% Zn addition on cement hydration rate. Error bars correspond to the standard deviations over three measurements.
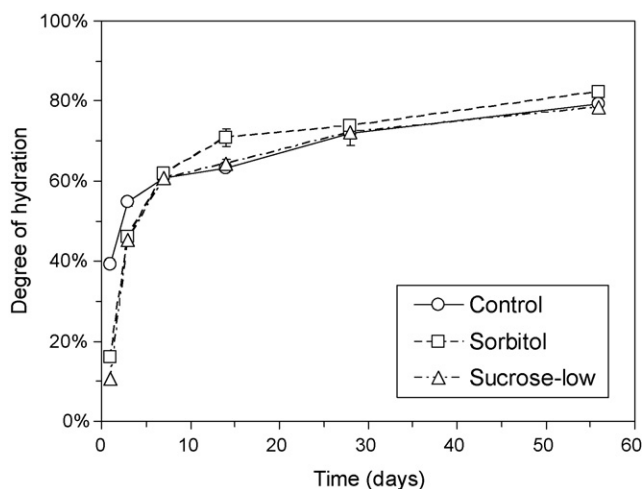
Fig. 3. Effect of sorbitol or sucrose addition on cement hydration rate.

Fig. 4. Effect of sorbitol or sucrose addition on cement hydration rate in samples containing 1% Pb + 1% Zn.

By contrast, previous studies of cement hydration in the presence of lead and zinc found that both metals retarded cement hydration. These studies, however, are not directly comparable to the present one because they were carried out with much larger metal concentrations [28,29] or were limited to early curing times of less than 17 h [30]. The retardation effect of Pb at early times has been explained by the rapid precipitation of colloidal lead hydroxide, sulfate, or hydroxysulfate as a protective membrane around unhydrated cement particles [29,30]. At high concentrations, Zn may precipitate as low permeability $CaZn_2(OH)_6 \cdot H_2O$ around unhydrated calcium silicate particles [28].

Fig. 3 reveals that, unlike added metal ions, sucrose and sorbitol did not radically alter the two-stage reaction profile that characterizes the hydration of pure Portland cement. However, the onset of stage-1 hydration was delayed by about 2 days in cements containing 0.15 wt% sucrose (Sucrose-low) or 0.40 wt% sorbitol (Sorbitol). Also, the sorbitol-containing mixture was slightly more hydrated after 7 days than either of the other two. The mechanisms by which certain sugars and sugar derivatives retard the hydration of cement are not fully understood. In the "half-salt" theory proposed by Thomas and Birchall [8,12], calcium ions react with sucrose in alkaline solution to form a soluble sucrose–calcium salt complex $Ca(OH)^+ \cdots R_{suc}^-$ (pK_{a1} of sucrose = 12.6). The pendant $Ca(OH)^+$ group in the half-salt is thought to adsorb onto growing calcium hydroxide (CH) nuclei and thus inhibit further precipitation of calcium and hydroxide ions on the poisoned surface. The precipitation of CSH gel, which relies on the deposition of silica on an existing CH lattice, is thought to be similarly inhibited by poisoning of the CH surface. Although published evidence supporting the existence of aqueous calcium-sucrose complexes is limited, Pannetier et al. [31] report formation of stable $Ca(OH)R_{suc}$ species in dilute alkaline solution and polymeric $[Ca(OH)R_{suc}]_n$ as the concentrations are increased. By contrast, no specific retardation mechanism has been proposed for sorbitol which, at best, interacts weakly with calcium ions (pK_{a1} = 13.6) [32]. Unlike sucrose, however, sorbitol is able to form $[HOSi(R_{sor})_2]^-$ and $[Si(R_{sor})_3]^{2-}$ complexes with aqueous silicon in high pH sur-

roundings [14]. These anionic complexes may play a role in delaying the hydration of cement (possibly through $Ca(OH)^+$ association) and contribute to the enhancement observed in the strength and final degree of hydration of cement mixtures containing sorbitol by crosslinking in the solid cement matrix.
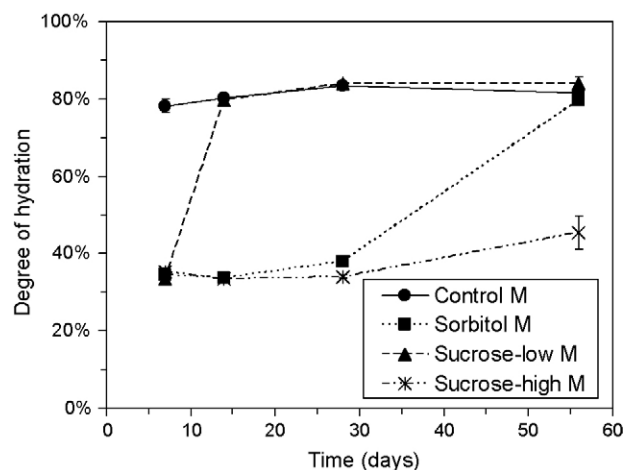
When added together with the metal ions, sucrose and sorbitol countered the accelerating influence of Pb and Zn on cement hydration, as demonstrated in Fig. 4. Surprisingly, they were more effective at inhibiting hydration for the cement containing Pb and Zn than for pure cement. Addition of 0.15 wt% sucrose (Sucrose-low M) or 0.40 wt% sorbitol (Sorbitol M) limited the degree of hydration to 35% for at least 7 or 28 days, respectively. Thereafter, the reaction quickly went to completion (80% degree of hydration), that is, without going through stage-2 hydration. Addition of 0.38 wt% sucrose (Sucrose-high M) maintained hydration at 35–40% through the entire 56 day experiment.

3.2. Grey level analyses

Grey level analyses were carried out on Control and Control M samples at 7 days. The percentage of unhydrated cement was lower in the Control M sample ($10.2 \pm 1.9\%$) than in the Control sample ($15.1 \pm 2.6\%$) at a confidence level of 99.997% (Student t-test). The degrees of hydration calculated from grey level analysis using Eq. (2) ($\alpha_{GL} = 65.9 \pm 5.9\%$ for the Control sample and $77.0 \pm 4.3\%$ for the Control M sample) are consistent with those independently calculated by loss on ignition using Eq. (1) ($\alpha_{LI} = 60.7 \pm 0.7\%$ for the Control sample and $78.1 \pm 1.7\%$ for the Control M sample, see Fig. 2). Hence, both methods of measuring degree of hydration show that the presence of 1% Pb and 1% Zn improves hydration at 7 days. By contrast, grey level analyses reported by Ouki and Hills [26] found that the addition of 1% Pb or 1% Zn *decreased* hydration of Portland cement at 29 days by 29% and 11%, respectively.

Table 2
Summary of sample setting status and main hydration products found by SEM-EDS[a]

Sample	Day 1	Day 7	Day 28	Day 56
Control	CH, CSH	CH, CSH	na	CH, CSH
Control M	na	CH, CSH, ettringite [b]	CH, CSH, ettringite [b]	CH, CSH, ettringite [b]
Sorbitol	CH	CH, CSH	na	CH, CSH
Sucrose-low	CH	CH, CSH	na	CH, CSH
Sorbitol M	na	ettringite, CH [b], CSH [b]	ettringite, CH, CSH	ettringite, CH, CSH
Sucrose-low M	na	ettringite, CSH [b]	ettringite, CH, CSH	ettringite, CH, CSH
Sucrose-high M	na	ettringite	ettringite, CH	ettringite, CH, CSH

[a] Shading indicates that the cement was not set. Light shading indicates that the cement was partially set. No shading indicates that the cement was set. CH: calcium hydroxide; CSH: calcium silicate hydrate; na: not analyzed.
[b] Only a small amount of this phase was detected.

3.3. Strength tests

Table 2 indicates the setting status (unset, set, or partially set) of all the samples at various stages of curing. Several of the samples (e.g., samples containing both metals and sorbitol at day 1 and day 7) were poorly solidified and friable when removed from the molds, exhibiting less than 400 psi (2.76 MPa) compressive strength and under 35% degree of hydration. Hence, they were deemed to be unset. By contrast, cement was considered to be set when compressive strength exceeded 2000 psi (13.8 MPa) and the degree of hydration was over 45%. Two samples (Sorbitol M at day 28 and Sucrose-high M at day 56) were deemed to be only partly set. They consisted of millimetre-sized pebbles of cured cement within a poorly consolidated matrix, while exhibiting less than 400 psi compressive strength and 35–45% hydration.
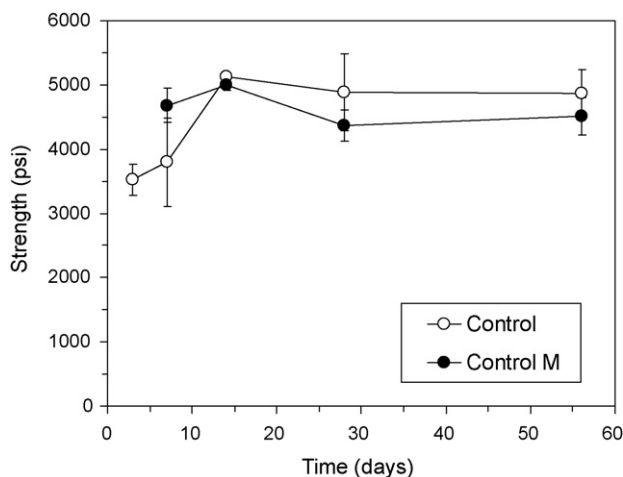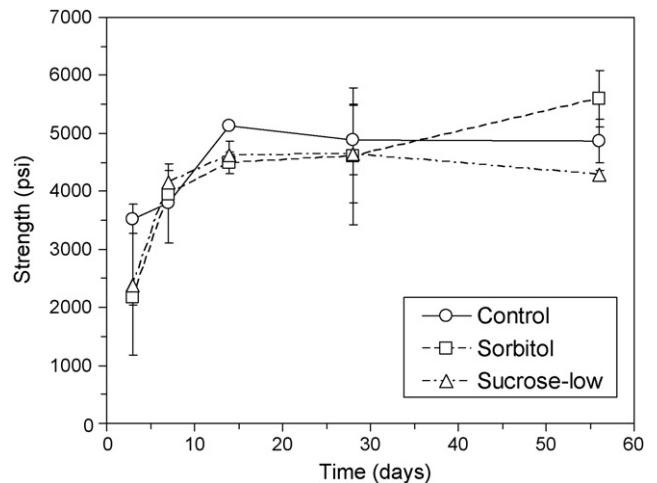

Fig. 6. Effect of sorbitol or sucrose addition on the development of cement strength.

Comparison between Figs. 5–7 and Figs. 2–4 reveals that evolution of compressive strength correlates closely with that of the degree of hydration.

Pure cement (Control) reached a maximum strength of *ca.* 5000 psi (34.5 MPa) after 14 days (Fig. 5). The addition of 1% Pb and 1% Zn (Control M) resulted in higher strength at day 7 compared to pure cement (86% confidence, based on Student *t*-test). This result reflects the higher degree of hydration for the Control M sample compared with the Control sample at day 7, and is also in accordance with the findings of Tashiro et al. [33] who reported increased strength for cement containing between 0.5% and 5% PbO·Pb(OH)$_2$ or 0.5% Zn(OH)$_2$ at 3 days and 28 days. In the present study, however, there was statistically no difference between the strengths observed for pure and metal-containing cement from day 14 onwards.

The effect of low sucrose and sorbitol addition on the compressive strength of metal-free cement is shown in Fig. 6. Strength was reduced at day 3 for samples containing 0.15 wt% sucrose or 0.40 wt% sorbitol, but caught up with that of pure cement by day 7. At day 56, the sample containing sorbitol was slightly stronger (81% confidence level), which confirms previ-

Fig. 5. Effect of 1% Pb and 1% Zn addition on cement strength. Error bars correspond to the standard deviations over three measurements.
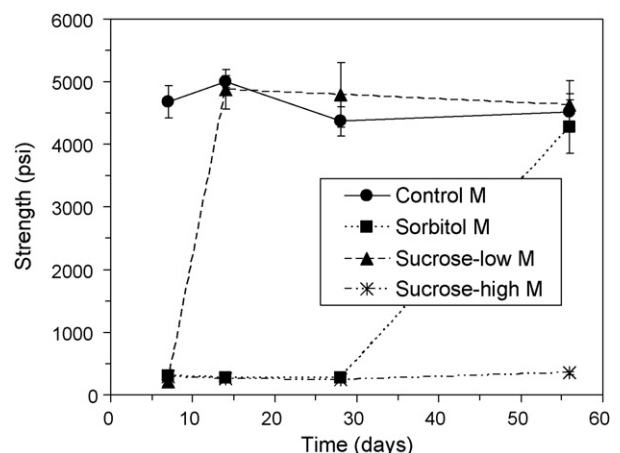

Fig. 7. Effect of sorbitol or sucrose addition on strength of samples containing 1% Pb + 1% Zn.
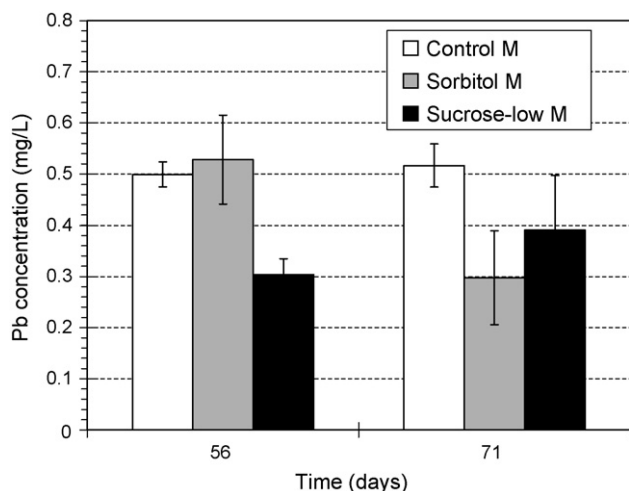
Fig. 8. Dissolved concentration of Pb in TCLP extracts. Error bars correspond to the standard deviations over three measurements.

Fig. 9. Dissolved concentration of Zn in TCLP extracts.

ous reports that sorbitol improves the strength of OPC after 28 days [16]. These results parallel the influence that sucrose and sorbitol had on the degree of hydration (Fig. 3).

Similarly, the influence of added sucrose or sorbitol on the strength of cement containing Pb and Zn (Fig. 7) parallels their effect on the hydration of these samples (Fig. 4). The addition of 0.15 wt% sucrose (Sucrose-low M) or 0.4 wt% sorbitol (Sorbitol M) delayed cement setting for at least 7 and 28 days, respectively, with the strength of these samples rising to that of Control M immediately thereafter. These findings have practical importance because they demonstrate that controlled addition of sucrose or sorbitol can delay the setting of S/S-treated metal waste for several days, thus adding flexibility for transportation to the final disposal site without negatively impacting the final product strength. However, excessive sucrose addition (Sucrose-high M; 0.38 wt%) delays setting beyond 56 days with unknown effects on final strength.

3.4. Leaching tests

Fig. 8 shows the average concentrations and standard deviations of dissolved Pb in the TCLP extracts at day 56 and day 71 for the Control M, Sucrose-low M, and Sorbitol M samples, all of which were fully set by this time. The leachability of Pb from the cement containing sorbitol decreased between the two curing periods, but remained constant within experimental uncertainty for the other samples. On day 71, the average leachability of Pb for the control sample was 0.52 ± 0.04 mg/L. Sucrose or sorbitol addition significantly inhibited lead leachability, the final values being 0.30 ± 0.09 mg/L for 0.40 wt% sorbitol (leaching inhibited with 96% confidence) and 0.39 ± 0.11 mg/L for 0.15% sucrose (84% confidence). It is worth noting that differences in leachability were not caused by pH variations in the TCLP extracts; the final extract pH after 18 h agitation was 12.4 for all the samples.

Fig. 9 shows the concentration of Zn in the TCLP extracts. Between 56 and 71 days, the zinc leachability decreased for the control and sorbitol-containing samples (93% and 84% con-
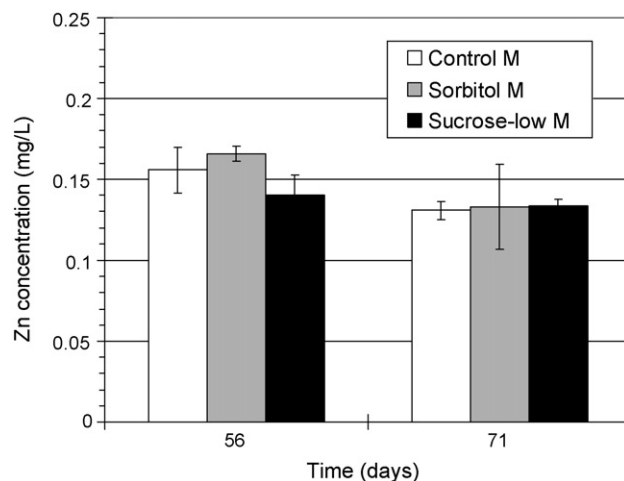
fidence, respectively) but did not significantly change for the sample containing sucrose. Unlike the results obtained for lead, the addition of sucrose or sorbitol to cement had no significant effect on Zn leachability by day 71.

3.5. Microstructure analyses

Table 2 lists the hydration products identified in each cement sample at different curing times and indicates whether or not the samples were set.

In agreement with previous studies [24], calcium hydroxide and CSH were the main hydration products of pure Portland cement (Control). Cement containing 1% Pb and 1% Zn (Control M) had the same microstructure as metal-free cement (Fig. 10). Shells of smooth-textured CSH surrounded unhydrated cement grains (C_3S primarily), while irregularly textured CSH occupied much of the void space that was originally filled with water. These two different CSH phases respectively correspond to what Diamond [34] terms "inner" and "outer" CSH.
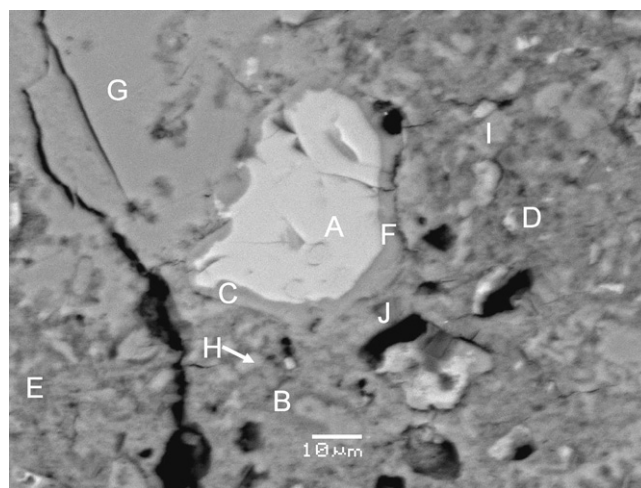

Fig. 10. Backscattered electron images of Control M sample (1% Pb + 1% Zn) at day 56 showing (A) C_3S, (C and F) inner CSH, (B, D, and E) outer CSH, (G, H and I) CH, and (J) ettringite.
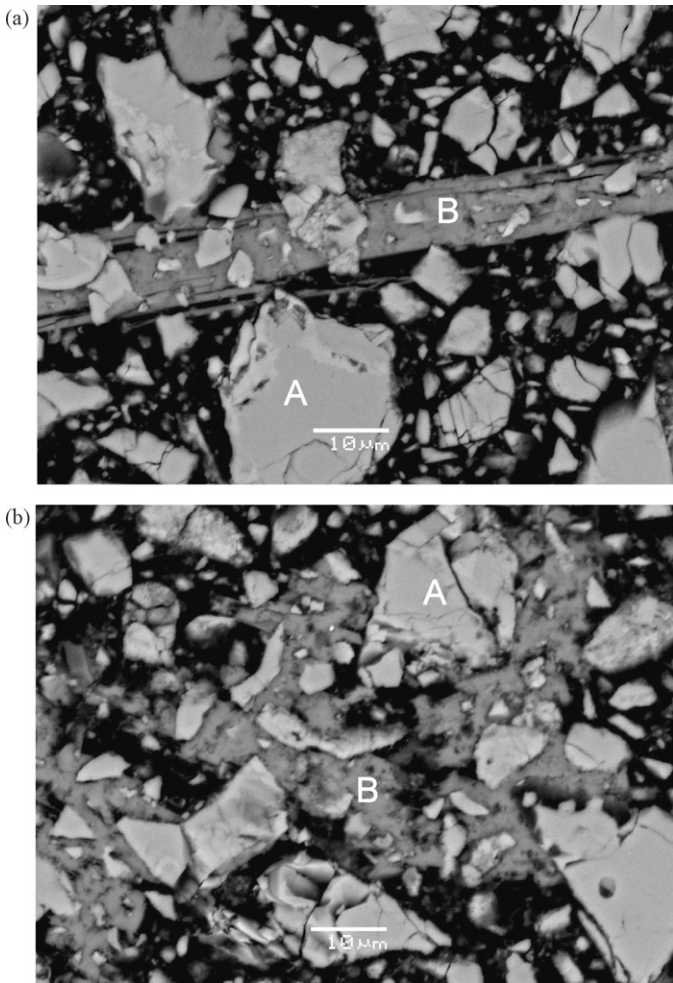
Fig. 11. Backscattered electron images of (a) Sucrose-low and (b) Sorbitol samples at day 1 showing the (A) unhydrated C_3S phase and (B) CH.
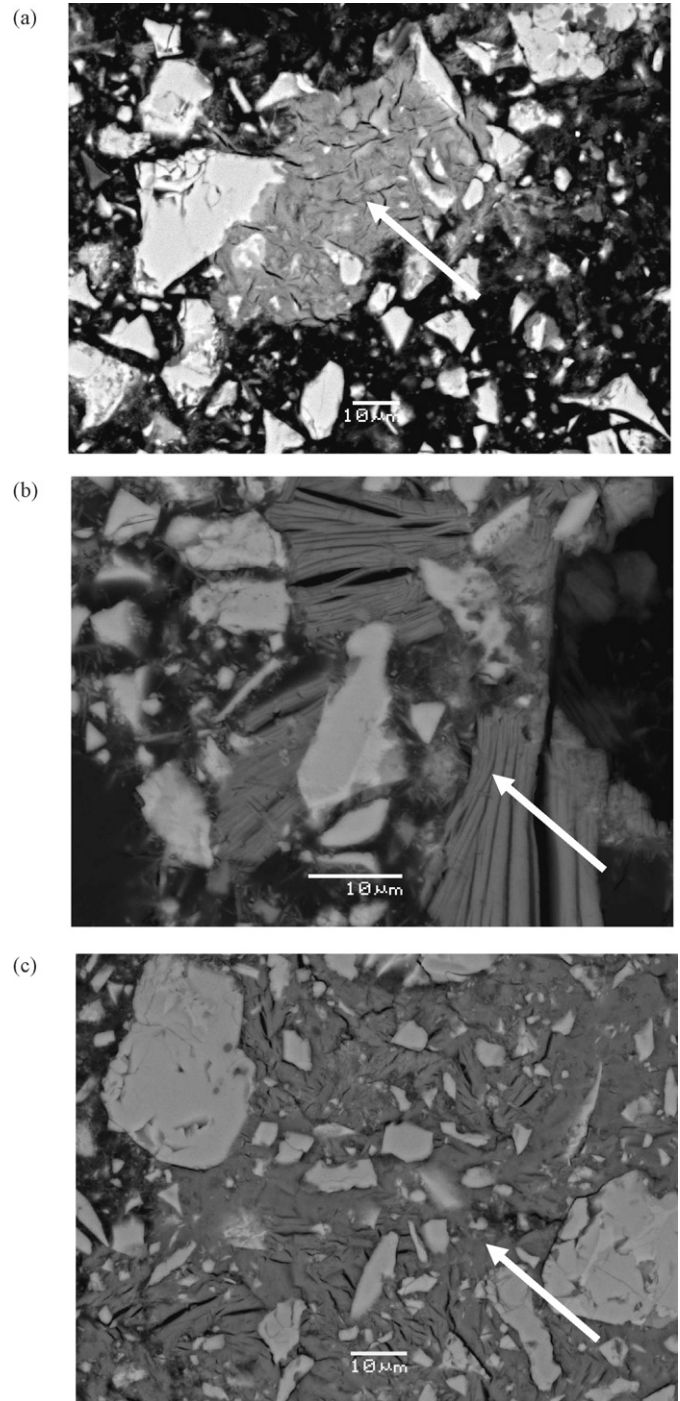

Fig. 12. Backscattered electron images of (a) Sorbitol M, (b) Sucrose-low M and (c) Sucrose-high M at day 7. The Al-rich phase is indicated by arrows. Bright areas are unhydrated cement consisting mainly of C_3S. None of these samples were set by day 7.

Small amounts of the Ca–Al-hydroxysulfate phases ettringite and monosulfate were disseminated throughout the sample and also might have been intermixed within the CSH as is suggested by the small amounts of Al and S detected in that phase (typically less than 2 atom%). Taylor [35] reports that Ca–Al-hydroxysulfate can intermix with CSH at the micrometer to single-layer scale which is too small to be resolved by SEM-EDS. Lead and zinc were mostly present in CSH at concentrations between 0.9 and 1.8 wt%. Ettringite and calcium hydroxide have much lower Pb and Zn concentrations (typically less than 0.8 wt%).

The addition of sorbitol or sucrose to metal-free cement delayed CSH formation. At day 1, CH was the only hydration product detected in the Sucrose-low and Sorbitol samples (Fig. 11). From day 7 onwards, however, these samples contained both CSH and CH.

When sucrose or sorbitol was added to cement in combination with Pb and Zn (Sucrose-low M, Sucrose-high M, Sorbitol M), the first hydration phase to appear consisted of platy Al-rich crystals (with cracks that were probably caused by drying; Figs. 12a–c). It was identified by X-ray diffractometry as ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ (Fig. 13). However, the average elemental composition determined by more than 50 independent EDS measurements – $Ca_{6.00}Al_{2.41}S_{0.45}O_{18.42}Fe_{0.11}Si_{0.57}Pb_{0.06}Zn_{0.11}$– indicates a much lower S/Ca ratio than that of ettringite. Therefore, it is likely that ettringite was intermixed with unhydrated C_3A, which would account for the low sulfur content. The presence of Fe, Si, Pb and Zn indicates that the ettringite contains impurities. As mentioned already, ettringite was also found in the absence of sucrose and sorbitol (Control M), but in
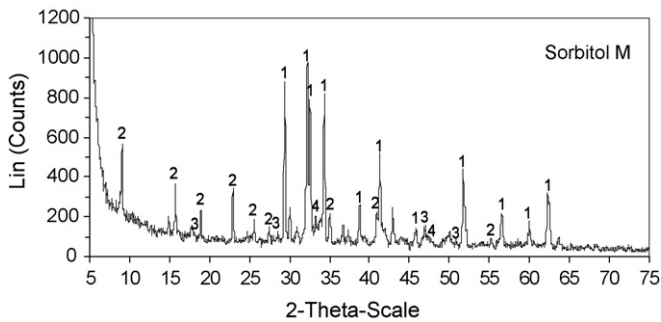
Fig. 13. X-ray diffractogram of the Sorbitol M sample at day 7, showing (1) C_3S or C_2S, (2) ettringite, (3) portlandite (CH), and (4) C_3A.
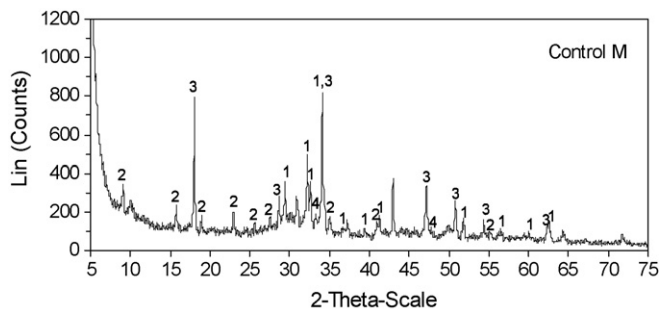

Fig. 14. X-ray diffractogram of the Control M sample at day 7, showing (1) C_3S or C_2S, (2) ettringite, (3) portlandite (CH), and (4) C_3A.

much smaller amounts and coexisting with CH and CSH (Figs. 10 and 14).

As the samples containing metal and sucrose or sorbitol began to set, the amounts of calcium hydroxide and CSH increased (Table 2). Fig. 15 shows a backscattered electron image of the Sucrose-high M sample at day 56, by which time partial setting had occurred. The image depicts ettringite coexisting with CSH (characterized by Ca/Si = 2.5–3.0:1) and a transition product which contains a significant concentration of Al (Ca/Al = 3–5:1) and a lower Si concentration than CSH (Ca/Si = 3–8:1).

The elemental composition at several points within the ettringite, CSH and transition product was measured by EDS on
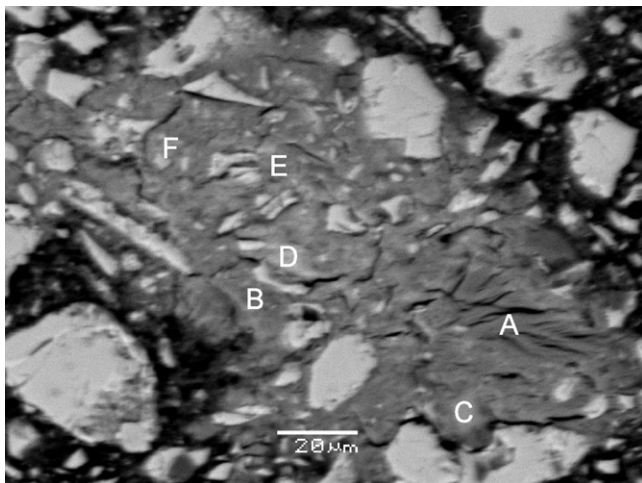

Fig. 15. Backscattered electron image of the Sucrose-high M sample at day 56, showing (A and B) ettringite, (C and D) CSH, and (E and F) transitional product.
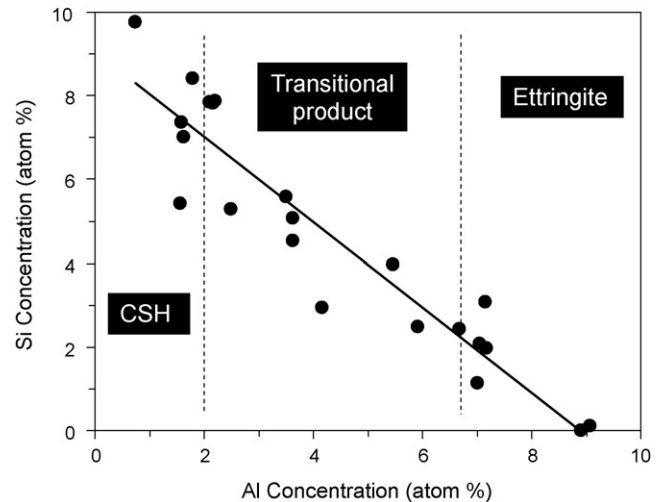

Fig. 16. Concentration of Si as a function of Al concentration in the Sucrose-high M sample at day 56.

several backscattered electron images of the Sucrose-high M sample at day 56 and plotted in Figs. 16 and 17. Three regions corresponding to CSH (low Al content), ettringite (high Al content) and the transitional product (intermediate Al content) are superimposed on the graphs. Similar results were obtained for the Sorbitol M sample (data not shown). The Si concentration increases almost linearly as the Al concentration decreases (Fig. 16), representing the transition from ettringite to CSH. Fig. 17 indicates that Pb and Zn concentrations vary widely, from 1 to 6 wt%, in CSH (corresponding to low Al concentration). By contrast, the range of Pb and Zn concentrations is relatively limited, less than 2 wt%, in ettringite. The larger capacity of CSH for immobilizing Pb and Zn is likely explained by structural differences: ettringite forms hexagonal prismatic or acicular crystals in which ion substitutions are the only significant immobilization mechanism [3], whereas CSH is an amorphous gel which allows Pb and Zn atoms to be immobilized through a variety of mechanisms such as sorption, coprecipitation, and formation of metallosilicates [3–7].
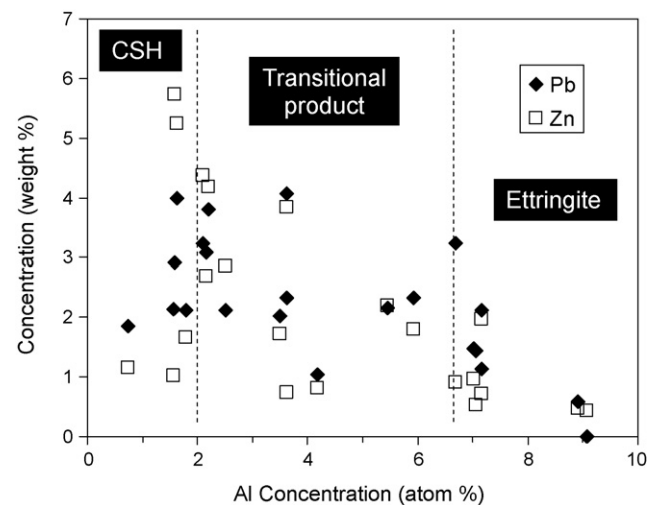

Fig. 17. Concentrations of Pb and Zn as a function of Al concentration in the Sucrose-high M sample at day 56.

4. Conclusions

1. The presence of 1 wt% Pb and 1 wt% Zn significantly shortens the time at which maximum hydration of Portland cement is achieved, but has relatively little effect on the final compressive strength.
2. The addition of 0.15 wt% sucrose or 0.40 wt% sorbitol to metal-free Portland cement retards hydration and strength development for 3 to 7 days.
3. The retardation effect of sucrose and sorbitol are considerably enhanced when Pb and Zn are present. Controlled sucrose or sorbitol addition to metal-cement mixtures can retard setting for up to 28 days without affecting the 56-day strength, thus adding flexibility to the handling of S/S-treated waste.
4. The long-term TCLP-based leachability of Pb may be somewhat reduced by the addition of sucrose or sorbitol; however, the long-term leachability of Zn is not significantly affected.
5. Cement setting correlates with the precipitation of CSH gel. Precipitation of ettringite was favored and the formation of CSH and CH were delayed when sorbitol or sucrose was added to metal-cement mixtures.
6. The ability of ettringite to immobilize Pb and Zn is inferior to that of CSH.
7. Sorbitol conferred a slightly higher degree of hydration and compressive strength than sucrose to Portland cement after 56 days.

Acknowledgement

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