



Metal leaching from monolithic stabilised/solidified air pollution control residues

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ABSTRACT

Portland cement (CEM I) and ground granulated blast furnace slag (ggbs) have been used to treat air pollution control (APC) residues from an energy-from-waste plant burning municipal solid waste. Stabilised/solidified (s/s) products were prepared with binder additions ranging from 10 to 50 wt.% of total dry mass and water/solids ratios between 0.40 and 0.80. Monolithic leach tests (EA NEN 7375:2004) indicated that 50% binder additions were necessary to meet the UK monolithic Waste Acceptance Criteria (monWAC) for Pb and Zn, and previous work indicated that chloride leaching exceeded WAC even at this binder addition. Lower binder additions (20 and 10%) did not sufficiently reduce leaching of Pb. Although the monWAC are based on an assumption that leaching is diffusion-controlled, evaluation of leaching mechanisms indicates that more complex processes than diffusion occur for s/s APC residues.

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1. Introduction

Incineration in modern energy-from-waste (EfW) plants is a major management option for municipal solid waste (MSW) that represents a viable alternative to landfill. Although the levels of recycling are increasing, the number of EfW plants in the UK is also expected to increase. Modern EfW plants have sophisticated air pollution control technologies to meet the emission requirements of the EC Waste Incineration Directive [1]. These use particulate removal systems such as electrostatic precipitators and neutralisation of acid gases using wet, dry or semi-dry lime or sodium bicarbonate scrubbers [2]. Activated carbon is used to adsorb heavy metals and dioxins and furans, with injection of dilute ammonia solution to reduce nitrogen oxides to nitrogen [3].

Air pollution control (APC) residues are the by-product from these systems. These consist of fine particulate matter that is typically between 3 and 5% of the total mass of MSW incinerated and are typically a mix of lime, fly ash and carbon [4]. APC residues are classified as hazardous waste according to European Waste Catalogue (19 01 07*) and they contain high concentrations of volatile heavy metals such as Pb, Cu and Zn and soluble salts [5].

Several technologies have been evaluated for the treatment of APC residues ranging from washing [6], plasma vitrification

[7] and electrokinetic extraction [8]. Comprehensive reviews of treatment technologies for APC residues have recently been completed [9,10]. Each technology has advantages and disadvantages in terms of contaminant immobilisation effectiveness, cost, by-products, process energy consumption and carbon footprint. Stabilisation/solidification (s/s) with hydraulic binders is a relatively inexpensive technology that is used for the treatment of metal-containing hazardous wastes. It involves encapsulation of wastes in a monolithic matrix with structural integrity and reduced surface area available for leaching. Contaminant immobilisation mechanisms may include chemical stabilisation as well as physical encapsulation [11].

Previous work has investigated s/s for the treatment of APC residues. Poletti et al. [12] showed that heavy metals, anions and alkalis in APC residues can significantly affect the mechanical properties of cement and that only partial stabilisation of contaminants may occur in hydration products. Geysen et al. [13] used the German standard DIN 38414-S4 test, a batch extraction with distilled water, to determine Pb leaching from s/s APC residues using standard types of cement and silica-containing materials. Results showed that treatment with cement failed to meet Flemish and German regulatory landfill limits (2 mg/L), but improved leaching results were achieved with the addition of silica-containing materials such as micro-silica. Other studies have evaluated re-using APC residues in construction, by direct application or following one or more pre-treatment stages [14–17].

The monolithic (tank) leaching test (Dutch standard NEN 7375:2004) is a dynamic test for assessing diffusion-controlled leaching and is used as the basis for the UK monolithic Waste

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Acceptance Criteria (monWAC) [18]. The objective of this research was to assess the effectiveness of s/s using commercial binders, in this case Portland cement and ground granulated blast furnace slag, for the immobilisation of contaminants in APC residues and evaluate compliance with the current WAC for monolithic wastes.

2. Experimental

2.1. Materials

Bulk samples (approximately 20 kg) of APC residues were provided by the operator of a major EfW plant in SE England with the capacity to burn 420,000 tonnes per year of MSW. This plant uses conventional mass-burn technology and generates approximately 34 MWh of electricity. Samples of APC residues were obtained directly from the bag house filters.

The mineralogy, elemental composition and leaching (EN12457-4) of these APC residues have previously been reported [5]. Major crystalline phases were $\text{Ca}(\text{OH})_2$, CaCO_3 , CaClOH and anhydrite (CaSO_4), and soluble salts present were NaCl and KCl . Concentrations of Pb and Zn leaching from the APC residues were greater than the granular WAC limits for inert waste landfill, and those for Pb were higher than the limit for hazardous waste landfill. The total amount of chloride present is typically 16–20 wt.%, and the leachable chloride of 140,000–170,000 mg/kg of dry matter is significantly greater than the granular WAC limits for hazardous waste landfill.

CEM I (Lafarge Cement) or ground granulated blast furnace slag (ggbs, Civil and Marine Slag Ltd.) and distilled water were used to prepare all s/s APC residue samples. Elemental composition of the ggbs used has previously been reported [19].

2.2. Stabilised/solidified product preparation

S/s products were prepared with varying APC residue/binder ratios and mix water contents. Samples were prepared with CEM I or ggbs additions of 10, 20 and 50 wt.% of total dry mass and water to solids (w/s) ratios between 0.4 and 0.8. CEM I or another alkali activator was not used with ggbs because the free lime and alkalis in the APC residues can activate the ggbs and initiate pozzolanic hydration reactions. The ranges for binder addition and w/s ratios were based on industrial applicability considerations for commercial viability (i.e. cost of binder) and workability, as well as performance of the S/S matrices.

Specimen preparation involved thoroughly mixing the binder with the APC residues using a 5 L capacity mortar mixer (ELE, UK). Distilled water was then added to achieve the desired w/s ratios. Mixing for 3 minutes produced homogenous pastes that were formed into 50 mm cube samples using a vibrating table (Controls, Italy) to remove air voids from the mix. Specimens were de-moulded after 24 hours and transferred to polyethylene resealable plastic bags containing a damp tissue to maintain a high humidity environment. This also minimised carbonation that could alter the properties and leaching characteristics of the solidified wastes. Specimens were prepared and cured at room temperature (20–24 °C) and pressure.

2.3. Stabilised/solidified product testing

2.3.1. Physical properties

Experimental techniques for determination of the physical properties of s/s APC residues have previously been reported [5,19]. Parameters determined included:

- unconfined compressive strength (UCS) at 7 and 28 days using an automated compression tester (Automax 5) and applying a loading rate of 300 kN/s;
- setting time (Vicat apparatus, BS EN 196-3:2005) and consistence (flow table applying 15 rapid vertical displacements, based on BS 4551);
- porosity (determined from bulk density, specific gravity (ASTM 5550-94) and water content).

Stegemann and Zhou [20] have identified performance threshold values for s/s products including:

- mix consistence of approximately 175 ± 10 mm;
- initial setting time between 2 and 8 hours with final setting occurring at before 24 hours;
- 28 day compressive strengths of greater than 1 MPa [21], before and after immersion.

2.3.2. Mineralogy

The crystalline phases of the s/s products were determined by X-ray diffraction (XRD) using a PANalytical X-Pert Pro MPD diffractometer with a Cu X-ray source. Samples cured for 7 and 28 days were dried at 60 °C and crushed to a fine powder. These were loaded onto a zero background silicon holder, and analysed from 5 to 60° 2θ using 0.04° 2θ step size and 30 s count time per step. Phase identification was carried out using the software X'Pert Highscore Plus.

2.3.3. Tank leaching test (NEN 7375:2004)

The tank test involves leaching of monolithic specimens in sealed containers, using distilled water as the leachant, to assess surface area related release. The leachant is renewed at 8 different times (fractions) over a period of 64 days and results are expressed in terms of emission of mass per unit surface area (mg/m^2).

Products that had a UCS greater than 1 MPa after water immersion were tested for diffusion-controlled leaching from the monolith. The 50 mm cube specimens, cured for 28 days, were immersed in distilled water at $V_L/V_S = 4.0$, where V_L is the volume of distilled water and V_S is the volume of the specimen, with renewal of the leachant at 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days. At each fraction the pH was measured using a pH meter (accuracy ± 0.05 pH units), calibrated using standard buffer solutions before each use. An aliquot of leachate was filtered through a 0.45 μm cellulose nitrate membrane filters (Whatman International Ltd.) and analysed for metals by Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP–OES) (Optima 4300 DV – Severn Trent Laboratories, UK). The liquid samples were preserved and matrix-matched to the ICP calibration by adding 1 ml of concentrated HCl (ARISTAR Grade, VWR, UK) to 9 ml of sample. These samples were stored in capped, 12 ml polystyrene test tubes, prior to analysis.

It is noted that samples were tested by ICP–OES for sulphur (S). However, due to the nature of the mixes it is assumed that the major sulphur species in the system is sulphate (SO_4^{2-}) and reference is made only to SO_4^{2-} hereafter. S emissions were corrected for the mass of SO_4^{2-} . Speciation of sulphur in commercial ggbs for use in concrete may comprise both sulphides and sulphates with maximum permissible contents of 2.0% and 2.5% by mass respectively, according to BS EN 15167-1:2006. A study by Roy [22] however, has shown that in activated slags it is likely that sulphides will be transformed to sulphates. Sulphur content in the ggbs used in this study was 0.05% [19].

Cumulative leaching according to NEN7375:2004 is calculated using the formula:

$$\varepsilon_n^* = \sum_{i=1}^n E_i \quad \text{for } n = 1 \text{ to } N \quad (1)$$

where ε_n^* is the measured cumulative leaching of a component for period n comprising fractions $i = 1$ to n , in mg/m^2 of sample surface area, E_i is the measured leaching of the component in fraction i in mg/m^2 and N is the total number of leachant renewal periods.

Cumulative derived leaching is also calculated according to the formula:

$$\varepsilon_n = E_i \times \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \quad (2)$$

where ε_n is the derived cumulative leaching for a component for period n comprising fraction $i = 1$ to n , in mg/m^2 , E_i is the measured leaching of the component in fraction i , in mg/m^2 , t_i is the replenishment time of fraction i in s and t_{i-1} is the replenishment time of fraction $i - 1$. Derived leaching values can be used to evaluate whether leaching is governed by diffusion.

3. Results

3.1. Physical properties

The physical properties of the *s/s* APC residues treated using CEM I or ggbs have previously been reported [5,19]. Compressive strengths of the products ranged between 0.5 and 20.6 MPa depending on binder and water addition. Ggbs mixes with binder additions lower than 50% exhibited compressive strengths below 1 MPa at 7 and 28 days. All CEM I mixes had compressive strengths greater than 1 MPa. Porosities for CEM I mixes ranged between 30.7 and 52.5 volume%, while the porosities of the ggbs samples ranged from 33.7% to 59.9%.

In the present study, mixes that satisfied the performance criteria outlined in Section 2.3.1 were 10 wt.% CEM I at w/s: 0.65, 20 wt.% CEM I at w/s: 0.65 and 50 wt.% CEM I at w/s: 0.55. None of the ggbs mixes satisfied all three criteria, in most cases being stiffer than the consistence performance threshold [19], which might not be a problem in industrial operations, depending on placement technique.

3.2. Mineralogy

Crystalline phases identified in the *s/s* products are presented in Fig. 1a–c. Fig. 1a shows the mineralogical composition of APC residues with 50% CEM I addition after 7 and 28 days. Major crystalline phases are $\text{Ca}(\text{OH})_2$, CaCO_3 (calcite) and the chloro-complex Friedel's salt, $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ and $\text{Ca}_2\text{Al}(\text{OH})_7\cdot 2\text{H}_2\text{O}$. Friedel's salt forms by the reaction between calcium aluminates and chloride compounds such as NaCl and CaCl_2 . The absence in the diffraction pattern of peaks related to the CaClOH previously found in the untreated APC residue indicates that this has been transformed into less soluble chloro-complex salts, but NaCl and KCl remain present.

Fig. 1b shows the XRD analysis of APC residues with 50% ggbs addition. During the hydration of ggbs, the $\text{Ca}(\text{OH})_2$ supplied by the APC residue is completely consumed, while CaClOH reacts to form Friedel's salt. The broad hump between 20° and 36° 2θ represents the poorly crystalline forms of the highly reactive phases present in ggbs.

The effect of CEM I addition on the mineralogical composition of APC residues at varying binder addition is presented in Fig. 1c. The comparison of the three solidified products shows the extent of the interaction between APC residues and CEM I.

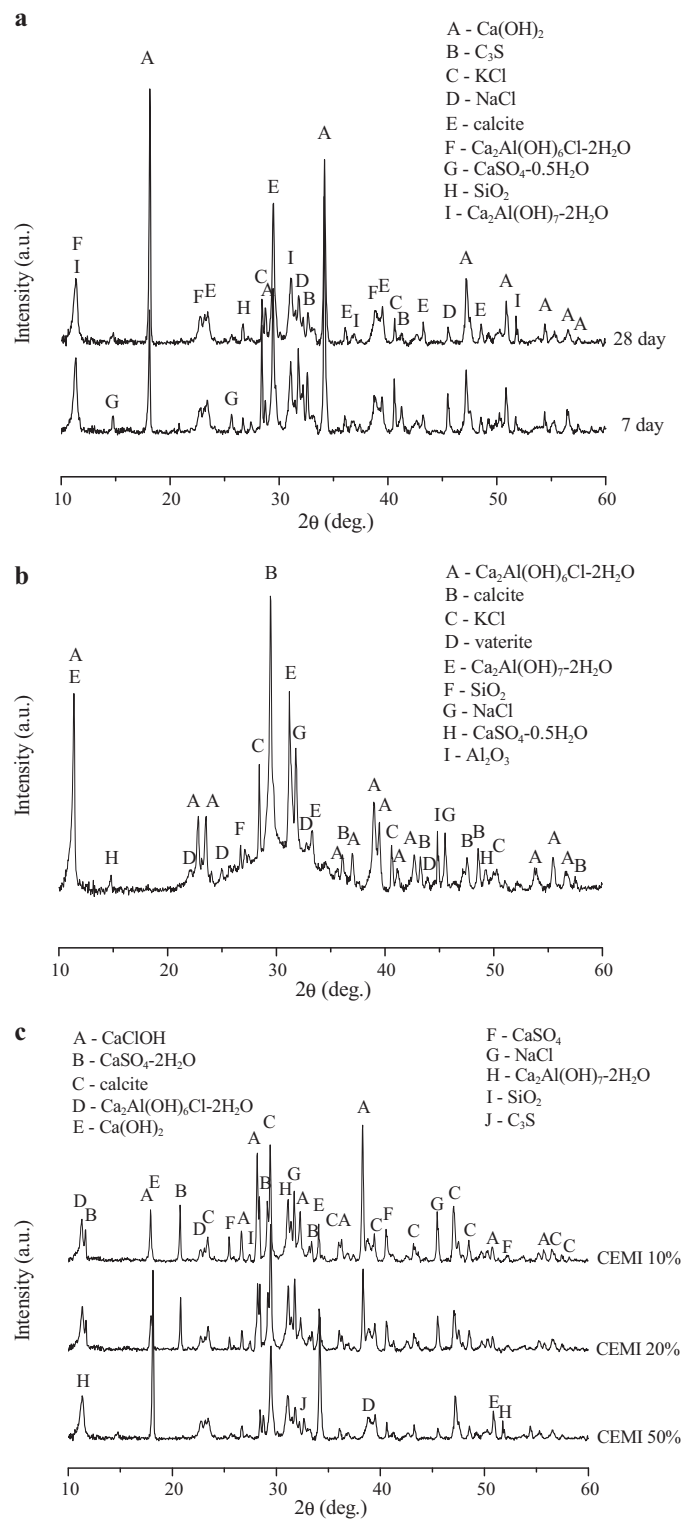


Fig. 1. XRD data of (a) APC residues with 50% CEM I addition after 7 and 28 day curing (w/s of 0.50), (b) APC residues with 50% ggbs addition after 28 day curing (w/s of 0.50) and (c) APC residues with 50%, 20% and 10% CEM I addition after 28 day curing (w/s of 0.50).

In *s/s* products with 10 and 20 wt.% CEM I, residual CaClOH was identified. It is also evident that tricalcium aluminate (C_3A in cement chemist's notation) reacted to form chloro-complex salts. Neither ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) or monosulphate ($\text{Ca}_4\text{Al}_2\text{SO}_4(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) were detected in the *s/s* products prepared with CEM I, while several calcium sulphates, anhydrite

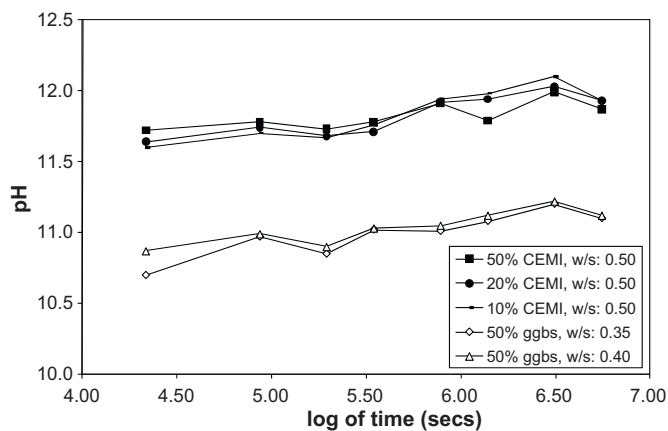


Fig. 2. pH values for the different fractions of the monolithic leaching test.

(CaSO₄), bassanite (CaSO₄·0.5H₂O) and gypsum (CaSO₄·2H₂O) were identified for 10 and 20% CEM I addition. It seems that C₃A may react with the chloride bearing phases to produce chlorocomplexes, and for this reason the sulphate phases remained unreacted.

3.3. Tank leaching data

The pH values determined for the different fractions of the tank leaching test for the s/s products are presented in Fig. 2. All CEM I mixes exhibit pH values ranging between 11.5 and 12.4, while ggbs mixes had lower pH values ranging between 10.7 and 11.2.

Results for measured cumulative leaching vs. time are presented in Figs. 3a, b and 4 on a double log scale. A similar presentation of results is also included in the draft prEN 15863 dynamic monolithic leaching test standard.

Element leaching data presented as log–log plots of cumulative derived leaching (ϵ_n) vs. time are also given in Figs. 3a, b and 4. Table 1 summarises the total measured amount of each element leached, expressed as emission of mass per unit of external surface area, as well as the diffusion controlled intervals, the slopes of the regression lines of log–log plots of the cumulative derived leaching vs. time for these intervals, and the estimated 64-day emissions based on the diffusion-controlled interval.

Rapid loss of Ca, Na and K was observed for all mixes. The ggbs samples exhibited lower Ca and Sr release compared to CEM I mixes with the same binder addition, but higher concentrations of Si and SO₄²⁻ were released. Results for 50 wt.% binder additions show that Pb and Zn were successfully immobilised; emissions were compared against the monWAC limits for hazardous waste landfill which are 20 mg/m² and 100 mg/m² for Pb and Zn, respectively. All 50 wt.% ggbs mixes exhibited concentrations below the detection limits for all fractions of leachate, while concentrations for 50 wt.% CEM I mixes ranged between 5.0 and 12.4 mg/m². Zn release for 50% binder additions ranged between 8.2 and 12.1 mg/m² for ggbs and 12.2 and 24.2 mg/m² for CEM I mixes, demonstrating a potential pH effect when comparing against the pH values in Fig. 2 [23]. 10 and 20 wt.% CEM I mixes failed to meet the monWAC permissible concentrations for Pb, with release ranging between 29.6 and 72.3 mg/m². It should be noted that s/s samples with lower ggbs additions could not be leach tested as they had poor structural integrity. Not all the mixes that met the performance thresholds were tested due to strength loss after immersion, and in some cases specimens totally disintegrated [19].

According to NEN 7375:2004, the gradient of a log–log plot of cumulative derived leaching vs. time indicates the predominant leaching mechanism. Gradients below 0.35 indicate either surface wash-off or depletion. Gradients between 0.35 and 0.65

indicate diffusion-controlled release, whereas gradients greater than 0.65 indicate dissolution. Examination of the slopes for different leaching intervals in Table 1, as well as the non-linear plots in Figs. 3a, b and 4 show diffusion control in early leaching intervals, with depletion, surface wash-off and/or dissolution occurring later. In the case of Na and K, a diffusion-controlled interval could not be established for CEM I mixes, due to early depletion. Leaching of Pb and Zn was governed mainly by diffusion. The diffusion-controlled interval was used to determine estimated 64-day emissions, which are presented in Table 1. Differences are observed between the measured and derived 64-day emissions. This is attributed to the fact that calculation of the derived emission assumes pure diffusion control, whereas measured emissions during the test may be influenced or controlled by other mechanisms. The data indicates that for elements under diffusion control, the estimated release is close to the measured release.

4. Discussion

The leachate pH values remained above 11.5 for all leachate fractions from the monolithic leaching test for CEM I mixes. Lower pH values were exhibited by the ggbs mixes, and this can be attributed to the consumption of free lime present in the mix resulting from slag activation. The values obtained are similar to those for a pure CaO–SiO₂–H₂O system where Na and K are present, according to data presented by Polettini et al. [12]. The high pH values for CEM I mixes are conducive to the release of amphoteric metals such as Pb and Zn whose solubility is pH dependent. It is noteworthy that the pH generally increases with the length of the leaching interval; this phenomenon may influence the test results.

XRD analysis identified the presence of Friedel's salt which is a hydrated chloride-containing calcium aluminate analogous to monosulphate in hydrated ordinary Portland cement. It forms from the reaction of chloride with aluminate phases, and is stable over a wide range of chloride concentrations [24]. The chloride binding capacity of cements through the formation of chlorocomplexes such as Friedel's salt has been previously investigated [25,26]. It was observed that for 50 wt.% binder additions, chlorocomplexes form and the peak of CaClOH disappears. Residual CaClOH peaks remain for 10 and 20 wt.% CEM I additions and this may be due to the reduced amount of C₃A present and the increased amount of CaClOH resulting from the greater waste addition. Friedel's salt formation is also observed for ggbs mixes and this supports the view that such chloro-complexes can form in the presence of Ca, Al and Cl without requiring initial addition of C₃A phases to the binder. Previous research [5,19] has shown that amounts of chloride leached from s/s APC residues are high, despite partial immobilisation in chlorocomplexes like Friedel's salt.

It was observed that relatively high amounts of Na and K were released during the leaching test. A diffusion-controlled increment could not be identified for CEM I mixes and the slopes of the log–log plots indicate surface wash-off and dissolution mechanisms. It is clear that the major release of Na and K results mainly from surface wash-off and dissolution at early stages and later depletion of the highly soluble salts present such as NaCl and KCl. However, the ratio of the sum of the molar amounts of Na and K to Cl ((Na + K)/Cl) ranged between 0.4 and 0.6, indicating that NaCl and KCl are not the only sources of chloride in the s/s products. Chloro-complexes that have formed may also be unstable and eventually lead to chloride leaching. Previous studies have shown that alkalis can affect the physical properties of mixes such as compressive strength, setting time and rheology. Alkalis can be incorporated in calcium silicate hydrate (CSH) gel, affecting the Ca:Si ratio [27] and the properties of the cement paste. Alkalis have also been reported to increase the

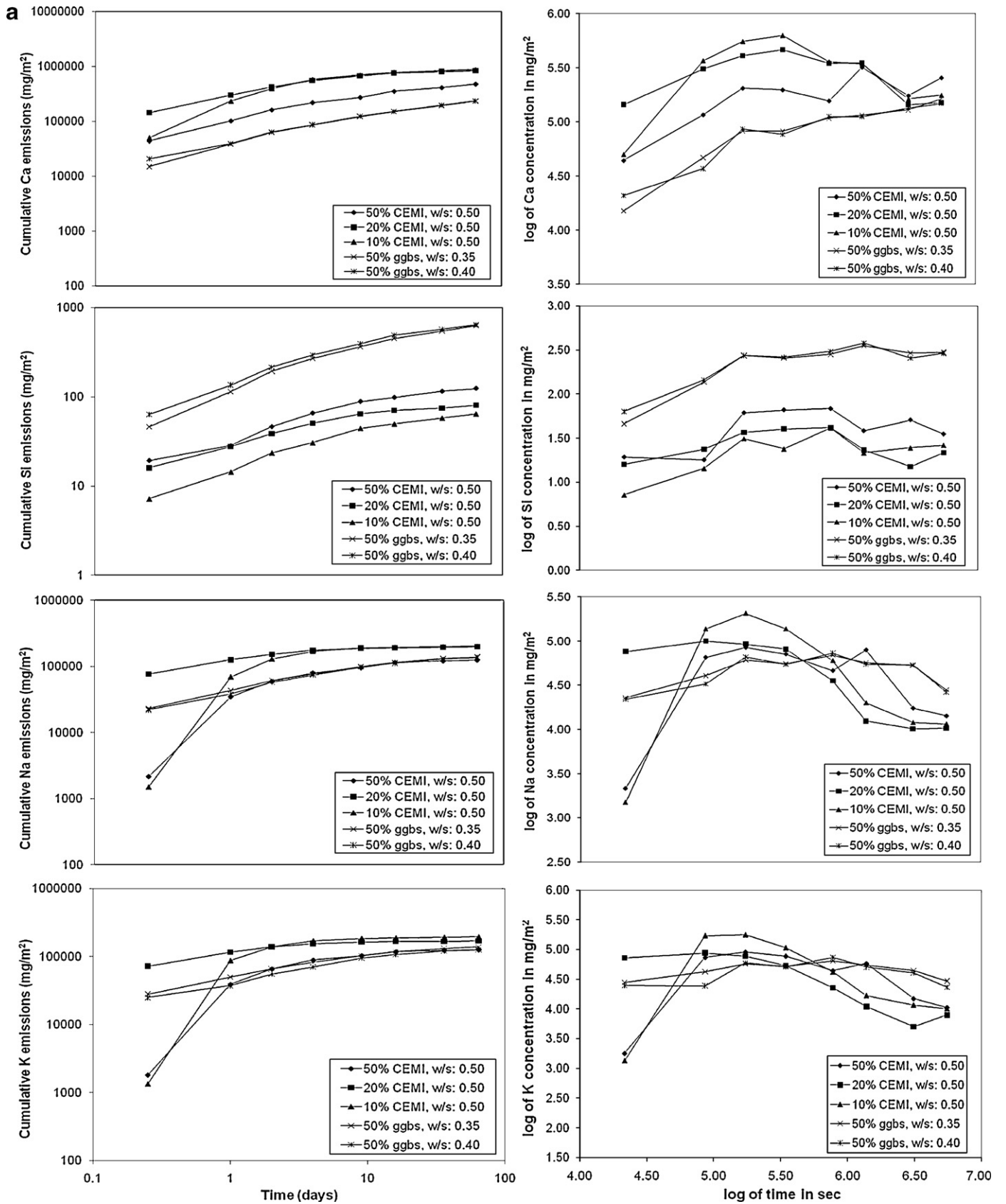


Fig. 3. Cumulative measured and derived leaching of (a) Ca, Si, Na and K and (b) Sr, Fe, Li and SO₂²⁻.

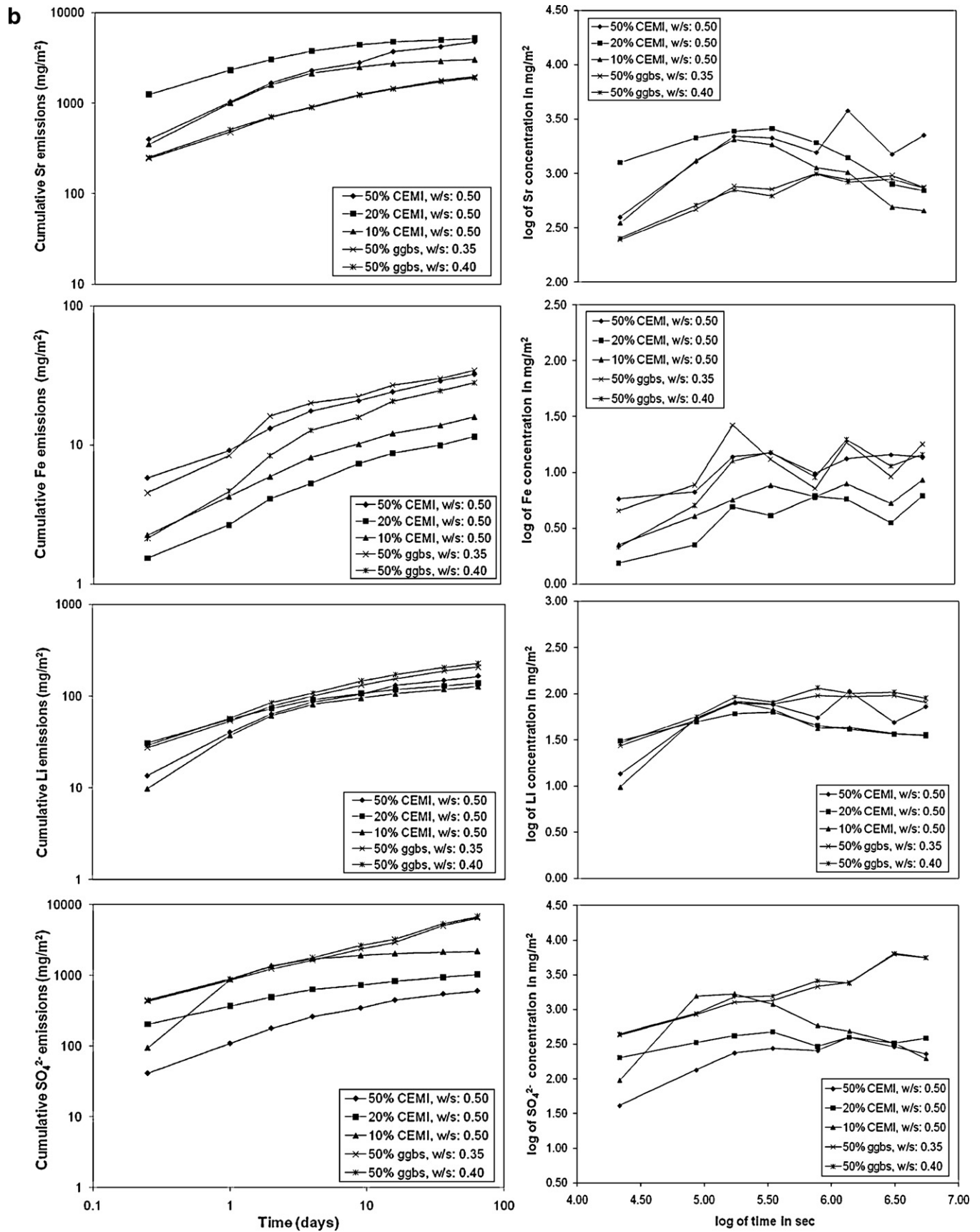


Fig. 3. (Continued)

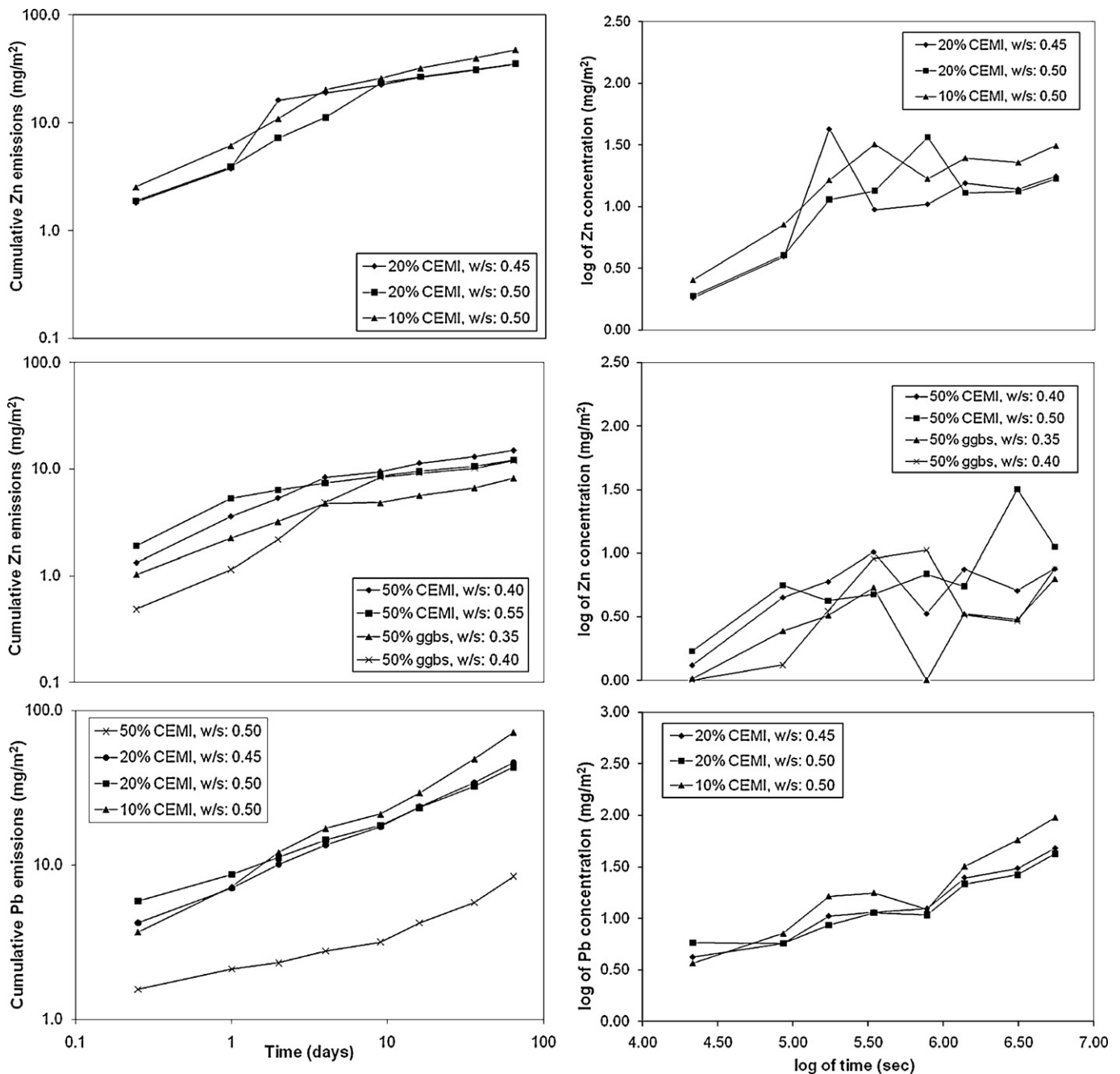


Fig. 4. Cumulative measured and derived leaching of Zn and Pb from s/s APC residues.

solubility of Friedel's salt and decrease the solubility of $\text{Ca}(\text{OH})_2$ [28,29].

The absence of $\text{Ca}(\text{OH})_2$ peak in the 50 wt.% ggbs mixes was attributed to consumption of the lime by reaction with the pozzolan. Leaching of Ca from ggbs mixes was also less compared to CEM I mixes, as CSH is less soluble than lime [30]. The slopes of the log-log plots for Ca indicate that depletion or a change in chemical form and release conditions may have occurred during the tank test, especially at low binder additions. However, this does not necessarily imply that Ca is being depleted. Calcium loss may occur due to leaching of soluble Ca-containing compounds such as CaClOH , a major phase in APC residues also detected in the 10 and 20 wt.% CEM I s/s products. Once Ca derived from such compounds is removed, Ca leaching may continue from other sources such as $\text{Ca}(\text{OH})_2$ and CSH at a much lower rate. Leaching of Ca

from portlandite and CSH leading to decalcification may result in a degradation of the s/s matrix. Decalcification of CSH is a slow process which results in a reduction in compressive strength and increased porosity [31,32]. Rapid leaching of soluble salts coupled with long-term decalcification may lead to an alteration in the physical properties of the matrix that are deleterious to the behaviour of the product, and changes to the effective diffusion coefficients of all species over time.

Leaching of sulphate is greater from 50 wt.% ggbs compared to all CEM I mixes tested, although both binders met the monWAC for SO_4^{2-} for hazardous waste landfills (20,000 mg/m²). Calcium sulphate hemihydrate, a potential source for leaching, was observed in the diffractograms for both CEM I and ggbs products. Comparison of leaching results indicates that immobilisation of sulphate may have taken place to a greater extent in CEM I mixes. However,

Table 1
Measured cumulative contaminant release (ε_n^*) of mixes tested according to the tank test and slopes of the log–log plots of derived cumulative leaching vs. time for diffusion controlled increments.

Element	Total content in APC residues (mg/kg) (Lampris et al. [5])	Binder addition (total dry mass)	Water-to-solids (ml/g)	ε_n^* (mg/m ²)	Diffusion controlled increment	$\Delta \log \varepsilon_n / \Delta \log t$ of diffusion controlled increment	Estimated 64 days release based on diffusion controlled interval (mg/m ²)
Ca	250,00–300,000	CEM I 50%	0.50	474,000	1–4	0.58	880,000
		CEM I 20%	0.50	844,000	1–4	0.44	2,223,000
		CEM I 10%	0.50	884,000	n/a ^a	n/a	n/a
		ggbs 50%	0.35	235,000	1–4	0.65	342,000
		ggbs 50%	0.40	233,000	2–5	0.44	338,000
Na	13,500–22,500	CEM I 50%	0.50	125,000	n/a ^a	n/a	n/a
		CEM I 20%	0.50	197,000	n/a ^a	n/a	n/a
		CEM I 10%	0.50	201,000	n/a ^a	n/a	n/a
		ggbs 50%	0.35	139,000	1–4	0.35	308,000
		ggbs 50%	0.40	136,000	1–4	0.38	294,000
K	9000–24,000	CEM I 50%	0.50	125,000	n/a ^a	n/a	n/a
		CEM I 20%	0.50	169,000	n/a ^a	n/a	n/a
		CEM I 10%	0.50	195,000	n/a ^a	n/a	n/a
		ggbs 50%	0.35	139,000	n/a ^a	n/a	n/a
		ggbs 50%	0.40	126,000	2–5	0.43	227,000
Pb	2500–5500	CEM I 50%	0.50	8.4	2–7	0.48	6.8
		CEM I 20%	0.50	42.9	2–7	0.41	40.4
		CEM I 10%	0.50	72.3	2–7	0.48	46.7
		ggbs 50%	0.35	<3.0 ^b	n/a	n/a	n/a
		ggbs 50%	0.40	<3.0 ^b	n/a	n/a	n/a
Zn	4000–18,500	CEM I 50%	0.50	24.2	2–7	0.40	23.7
		CEM I 20%	0.50	35.2	n/a ^a	n/a	n/a
		CEM I 10%	0.50	47.5	2–5	0.42	74.3
		ggbs 50%	0.35	8.2	1–4	0.58	18.9
		ggbs 50%	0.40	12.1	1–6	0.63	14.9

^a A diffusion controlled interval was not identified.

^b Concentrations below the laboratory detection limit for all fractions of the leaching test. Emissions in mg/m² were calculated based on the detection limit of 10 µg/L.

other sulphur-containing minerals were not detected in the diffractograms of either the ggbs or CEM I mixes, though previous studies report formation of ettringite in s/s APC residues [33]. While high concentrations of chloride have been reported to destabilise monosulphate and ettringite in favour of the production of Friedel's salt [34–36], the form of the sulphate in the 50 wt.% CEM I s/s products remains an open question. Previous studies [34] identified the presence of a Cl and SO₄-containing calcium aluminate hydrate known as Kuzel's salt, although this was not investigated in the present study.

Release of other minor elements, such as Li and Fe, is similar for ggbs and CEM I at the same binder addition. However, release of these elements is not fully diffusion-controlled, and different mechanisms are observed throughout the test. Sr release was lower for ggbs mixes. This can be attributed to the increased amounts of Al in ggbs compared to CEM I, which may result in the formation of greater amounts of calcium aluminates hydrates (Ca₂Al(OH)₇·2H₂O). Sr has been previously reported to substitute for Ca in calcium aluminate hydrates [37]. The higher amount of Al in the ggbs products may also contribute to the higher Friedel's salt diffractogram peaks, relative to the CEM I products, though this was not quantitatively investigated [38,39].

The leaching results for Pb showed that the monWAC limit of 20 mg/m² for hazardous waste landfills was exceeded for mixes with 10 and 20% CEM I addition, but was met for 50 wt.% CEM I. Pb release was found to be diffusion-controlled, as demonstrated by the slopes of the leaching increments in Table 1 and Fig. 4. The ggbs mixes exhibited undetectable Pb release for 50 wt.% binder addition compared to CEM I. This may be partially attributed to the lower pH values for all fractions of the leaching tests for ggbs mixes, which reflect lower pore water pH, and therefore a lower driving force for diffusion.

Zn was effectively contained in the matrices and its leaching was below the monWAC of 100 mg/m² for hazardous waste landfill. Diffusion-controlled release was observed in the early stages and changes in the chemical form or release conditions at later stages. Similar release behaviour for Zn has been reported by van der Sloot et al. [40]. Pb or Zn bearing minerals were not identified in the XRD data for the s/s products or the untreated APC residues. The metals may remain with the phases of the APC residue itself, or may be taken up into crystalline hydration products by isomorphic substitution, or they may be present in amorphous materials not detected by XRD. Pb has been found to replace Ca²⁺ in CSH, inhibiting gel formation [37]. Zn has been reported to be retained by CSH without the replacement of Ca or Si in the gel but by the linkage of tetrahedral Zn to CSH tetrahedral silicate chains [37,41]. Pb and Zn have previously been reported to adversely affect the hydration of Portland cement and impair physical properties. At high pH values Pb(OH)₄²⁻ and Zn(OH)₄²⁻ have been reported to form Ca-complexes which precipitate and coat cement grains [42]. Thus, the fate of the Pb and Zn in the ggbs or CEM I system is not straightforward, and several mechanisms probably occur simultaneously that compete for the available Pb and Zn species.

5. Conclusions

Although s/s APC residues containing 50 wt.% of CEM I or ggbs can meet the UK monWAC leaching limits for hazardous waste landfill, the limits were exceeded for Pb at lower binder additions and for chloride at all binder additions. Current UK monWAC were developed based on modeling of diffusion-controlled leaching from a semi-infinite medium with constant porosity and a constant leaching mechanism. However, as determined in the present study, the release mechanisms of some contaminants are not con-

stant, leading to changes in the effective diffusion coefficient with time. Furthermore, the rapid leaching of high concentrations of soluble contaminants may result in changes to the physical matrix, compromising its integrity and affecting the rate of mass transfer, such as increase in porosity or even disintegration of the monolith in the long-term. Contaminant release and leachate composition are also influenced by the complex geochemistry of the s/s system as demonstrated by the mineralogy and leaching results. Chemical reactions between contaminant species and hydration products and/or other phases can influence the release mechanism and pattern of contaminants, and therefore affect leachate composition.

Thus, it seems that s/s of APC residues results in complex monoliths, which do not fulfill the assumptions underlying the monWAC. Nevertheless, monWAC probably represents a conservative approach.

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References

- [1] EC Waste Incineration Directive, Directive 2000/76/EC of the European Parliament and of the Council on Incineration of Waste, European Commission, Brussels, 2000.
- [2] F. Bodéan, Ph. Deniard, Characterisation of the flue gas cleaning residues from European solid waste incinerators: assessment of various Ca-based sorbent processes, *Chemosphere* 51 (2003) 335–347.
- [3] P.T. Williams, *Waste Treatment and Disposal*, second ed., John Wiley & Sons Ltd, Chichester, 2005.
- [4] J. Todorovic, H. Ecke, A. Lagerkvist, Solidification with water as a treatment method for air pollution control residues, *Waste Manage.* 23 (2003) 621–629.
- [5] C. Lampris, J.A. Stegemann, C.R. Cheeseman, Solidification/stabilisation of air pollution control residues using Portland cement: physical properties and chloride leaching, *Waste Manage.* 29 (2009) 1067–1075.
- [6] J.M. Chimenos, A.I. Fernandez, A. Cervantes, L. Miralles, M.A. Fernandez, F. Espiel, Optimising the APC residue washing process to minimise the release of chloride and heavy metals, *Waste Manage.* 25 (2005) 686–693.
- [7] D. Amutha Rani, E. Gomez, A.R. Boccaccini, L. Hao, D. Deegan, C.R. Cheeseman, Plasma treatment of air pollution control residues, *Waste Manage.* 28 (2008) 1254–1262.
- [8] L.M. Ottosen, A.T. Lima, A.J. Pedersen, A.B. Ribeiro, Electrolytic extraction of Cu, Pb and Cl from municipal solid waste incineration fly ash suspended in water, *J. Chem. Technol. Biotechnol.* 81 (2006) 553–559.
- [9] D. Amutha Rani, A.R. Boccaccini, D. Deegan, C.R. Cheeseman, Air pollution control residues from waste incineration: current UK situation and assessment of alternative technologies, *Waste Manage.* 28 (2008) 2279–2292.
- [10] M.J. Quina, J.C. Bordado, R.M. Quinta-Ferreira, Treatment and use of air pollution control residues from MSW incineration: an overview, *Waste Manage.* 28 (2008) 2097–2121.
- [11] J.A. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*, Van Nostrand Reinhold, New York, 1990.
- [12] A. Poletini, R. Pomi, P. Sirini, F. Testa, Properties of Portland cement-stabilised MSWI fly ashes, *J. Hazard. Mater.* B 88 (2001) 123–138.
- [13] D. Geysen, C. Vandecasteele, M. Jaspers, G. Wauters, Comparison of immobilization of air pollution control residues with cement and with silica, *J. Hazard. Mater.* B 107 (2004) 131–143.
- [14] J.E. Aubert, B. Husson, A. Vaquier, Use of municipal solid waste incineration fly ash in concrete, *Cem. Concr. Res.* 34 (2004) 957–963.
- [15] C. Collivignarelli, S. Sorlini, Reuse of municipal solid waste incineration fly ash in concrete mixtures, *Waste Manage.* 22 (2002) 909–912.
- [16] H.-S. Shi, L.-L. Khan, Leaching behaviour of heavy metals from municipal solid waste incineration (MSWI) fly ash used in concrete, *J. Hazard. Mater.* 164 (2009) 750–754.
- [17] Y. Xue, H. Hou, S. Zhu, J. Zha, Utilisation of municipal solid waste incineration fly ash in stone mastic asphalt mixture: pavement performance and environmental impact, *Constr. Build. Mater.* 23 (2009) 989–996.
- [18] D.H. Hall, D. Drury, J. Gronow, Modelling in support of setting the waste acceptance criteria for monolithic waste, in: A. Al-Tabbaa, J.A. Stegemann (Eds.), *Proceedings of the International Conference on Stabilisation/Solidification Treatment and Remediation*, A.A. Balkema Publishers, 2005, pp. 107–116.
- [19] C. Lampris, J.A. Stegemann, C.R. Cheeseman, Chloride leaching from air pollution control residues solidified using granulated ground blast furnace slag, *Chemosphere* 73 (2008) 1544–1549.
- [20] J.A. Stegemann, Q. Zhou, Screening tests for assessing treatability of inorganic industrial wastes by stabilisation/solidification with cement, *J. Hazard. Mater.* 161 (2009) 300–306.
- [21] Environment Agency, *Guidance for waste destined for disposals in landfills (Version 2 2006), Interpretation of the Waste Acceptance Requirements of the Landfill (England and Wales) Regulations 2002 (as amended)*. Available from: <http://www.ea-transactions.com/static/documents/Business/wacv2.1006008.pdf> (accessed 19.08.10).
- [22] A. Roy, Sulfur speciation in granulated ground blast furnace slag: an X-ray absorption spectroscopic investigation, *Cem. Concr. Res.* 39 (2009) 659–663.
- [23] M.J. Quina, J.C. Bordado, R.M. Quinta-Ferreira, The influence of pH on the leaching behaviour of inorganic components from municipal solid waste APC residues, *Waste Manage.* 29 (2009) 2483–2493.
- [24] F.P. Glasser, J. Marchand, E. Samson, Durability of concrete-degradation phenomena involving detrimental chemical reactions, *Cem. Concr. Res.* 38 (2008) 226–246.
- [25] H.A.F. Dehwah, Effect of sulphate contamination on chloride-binding capacity of plain and blended cements, *Adv. Cem. Res.* 18 (2006) 7–15.
- [26] A.K. Suryavanshi, J.D. Scantlebury, S.B. Lyon, Mechanism of Friedel's salt formation in cements rich in tri-calcium aluminate, *Cem. Concr. Res.* 26 (1996) 717–727.
- [27] S.-Y. Hong, F.P. Glasser, Alkali binding in cement pastes part I. The C–S–H phase, *Cem. Concr. Res.* 29 (1999) 1893–1903.
- [28] S. Rémond, D.P. Bentz, P. Pimienta, Effects of the incorporation of municipal solid waste incineration fly ash in cement pastes and mortars, *Cem. Concr. Res.* 32 (2002) 565–576.
- [29] J. Duchesne, E.J. Reardon, Measurement and prediction of portlandite solubility in alkali solutions, *Cem. Concr. Res.* 25 (1995) 1043–1053.
- [30] J.A. Stegemann, R.J. Caldwell, C. Shi, Response of various solidification systems to acid addition, in: J. Goumans, J. Senden, H. van der Sloot (Eds.), *Waste Materials in Construction: Putting Theory in Practice (Studies in Environmental Science 71)*, Elsevier Science B.V., Amsterdam, 1997, pp. 803–814.
- [31] J.J. Chen, J.J. Thomas, H.M. Jennings, Decalcification shrinkage of cement paste, *Cem. Concr. Res.* 36 (2006) 801–809.
- [32] J. Jain, N. Neithalath, Analysis of calcium leaching behaviour of plain and modified cement pastes in pure water, *Cem. Concr. Compos.* 31 (2009) 176–185.
- [33] I. Baur, C. Ludwig, C.A. Johnson, The leaching behavior of cement stabilized air pollution control residues: a comparison of field and laboratory investigations, *Environ. Sci. Technol.* 35 (2001) 2817–2822.
- [34] M. Balonis, B. Lothenbach, G. Le Saout, F.P. Glasser, Impact of chloride on the mineralogy of hydrated Portland cement systems, *Cem. Concr. Res.* 40 (2010) 1009–1022.
- [35] R. Loser, B. Lothenbach, A. Leeman, M. Tuchsmit, Chloride resistance of concrete and its binding capacity—comparison between experimental results and thermodynamic modelling, *Cem. Concr. Compos.* 32 (2010) 34–42.
- [36] U.A. Birnin-Yauri, F.P. Glasser, Friedel's salt, $\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$: its solid solutions and their role in chloride binding, *Cem. Concr. Res.* 28 (1998) 1713–1723.
- [37] N.D.M. Evans, Binding mechanisms of radionuclide to cement, *Cem. Concr. Res.* 38 (2008) 543–553.
- [38] R.K. Dhir, M.A.K. El-Mohr, T.D. Dyer, Chloride binding ggbs concrete, *Cem. Concr. Res.* 26 (1996) 1767–1773.
- [39] R. Luo, Y. Cai, C. Wang, X. Huang, Study of chloride binding and diffusion ggbs concrete, *Cem. Concr. Res.* 33 (2003) 1–7.
- [40] H.A. van der Sloot, A. van Zomeren, J.C.L. Meeusen, P. Seignette, R. Bleijerveld, Test method selection, validation against field data and predictive modeling for impact evaluation of stabilized waste disposal, *J. Hazard. Mater.* 141 (2007) 354–369.
- [41] F. Ziegler, C.A. Johnson, The solubility of calcium zincate ($\text{CaZn}_2(\text{OH})_6\cdot 2\text{H}_2\text{O}$), *Cem. Concr. Res.* 31 (2001) 1327–1332.
- [42] S. Asavapisit, G. Fowler, C.R. Cheeseman, Solution chemistry during cement hydration in the presence of metal hydroxide wastes, *Cem. Concr. Res.* 27 (1997) 1249–1260.