Pergamon

Cement and Concrete Research 29 (1999) 55–61

CEMENT AND CONCRETE RESEARCH

Encapsulation of steel foundry bag house dusts in cement mortar

Ian W. Hamilton [a], Nigel M. Sammes [b,*]

[a]Golden Bay Cement, Portland, Whangarei, New Zealand
[b]Department of Technology, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Manuscript received 6 November 1997; accepted manuscript 17 September 1998

Abstract

The purpose of this study was to investigate the properties of bag house dusts generated by steel foundries when stabilized with Portland cement at high levels of cement addition. The main bag house dust studied was obtained as a byproduct of steel manufacture, at Pacific Steel Limited in Auckland, New Zealand, whereas others were sourced from BHP New Zealand Steel, Masport, and A&G Price foundries. The main examination techniques used in this study were leachate testing, scanning electron microscopy, X-ray diffraction, and compressive strength measurements. The findings showed that all the dusts investigated varied in their composition and physical makeup. Those bag house dusts that contained elevated levels of zinc severely retarded the hydration of cement within the first 2 weeks, but accelerated the strengths at late ages (28 days). The zinc was predominantly in the form of zinc oxide, which, when mixed with cement, produced the complex, calcium zinc hydrate. When cement was doped with zinc oxide, it was also found to display the same type of retardation as was found with the high ZnO bag house dusts. Lead also displayed a slight accelerating phenomena at 28 days, but the retention of lead in stabilized materials, as measured by the toxicity characteristic leaching procedure, was higher than that for zinc. The Masport, A&G Price, and two BHP New Zealand Steel bag house dusts did not show accelerating characteristics; however, Pacific Steel and the other two BHP New Zealand Steel zinc oxide-containing bag house dusts did. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Waste management; Mortar; Reaction; Heavy metals

Solidification and stabilization technologies are being used to treat a variety of wastes that have been previously land filled or dumped, without any form of treatment. Solidification is the process of encapsulating wastes, whether as solutions or solids, and forming a monolithic structure [1]. This structure should have mechanical integrity and thus be able to take some weight without disintegrating. Solidification does not necessarily reduce leaching or affect the hazard capacity of the wastes. Solidification sets up a barrier between waste and the environment, thus limiting permeability of the waste to water and reducing the surface area available for diffusion. To reduce leaching, a stabilization process must take place [2]. This process of stabilization reduces the leachability of certain constituents by chemical means such as altering the pH, as shown by lead and zinc stabilization.

1. Stabilization

1.1. Lead

At below pH 8 and above pH 12, there is an increase in the amount of lead leaching [3]. Lead compounds react differently with cement depending upon their solubility to solutions. Lead compounds that are soluble in alkaline solutions retard the set of cement, whereas lead salts that are insoluble in water have not been found to retard the cement reaction [4]. Lead shows normal hydration after a period of retardation giving superior strengths at 28 days and beyond. Due to lead not being detected [5] by x-ray diffraction, it can be postulated that the lead compounds in the cement are amorphous.

1.2. Zinc

Zinc leaching is also strongly controlled by pH, and, in a similar way to lead, its hydroxides are least soluble at specific pH ranges [6]. If zinc is present as a hydroxide, the stabilization system must be tailored to approximately pH 9. It has also been found that zinc is preferentially deposited on the surface of the cement particles. Stabilization, using a Portland cement/sodium silicate mix [7], showed that, although the material was porous, the amount of leached zinc was low. This would indicate that permeability was not an important factor for determining the movement of this metal through the material. Chemical stabilization rather than encapsulation is believed to reduce movement of zinc in stabilized waste [8].

---

* Corresponding author. Tel.: 64-7838-4065; Fax: 64-7838-4835; E-mail: n.sammes@waikato.ac.nz.

0008-8846/99/$–see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(98)00169-0

Table 1
Chemical composition of the bag house dusts, fly ash, and cement

Element	Percent of each element detected Pacific Steel	A&G Price	Masport	Meter metal side fume	Electric arc furnace	Meter metal slag side fume	KOMB secondary fume
O	15.4	6.5	56	29	7	4.5	28
Na	4.7	2.9	2.8	0.9	1.3	2.4	1
Mg	0.8	15.8	0.8	0.4	2	1.9	2.5
Al	0.2	0.6	2.2	0.1	0.3	0.3	0.2
Si	1.2	4.8	10.9	0.4	1.2	1	0.7
P	0.2	0.2	0.1	0.1	0.1	0.2	0.1
S	0.8	1.6	0.5	0.2	0.9	0.9	0.2
Cl	2.2	1.6	2.7	0	1.2	1.2	0.2
K	1.3	1.6	0.6	0	1.1	1	0.2
Ca	1.4	9	0.7	0.6	2.6	2.3	2.6
Ti	0	0	0	0.2	0.2	0.2	0.1
V	0	0	0	0.2	0.2	0.2	0.3
Cr	0.2	0.5	0.1	0	0.1	0.1	0.1
Mn	1.1	10.5	1.3	0.4	2.4	1.9	0.6
Fe	14.8	34.6	9.4	66.2	39.9	34.3	61.9
Cu	0.1	0.3	0	0	0.1	0.1	0
Zn	49.8	7.7	8.2	1.2	37.6	45	1.2
Sr	0	0	0	0	0	0	0
Zr	0	0.1	0	0	0	0	0
Pb	4.9	1.5	3.5	0	1.7	2.3	0.1
Total	99.1	99.8	99.8	99.9	99.9	99.8	100

Sc, Rh, Ag, In, Sb, Te, I, Ce, Nd, Sm, Gd, Dy, Hf, Ta, Pt, Au, Hg, Tl, Th, Th, and U were not detected.

Zinc in different forms (for example, zinc oxide and zinc sulfate) has been understood for many years to retard the hydration of cement [9]. Although ZnO severely retards cement hydration during an initial period, it has also been found to increase the strength at late ages (28 days and more) [10]. This retarding effect is believed to be due to the zinc forming a protective cover of an amorphous zinc hydroxide or some other form of oxy-compound on the grain surfaces [11]. Lieber [12] found that no $Ca(OH)_2$ was formed during the period of retardation. It is believed that, after this retardation period, high concentrations of Ca^{2+} and OH^- present in the pores transform zinc hydroxide to crystalline calcium zinc hydroxide, $Ca[Zn(OH)_3H_2O]_2$ [13]. This calcium zinc compound starts to diminish, and the hydration of C_3S commences with the subsequent formation of $Ca(OH)_2$. With the hydration of C_3S, no new zinc compounds were detected; thus, it would be concluded that the zinc has entered the crystal lattice.

2. Experimental methods

2.1. Materials

The cement used was manufactured by Golden Bay Cement, Whangarei, New Zealand, and was type GP–general purpose Portland cement with no mineral additions. The primary dust studied was obtained from Pacific Steel, Auckland, New Zealand. Bag house dusts were also sampled from Masport Limited, Auckland, A&G Price, Thames, and four samples from BHP New Zealand Steel, Glenbrook. The samples were received in a dry state, and all bag house dusts were used as received.

2.2. Chemical analysis

Chemical analysis of the materials was carried out using a Siemens SRS303 sequential x-ray fluorescence spectrometer. The powders were pressed into 40-mm discs, using a 30-ton press before being subjected to x-ray analysis. A

Table 2
Summary of the XRD trace for bad house dust inspected

	Pacific Steel	A&G Price	Masport	Meter metal side fume	Electric arc furnace	Meter metal slag side fume	KOMB secondary fume
$ZnFe_2O_4$	Detected	Detected			Detected	Detected	
ZnO	Detected		Detected		Detected	Detected	
Fe_2O_3				Detected			Detected
Fe_3O_4				Detected			Detected
SiC			Detected				
C			Detected				

Table 3
SEM observations showing the comparison of hydration of cement and Pacific Steel bag house dust/cement mixtures (10:90 ratio)

Day	Cement	Pacific Steel/cement mixtures
1	Calcium silicate hydrate and $Ca(OH)_2$ are visible	Two different particles are visible in the cement and bag house dust; no hydration product present
3	Voids are visible and the calcium silicate hydrate appears to have grown into the void; cement grains are visible and $Ca(OH)_2$ can be seen to fill the spaces in between the grains	No hydration prodcucts present
7	It is difficult to distinguish the $Ca(OH)_2$; however needle-like calcium silicate hydrate and shrinkage cracking are visible	A porous weak solid has developed with $Ca(OH)_2$ present in long needle arrangement, in one direction; these “needles” are surrounded by the dust particles; no calcium silicate hydrate is present and it is likely that the $Ca(OH)_2$ is possibly holding the structure together
14	Difficult to distinguish $Ca(OH)_2$ and calcium silicate hydrate. Shrinkage cracking visible	The paste appears to be like hydrated cement with large $Ca(OH)_2$ crystals present on the 5 μm micrograph. A cleaved cement grain can be seen

continuous scan was collected over a wide range of the x-ray spectrum. These data were then compared against data collected from Siemens multielement standards, and the concentrations were calculated.

2.3. X-ray diffraction

The samples were prepared by mixing 4 g of water to each 10 g of solid, for 1 min, undertaken in small plastic containers. The pastes were then stored at 20°C and a relative humidity of approximately 70% for the specified days. The samples were ground by mortar and pestle before being transferred to the powder x-ray diffractometer. The x-ray diffractometer was a Phillips X’PERT system using CuKα radiation, operated at 45 kV and 40 mA. Scanning from 6° to 150° 2ϑ at a rate of 0.75°/min, was performed. Data storage and manipulation were carried out using an IBM personal computer.

2.4. Scanning electron microscopy

Samples were dry mixed before being combined with water at a water-to-solids ratio of 0.4. The pastes were hand mixed for 1 min, then placed into labeled test tubes. The samples were stored at 20°C before being examined in a Hitachi S-4000 scanning electron microscope. The microscope was operated at 20.0 KeV accelerating voltage with a sample incidence angle of 90.0° and an x-ray emergence angle of 68.0°.

2.5. Leaching testing

The samples were mixed to a water-to-solids ratio of 0.4. This was done by mixing 40 g of distilled water to 100 g of

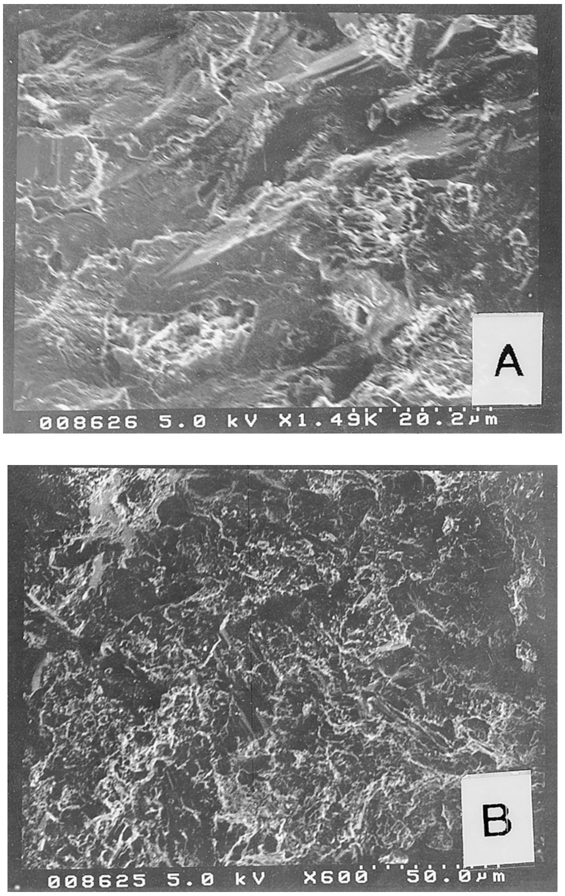

Fig. 1. Micrographs of hydrated cement (A) and Pacific Steel bag house dust/cement mixtures (B).

Table 4
Summary of the XRD traces for ZnO cement doped cement bag house dust inspected after 28 days

	1%	5%	10%	20%
Ca_3SiO_5	Detected	Detected	Detected	Detected
$Ca(OH)_2$	Detected	Detected	Detected	Detected
ZnO				Detected
$Ca(Zn(OH)_3)_2 \cdot 2H_2O$			Detected	Detected

Table 5
Summary of the XRD traces for PbO cement doped cement bag house dust inspected after 28 days

	1%	5%	10%	20%
Ca_3SiO_5	Detected	Detected		
$Ca(OH)_2$	Detected	Detected	Detected	Detected
ZnO	Detected		Detected	Detected
Lead compound	None	None	None	None

Table 6
Summary of the XRD traces for Pacific Steel bag house dust doped cement

	10% cured to 1 day	10% cured to 28 days	20% cured to 28 days	30% cured to 28 days	40% cured to 28 days	50% cured to 28 days
$ZnFe_2O_4$	Detected	Detected	Detected	Detected	Detected	Detected
Ca_3SiO_5	Detected	Detected	Detected	Detected	Detected	Detected
Ca_3SiO_4		Detected	Detected	Detected		
$Ca(OH)_2$		Detected	Detected	Detected		
ZnO	Detected				Detected	Detected
$Ca(Zn(OH)_3)_2 \cdot 2H_2O$				Detected	Detected	Detected

sample. The samples were stored in the laboratory for 28 days at 20°C and a relative humidity of approximately 65%. The samples were crushed to pass through a 9.5-mm sieve and be retained on a 2.36-mm sieve. One hundred grams of sample was added to 2000 g of buffered acetic acid solution at a pH of 4.9 (except for the 100% Pacific Steel bag house dust sample, in which a buffered acetic acid of pH 2.9 was used). The sample and solution were continually tumbled, end over end (30 rpm), for 18 h in a plastic bottle. After 18 h, the leachate was separated by filtering through a borosilicate glass fiber filter. The filtrate was analyzed for zinc and lead using an GBC 901 atomic absorption spectrophotometer.

3. Results and discussion

3.1. Characterization of materials

A critical aspect of stabilization is the characterization of the material to be stabilized. Seven bag house dusts were considered: Pacific Steel, A&G Price, Masport, and four dusts from BHP New Zealand Steel.

3.2. Chemical analysis

The seven bag house dusts (Table 1) were widely different in composition. The results for the iron present ranged from 9.4% to 66.2% because of the way the iron is manufactured at the different foundries. At BHP New Zealand Steel, iron is produced from iron sand, whereas at Pacific Steel, scrap iron is used (scrap contains galvanizing, which uses zinc). All the dusts had relatively high levels of iron when compared to cement. Three of the dusts examined were high in zinc: Pacific Steel, Melter metal slag side fume, and A&G Price. The zinc in these samples was in the range from 35% to 50%. At A&G Price and Masport, only 8% zinc was present; Melter metal side fume and KOBM contained only 1%. A&G Price contained the highest levels of magnesium and manganese. The maximum level of silica was detected in the Masport bag house dust, which also showed a high loss on ignition

3.3. X-ray diffraction

Table 2 summarizes the analysis of some bag house dusts by x-ray diffraction. These results indicate a wide variation in the bag house dusts surveyed. The x-ray diffraction trace for Pacific Steel bag house dust confirms that the zinc is predominately in the oxide form (ZnO). The iron is associated with zinc, as zinc iron oxide ($ZnFe_2O_4$). Where zinc was detected in the other bag house dusts, it also was predominantly in the form of zinc oxide (ZnO). A&G Price bag

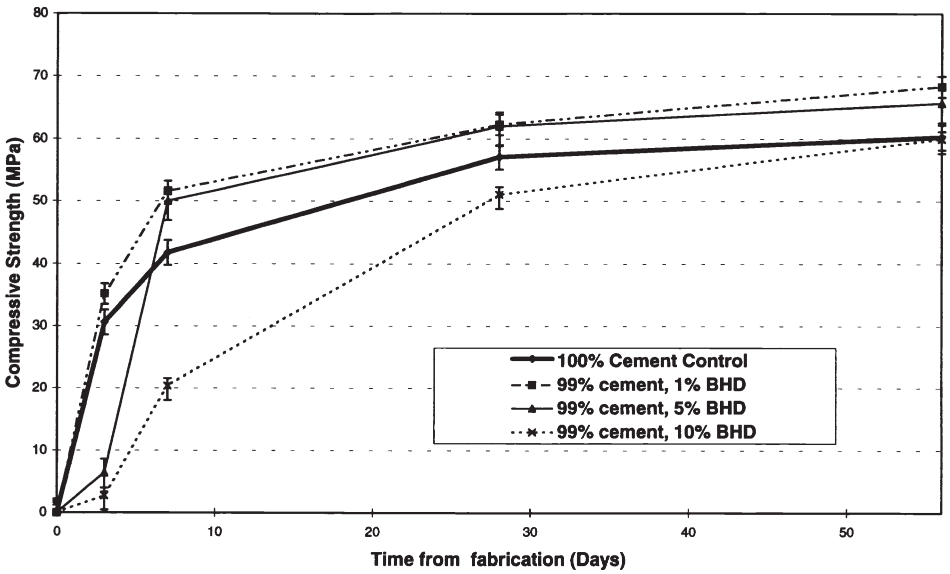

Fig. 2. Compressive strength results of cement and Pacific Steel bag house dust mixtures

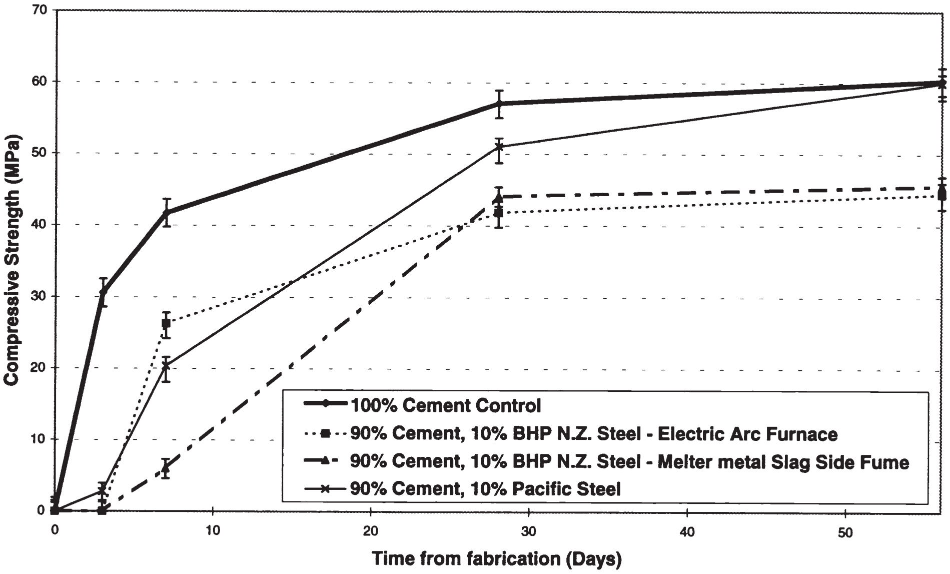

Fig. 3. Compressive strength results for cement and different bag house dusts containing significant amounts of zinc.

house dust was the exception, where the zinc was only detected as $ZnFe_2O_4$. The x-ray diffraction results for Masport bag house dust show that carbon, in the form of graphite, also was present.

In the KOBM and Melter metal side fume samples, iron compounds predominated. The compounds that predominated in Melter metal side fume were hematite, Fe_2O_3, with lesser amounts of magnetite, Fe_3O_4. In contrast, KOBM contained predominately magnetite (Fe_3O_4), with lesser amounts of hematite (Fe_2O_3).

3.4. Scanning electron microscopy

Table 3 presents the findings from the mixture of Pacific Steel bag house dust, compared to normal cement, during the first 14 days of hydration. Calcium silicate and $Ca(OH)_2$, which are the main hydrate products of cement hydration, appear in the first few days.

At 14 days, both pastes appeared to be well hydrated. The material was very brittle, with blunt fracture surfaces. In the Pacific Steel bag house dust mixture, no distinct particles can be seen, and it appears that the bag house dust has been dispersed throughout the whole sample (Fig. 1).

3.5. X-ray diffraction

Cement was doped with differing amounts of zinc oxide and interesting results were obtained (Table 4). At 1% and 5% zinc oxide, $Ca(OH)_2$ was present, but zinc compounds were

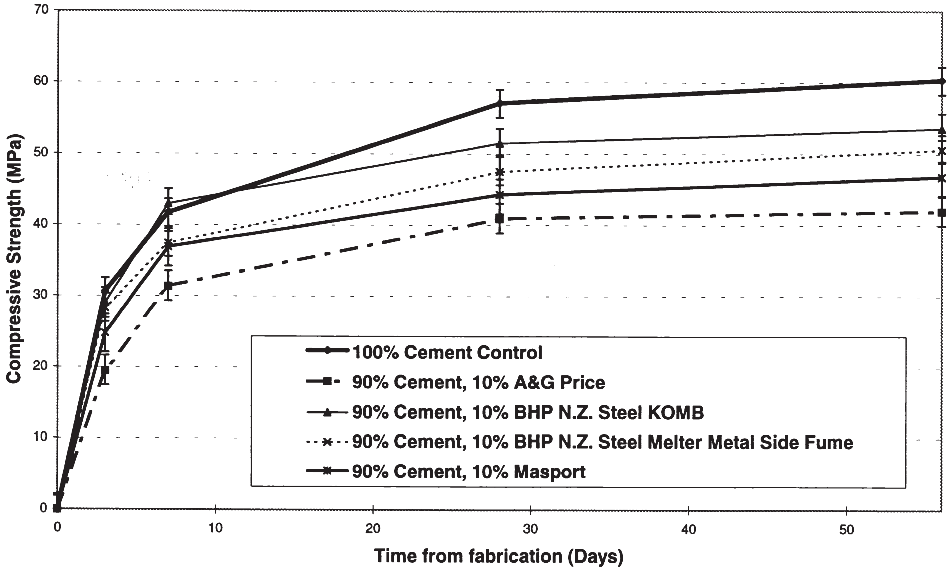

Fig. 4. Compressive strength results for different mixtures of cement and bag house dusts with low levels of zinc.

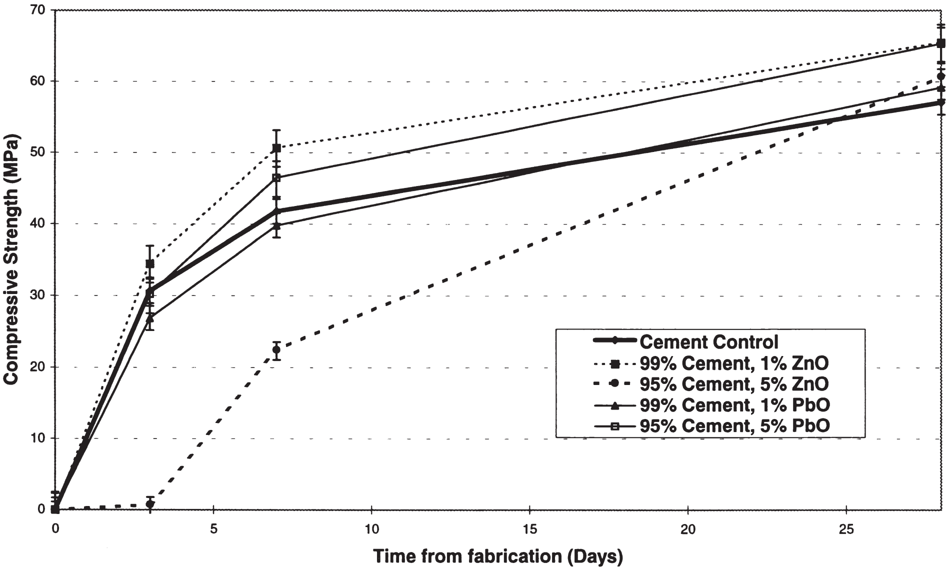

Fig. 5. Compressive strength results zinc and lead doped cement.

not, possibly due to the low level used. As the zinc oxide level was increased to 10% and 20%, calcium zinc hydrate was detected (Eq. 1). Only at 20% was any ZnO detected.

$$ZnO + Ca(OH)_2 + 4H_2O \rightarrow Ca[Zn(OH)_3H_2O]_2 \qquad (1)$$

When cement was doped with lead oxide, no lead compounds were detected (Table 5), even at 20%, which is in agreement with the findings of Rossetti and Medici [15]. However, Portlandite was detected, which is to be expected with normal cement hydration.

A summary of results for cement doped with Pacific Steel bag house dust is shown in Table 6. These results indicate that there is ZnO in the 1-day pastes but none in the 28-day pastes, while $ZnFe_2O_4$ is also present in both the 1-day cured and the 28-day maturity. This is likely due to the fact that $ZnFe_2O_4$ is insoluble in alkali, whereas ZnO is soluble in alkali.

$ZnFe_2O_4$ was detected for all the other combinations, i.e., 20%, 30%, 40%, and 50% mixtures. Calcium zinc hydrate also was detected, being more intense in the 10%, 20%, and 30% mixtures than in the 40% and 50% mixtures. ZnO also was detected in the 30%, 40%, and 50% samples. Due to the zinc retardation, no $Ca(OH)_2$ was detected in the 40% and 50% mixes.

3.6. Compressive strengths

The addition of Pacific Steel bag house dust to cement (Fig. 2), depresses the strengths at 3 days, but increases it after 7 days. Cements doped with 1% and 5% bag house dust were found to have greater strengths than the control cement after 7 days, whereas in the 10% bag house dust, doped cement equal strengths were not reached until 56-day maturity. The 1% doped cement showed similar behavior to the control sample (which may be due to the retardation period being less than 3 days). These results confirm the findings of Sammes and Hamilton [14].

The BHP electric arc furnace, Melter slag side fume, and Pacific Steel bag house dusts contain significant amounts of ZnO and all show the same type of strength growth (Fig. 3), i.e., retardation of strength followed by acceleration.

Four of the bag house dusts studied had lower levels of zinc. The dusts showing slight retardation were those with 8% zinc. Melter metal side fume bag house dust (MMSF) strengths are approximately 10% below the control results (Fig. 4). This would be expected if there are no cementitious compounds in the dust.

When cement was doped with zinc oxide and lead oxide, interesting results were observed. The 5% ZnO/95% cement showed normal retardation, as was observed when cement was doped with Pacific Steel bag house dust (Fig.5). The 1% zinc oxide accelerates the hydration of cement at 3 days and continues to increase at 28 days.

3.7. Leaching

Various quantities of lead and zinc were mixed with cement, and an increase was detected in both the lead and zinc

Table 7
Leachate results for lead and zinc doped cement

	Lead (mg/L)	Zinc (mg/L)
100% Cement	0.3	0.0
99% Cement, 1% PbO	0.5	—
95% Cement, 5% PbO	4.7	—
90% Cement, 10% PbO	12.7	—
80% Cement, 20% PbO	50.1	—
99% Cement, 1%ZnO	—	0.2
95% Cement, 5% ZnO	—	1.1
90% Cement, 10% ZnO	—	2.1
80% Cement, 20% ZnO	—	2.7

Table 8
Leachate results for Pacific Steel bag house dust/cement mixes

	Zinc (%)	Lead (%)	TCLP extract lead (mg/L)	TCLP extract zinc (mg/L)
100% Cement	0	0	0.3	<0.1
90% Cement, 10% bag house dust–Pacific Steel	0.5	5	0.3	0.5
80% Cement, 20% bag house dust–Pacific Steel	1	10	0.3	1.5
70% Cement, 30% bag house dust–Pacific Steel	1.5	15	0.4	0.9
60% Cement, 40% bag house dust–Pacific Steel	2	20	2.3	1.7
50% Cement, 50% bag house dust–Pacific Steel	2.5	25	2.2	1.6
100% Bag house dust–Pacific Steel	5	50	197	2470
US EPA regulatory level			5	No requirement

leached (Table 7). There is also an increased retention of zinc compared with lead (e.g., 20% lead/80% cement leached 50.1 mg/m^3, whereas 20% zinc/80% cement leached 2.7mg/m^3). Table 7 shows the detection level of zinc is 0.0 mg/L, whereas lead had a level of 0.3 mg/L.

Lead starts to leach in detectable levels when the percentage of Pacific Steel bag house dust reached 40% (Table 8), whereas the quantity of zinc leached remained at 1 to 2 mg/L, even up to 50% Pacific Steel bag house dust/50% cement.

4. Conclusions

The major area of this study was to determine the properties of the dusts stabilized with Portland cement and Portland cement/fly ash mixtures, at high levels of cement addition.

Initially, only Pacific Steel bag house was studied. From this initial investigation, it was found that there was retardation, as well as potential strength-enhancing properties, with the addition of Pacific Steel bag house dust. Further investigation was undertaken to see if any other dusts contained these properties. The findings showed that all the dusts studied varied in their composition and physical makeup. Those bag house dusts that contained elevated levels of zinc severely retarded the hydration of cement within the first 2 weeks, but accelerated the strengths at late ages (28 day).

The zinc was predominantly present as zinc oxide, which, when mixed with cement, produced the complex, calcium zinc hydrate.

Pacific Steel bag house dust was found to exhibit the best 28-day strengths of the high zinc bag house dust/cement mixes. This may have been due to the high surface area, which enabled it to react quicker than the other dusts, thus producing calcium zinc hydrate earlier. This, in turn, would allow it to move through the retardation and on to the stage in which hydration could take place, therefore producing hydrated material quicker than bag house dust containing zinc.

When cement was doped with zinc oxide, it also was found to display the same type of retardation as was found with the high ZnO bag house dusts. Lead also displayed a slight accelerating phenomenon at 28 days, but the retention of lead in stabilized materials, as measured by the toxicity characteristic leaching procedure, was higher than for zinc.

The Masport, A&G Price, and two BHP New Zealand Steel bag house dusts did not show accelerating characteristics, unlike Pacific Steel and the other two BHP New Zealand Steel zinc oxide containing bag house dusts. The results showed that all the dusts can be successfully stabilized using cement at the 90% level, with good compressive strengths and low leachate levels for zinc and lead.

References

[1] W.S. Adaska, S.W. Tresouthick, P.B. West, Solidification and Stabilisation of Wastes Using Portland Cement, Portland Cement Association, 1991.

[2] J.R. Conner, Chem Eng 92 (1986) 79–85.

[3] M. MacKay, J. Emery, Cement industry solutions to waste management, in: Proceedings of the First International Symposium, Canadian Portland Cement Association, Calgary, 1992, p. 135.

[4] F.M. Lea, The Chemistry of Cement and Concrete, Chemical Publishing Company Inc., New York, NY, 1971.

[5] V. Alunno-Rossetti, F. Medici, Cem Concr Res 25 (1995) 1147–1152.

[6] J.R. Conner, Chemical Fixation and Solidification of Hazardous Wastes, Van Nostrand Reinhold, New York, NY, 1990.

[7] C.J. Sollars, R. Perry, IWEM 88 Conference Paper, 1989.

[8] C.S. Poon, A.I. Clark, R. Perry, A.P. Barker, P. Barnes, Cem Concr Res 16 (1986) 161–172.

[9] I. Jawed, J. Skalny, J.F. Young, Structure and Performance of Cements, Applied Science Publishers, Barking, Essex, UK, 1983.

[10] J.I. Bhatty, Role of minor elements in cement manufacture and use, Research and Development Bulletin RD109T, PCA, 1995.

[11] H.F.W. Taylor, The Chemistry of Cements, Academic Press, New York, NY, 1964.

[12] W. Lieber, Proceedings of the Fifth International Symposium on the Chemistry of Cement, Tokyo, 1968, p. 444.

[13] G. Arliguie, J. Grandet, Cem Concr Res 20 (1990) 517–524.

[14] N.M. Sammes, I.W. Hamilton, IPENZ Trans 23 (1) (1996) 33–39.