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SOLIDIFICATION/STABILIZATION OF AIR POLLUTION CONTROL RESIDUES USING PORTLAND CEMENT: PHYSICAL PROPERTIES AND CHLORIDE LEACHING

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Abstract

Portland cement (CEMI) was used to solidify air pollution control (APC) residues from an energy-from-waste plant burning municipal solid waste. APC residue/CEMI mixes were prepared with CEMI additions ranging from 0 to 50 weight (wt) % of total dry mass and water/solids ratios between 0.40 and 0.80. Isothermal conduction calorimetry was used to assess the effect of APC residues on the hydration of CEMI. Although up to 30 wt% additions of APC residues accelerated CEMI hydration, the total heat of hydration during the initial 98 hours was significantly reduced. Higher levels of APC residues severely inhibited CEMI hydration. The consistence, setting time, compressive strength, porosity, and chloride leaching characteristics of the solidified products were determined. As might be expected, increasing the CEMI addition and reducing the water content resulted in increased compressive strengths. All mixes achieved compressive strengths greater than 1 MPa at 7 and 28 days but only 50 wt% samples did not show significant strength reduction when tested after immersion in water. Monolithic leaching tests indicated low physical immobilisation of chloride in the CEMI-solidified APC residues, with chloride leaching in excess of relevant EU landfill waste acceptance criteria (WAC). The results of this study show that greater than 50% CEMI additions would be required to effectively treat APC residues to meet current WAC limits.

Keywords: APC residues; solidification; soluble salts; incineration; chloride leaching

1.   Introduction

There are currently 19 energy-from-waste (EfW) plants operating in the UK, which range in capacity from processing 55,000 to 600,000 tonnes of municipal solid waste (MSW) per annum. Although increasing restrictions on MSW disposal to landfill will result in greater recycling and use of other treatment or disposal options, it is expected that the number of EfW plants will also increase in the UK and many other countries.

Compliance with the European Union Waste Incineration Directive requires advanced air pollution control systems (EC Directive, 2000/76; Williams, 2005). These typically involve particulate removal systems such as electrostatic precipitators, neutralisation of acid gases using wet, dry or semi-dry lime or sodium bicarbonate scrubbers (Bodénan and Deniard, 2003), activated carbon to absorb heavy metals and dioxins and injection of dilute ammonia solution to reduce nitrogen oxides to nitrogen. The resulting particulate matter is a mixture of lime, fly ash and carbon which is removed from the gas stream by bag filters before the cleaned emission gasses are released to air. These air pollution control (APC) residues are a fine particulate material that represents between 3 and 5 weight (wt) % of the total MSW input to the EfW plant (Todorovic et al., 2003; Xiaomin Li et al., 2006). APC residues are classified as hazardous waste in the European Waste Catalogue (19 01 07*), primarily due to their high alkalinity and high levels of soluble salts and volatile heavy metals such as cadmium, lead, copper and zinc. They also contain trace levels of organic pollutants including dioxins and furans.

UK waste incineration currently produces approximately 128,000 tonnes per annum of APC residues. By far the majority is produced from MSW EfW plants, but clinical waste incineration produces around 10,000 tonnes per annum and sewage sludge incineration a further 3,500 tonnes per annum. An additional 40,000 tonnes per annum of APC residues are expected to be generated from additional UK MSW incineration capacity in the near future.

The main disposal method for APC residues in the UK involves conditioning with aqueous wastes prior to placement directly into monofill cells at a hazardous waste landfill (Environment Agency, 2002). Mixing with wastewater is used to adjust the pH to the lower alkaline range and form a treated product that solidifies and has some strength. This also aids handling of APC residues, as it prevents wind-blown dispersal at the landfill. Detailed analysis of post-disposal behaviour of APC residues and the long-term durability of the wastewater-hardened material has not been reported. APC residues treated in this way leach total dissolved solids at less than three times the waste acceptance criteria (WAC) limit and this is currently considered appropriate for disposal in the UK (Environment Agency, 2006).

The EU Landfill Directive requires pre-treatment of wastes prior to landfill to an appropriate level. Solidification using cementitious binders is a pre-landfill treatment process that is used to encapsulate hazardous wastes in a monolithic solid with structural integrity and reduced surface area for contaminant leaching by diffusion. It does not necessarily involve chemical interaction between

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the waste and the solidification binder to reduce contaminant solubility (termed "stabilisation"), but may physically contain the hazardous components within the monolith (Conner, 1990).

Solidification/stabilization (s/s) binders used commercially for treating various types of wastes include Portland cement (CEMI), pulverised fuel ash, ground granulated blast furnace slag (ggbs) and lime, and these are often used in combination.

Current treatment technologies for APC residues including s/s have recently been reviewed (Amutha Rani et al., 2007, Quina et al. 2007). Studies included in these reviews have focused on leaching of metals and soluble salts but no comparison was made against the monolithic UK WAC limits. The objective of this research was to assess the effectiveness of CEMI as an s/s binder for APC residues. This involved systematically varying the mix design (CEMI content and water/solids ratio) and evaluating key processing and performance indicators of the s/s treated APC residues.

2. Experimental

2.1 Materials

APC residues were obtained from 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 34 MWh of electricity.

The as-received APC residues were examined by scanning electron microscopy (JEOL-JSM-840A). A typical image, shown in Figure 1, shows that APC residues consist of agglomerated spherical particles with a mean particle size of approximately 25 μm.

Crystalline phase analysis of as-received APC residues was completed using X-ray diffraction (XRD, Philips PW1700 series) with Cu Kα radiation and a secondary graphite crystal as mono-chromator. An XRD trace is shown in Figure 2. The major Ca-containing phases were identified as $Ca(OH)_2$, $CaCO_3$ and CaClOH, and soluble salts present were NaCl and KCl.

Typical elemental composition and leaching data (liquid-to-solid, L/S, ratio of 2-10 determined according to EN12457-4) and regulatory WAC limit values for compliance leach testing using EN12457-4 for APC residues are given in Table 1 (Resource Recovery Forum, 2004; Environment Agency, 2006). It can be seen that the concentrations of Pb and Zn that leach from the APC residues are greater than the WAC limits for inert waste landfill and those for Pb are higher than the limits for hazardous waste landfills. The mineral and elemental composition data indicates APC residues contain high levels of soluble salts. The total amount of chloride present is typically around 16 wt % and the leachable chloride of 140,000 - 170,000 mg kg^{-1} of dry matter is much greater than the WAC limits for hazardous waste landfill.

CEMI (supplied by Lafarge Cement) and distilled water were used to prepare all CEMI s/s treated APC residue samples.

2.2 Isothermal conduction calorimetry

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The interaction between APC residues and CEMI was investigated using isothermal conduction calorimetry (Wexham Developments, JAF calorimeter). This measures the rate of heat evolution from hydration reactions with curing time. In these experiments, mixes have been prepared with high CEMI/low APC residue additions (0, 10 and 30 wt % of total dry mass) and low CEMI/high APC residue additions (50, 70 and 100 wt %). For both sets of samples, the CEMI was thoroughly mixed with the APC residues using a water/solids ratio of 0.5, and 25 g of the paste transferred to a polyethylene bag for testing. This was carefully placed around the heat sensor of the calorimeter and the chamber then placed in a water bath set at 20°C. Hydration was monitored for 98 hours.

2.3   Solidified product preparation

The main variables affecting the performance and properties of the solidified products were expected to be the APC residue/CEMI ratio and the mix water content (water/solids, or w/s, ratio). Solidified products were prepared with 0, 10, 20 and 50 wt % of total dry mass CEMI. The CEMI was thoroughly mixed with the APC residues prior to water addition using an ELE Automatic/Manual mortar mixer with a 5L capacity. Distilled water was then added to achieve the desired w/s ratios, with these ranging from 0.4 to 0.8. Mixing for 3 minutes produced a homogenous paste that was formed into 50 mm cube samples using a vibrating table (Controls 55-C0159/H) to remove air voids from the mix. Specimens were de-moulded after 24 hours and transferred to polyethylene re-sealable 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 cured at room temperature.

2.4   Solidified product testing

2.4.1   Physical Tests

All products were tested for consistence, setting time, bulk density, water content, specific gravity and unconfined compressive strength.

Consistence was determined using a flow table with a disc diameter of 255 mm and a 100 mm diameter conical mould. The test involves removing the conical mould from the mixed slurry sample, applying 15 rapid vertical displacements to the disc and measuring the diameter of spread of the sample (BS EN 1015-3:1999). Initial and final setting times were determined using the Vicat test (BS EN 196-3:2005). Water content was determined by drying samples at 60°C to constant weight after immersing samples in acetone to prevent further hydration, and the results were calculated on a wet mass basis. The specific gravity of samples was determined using a He gas volume expansion meter (Robertson Research, ASTM D5550-94). Specimen porosity (p) was calculated from the bulk density, water content and specific gravity using the equation (Stegemann and Côté, 1991):

$$\text{Porosity (p)} = 1 - \left[\frac{BD \times (1-WC)}{SG \times d} \right] \qquad (1)$$

where BD = bulk density (g/cm^3), WC = water content (w/ww), SG = specific gravity (g/cm^3) and d = density of water (1 g/cm^3).

Solidified product specimens were tested in triplicate at 7 and 28 days for unconfined compressive strength (UCS, Automax 5) using a loading rate of 300 N/s. Water-saturated 28 day UCS data was obtained by curing samples for 21 days as described above and then immersing them in water for 7 days before UCS measurement.

To provide a basis for continued development of the experimental programme, solidified product with the following performance were deemed to be of sufficient quality (Stegemann and Zhou, 2008):

- mix consistence (i.e., flow table spread) of approximately 175 ±10 mm, as this was measured for a cement paste of standard consistence;
- 2< initial setting time < 8 hours and final setting time occurring at < 24 hours;
- 28 day compressive strengths > 1 MPa (Environment Agency, 2006).

2.4.2 Acid Neutralisation Capacity (ANC)

Hydration of cement-based binder systems produces alkaline hydration products that control the acid neutralisation capacity of solidified products, and therefore the solubility of metal contaminants. The acid neutralisation capacity of the solidified wastes was determined using a three-point ANC test, based on the Environment Canada ANC method (Stegemann and Côté, 1991), with HNO$_3$ acid additions of 0, 1 and 2 meq/g dry mass. Samples cured for 28 days were dried at 60°C, crushed using a mortar and pestle and sieved to <150μm. The crushed sample was then placed in 100 mL plastic bottles and distilled water and 1M HNO$_3$ added to give a liquid-to-solid ratio of 10 and the desired acid addition. The bottles were sealed and rotated end over end for 48 hours. Leachate was extracted, centrifuged at 10,500 rpm for 10 minutes (Sorvall RC6 centrifuge) and the pH determined. Part of the leachate was filtered through a 0.45 μm cellulose nitrate membrane filter (Whatman International Ltd.) and analysed for chloride using the argentometric method (AWWA, 2005). This involves titrations using silver nitrate (AgNO$_3$) as the titrant and potassium chromate (K$_2$CrO$_4$) as indicator.

2.4.3 Tank Leaching Test (NEN 7375:2004)

Products that had a UCS after water immersion > 1MPa were tested for diffusion-controlled leaching from the monolith. 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 8 different times over a total period of 64 days. An aliquot of leachate

was filtered through 0.45 µm cellulose nitrate membrane filters (Whatman International Ltd.) for chloride analysis by the argentometric method.

3. Results

3.1 *Heat of hydration*

Figure 3 shows the results for high CEMI/low APC residue additions (0, 10 and 30 wt % of total dry mass). Figure 4 shows the effect on the heat of hydration for low CEMI/high APC residue addition (50, 70 and 100 wt.% of total dry mass) samples. Table 2 gives quantitative data from the conduction calorimetry experiments.

For APC residue additions up to 30 wt %, the main CEMI hydration peak occurs earlier than for 100% CEMI and the maximum rate of heat evolution increases. However, the total energy evolved is reduced with increasing APC residue addition. The total predicted heat evolution calculated based on the amounts of APC residues and CEMI in each mix, is also greater than actually evolved, indicating retardation of cement hydration. The hydration curves for samples containing 50%, 70% and 100% APC residues show no peak associated with CEMI hydration and the total heat evolved is much lower than for 100% CEMI samples.

3.2 *Setting time and consistence*

Setting time and consistence data for different CEMI /APC residue samples are presented in Figures 5 a-d. Both parameters are highly correlated with water addition, with correlation coefficients (R^2) for a fitted exponential curve ranging between 0.97-0.99 for consistence, 0.88-0.97 for initial setting time and 0.94-0.99 for final setting time.

Achievement of a target consistence of 175 ± 10 mm was desired, to provide a mix that was sufficiently flowable to allow compaction. However, the water demand of the APC residue was high, and this target could not easily be achieved for the 0% CEMI mixes, even with high water additions. The consistence criterion could be satisfied for CEMI-containing mixes, but the water additions are higher than typical water/solids ratios used for concrete. Increasing the amount of APC residues in the mix resulted in a decrease in consistence value for the same water addition.

3.3 *Porosity*

Calculated porosities are presented in Figure 6. Porosity increases linearly with increasing water addition; porosities ranged from ~30 volume % for 50 wt % CEMI at w/s = 0.4, to ~60 volume % for 0 wt % CEMI at w/s = 0.8 w/s. Porosity and water addition are highly correlated with correlation coefficients ranging between 0.89 and 0.99.

3.4 *Unconfined compressive strength*

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UCS data are presented in Figures 7 a-d. Values reported are the average of three replicates. Standard deviations (s^2) for all mixes ranged from 0.03 to 1.21, with differences between the individual samples and the average for each mix being less than 10%, indicating the low variability of the results obtained. Increasing water or reducing CEMI content reduced compressive strengths. 50 wt % CEMI mixes achieved average 28 day UCS values ranging from 8 to 17 MPa depending on the w/s ratio. Solidified products without any CEMI (Figure 7a) exhibited very low strength, with a maximum 28 day UCS of ~1 MPa exhibited by the mix with w/s = 0.4.

The percentage reduction in UCS after water immersion increased with increasing APC residue and water addition and was ~80% for 10% CEMI samples with low water content (w/s of 0.50 or 0.55). Specimens with low CEMI content (0 and 10%) and high water additions (w/s of 0.60 or 0.65) disintegrated during 7 days water immersion. However, the strength of solidified products containing 50% CEMI did not decrease after immersion, with the data actually show a marginal increase in UCS.

3.5 ANC test and leaching data

Leachate pH results and chloride leaching data are presented in Table 3. The leachate pH of all the products was high, typically ~ 12.1-12.6 and this is a range where many metal hydroxides such as zinc and lead exhibit relatively high solubility. Up to 2 meq/g of acid addition had no effect on the leachate pH of the 0% CEMI mixes. A greater effect is observed for the 10%, 20% and 50% CEMI mixes, which exhibited a higher pH initially, although pH reduced by less than 0.6 units. No difference in pH was observed between 1 meq/g and 2 meq/g acid additions for all mixes. Leaching of the finely crushed solidified products in the ANC test is indicative of the level of chemical stabilisation and the data show that most of the chloride remained soluble. 0% CEMI mixes leached high levels of chloride, which are within the range of the amounts potentially available for leaching given in Table 1. This demonstrates that curing of APC residues mixed with water has no significant effect on chloride solubility. Lower chloride leaching was achieved with higher CEMI additions, in part due to the reduced amount of chloride in the solidified waste samples.

3.6 Tank leaching data

The cumulative fractions of total chloride leached from the solidified APC residues are presented in Figure 8 as a function of the square root of time, for specimens containing 10%, 20% and 50% of total dry mass CEMI at a w/s ratio of 0.5. Cumulative measured leaching was calculated according to the formula:

$$\varepsilon_n^* = \sum_{i=1}^{n} E_i \qquad \text{for n = 1 to N} \qquad (2)$$

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.

Chloride leaching data presented as log-log plots of cumulative derived leaching (ε_n) vs. time are given in Figure 9. Cumulative derived leaching was calculated according to the formula:

$$\varepsilon_n = E_i \times \frac{\sqrt{t_i}}{\sqrt{t_i} - \sqrt{t_{i-1}}} \qquad (3)$$

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. Table 4 summarises the total measured amount of chloride leached expressed as emission of mass per unit surface area, as well as the diffusion controlled intervals and the slopes of the regression lines of log-log plots of the cumulative derived leaching vs. time for these intervals.

According to NEN 7375:2004, the gradient of a log-log plot of cumulative 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 Figure 9 shows diffusion control in early leaching intervals (1-4), with depletion of chloride from the specimens in later leaching intervals (as is also demonstrated by the nonlinear plots in Figure 8). The results for the diffusion-controlled period were used to estimate 64 day emissions, which are shown in Table 5. It should be noted that this approach is a deviation from the standard NEN method, which was carried out to obtain an indication of probable emissions, despite the rapid depletion of chloride from the specimen; the results should be considered as approximations only.

A subsequent paper will report the metal leaching data from monolithic CEMI solidified APC residue samples.

4. Discussion

Conduction calorimetry demonstrates that APC residues have a significant effect on CEMI hydration. A 10% APC residue addition to CEMI caused the main CEMI hydration peak to occur after 5.2 hours compared to 8.9 hours, while the total heat evolved during the 98 hour monitoring period was reduced. This level of APC residue addition is equivalent to the addition of ~ 2.4 wt % Cl$^-$ ion to the CEMI and this is in the range of Cl$^-$ ion additions used to accelerate CEMI hydration (1.0 % - 3.0 wt %) (Lea, 1970). Similar observations apply to samples prepared with 30 wt % CEMI additions.

The main CEMI hydration peak was no longer observed in solidified mixes containing low CEMI/high APC residue, although there was significant heat evolved during at least the initial 10 hours after mixing. There is no evidence of hydration reactions occurring for the 100% APC residue samples and the early heat evolved can be attributed to the exothermic reaction of free lime with water.

Setting time and consistence were affected both by the amount of CEMI in the mix and the amount of water. The correlation coefficients show that setting times and consistence are highly related to water addition. A less flowable consistence was observed for high APC residue additions. The presence of soluble salts combined with the fineness of APC residues means that high levels of water are required to obtain workable mixes containing high APC residue additions. Salts such as NaCl and KCl are deliquescent and readily adsorb large amounts of moisture from the environment. The consistence criterion of 175 mm chosen for this experimental work cannot be achieved with low water additions. Whereas all mixes satisfied the requirements for maximum initial (< 8 hours) and final (< 24 hours) setting time, the mixes with short setting times (e.g. less than 2 hours) could cause operational difficulties in a full-scale facility.

The target of 1 MPa for dry UCS was satisfied by all CEMI-containing mixes at both 7 and 28 days. APC residues solidified specimens containing 50% CEMI had maximum compressive strengths of 17.3MPa. These were reduced to 10.4 MPa at 20% and 5.5MPa at 10% CEMI additions, and the significance of these results as indicators of hydration is questionable, considering that no hydration peak was observed for these mixes by calorimetry. Certain heavy metal oxides are known to inhibit CEMI hydration reactions and this produces poor mechanical properties (Fernandez, 2001; Asavapisit, 1997). Zinc hydroxy anions present at pH values between 12 and 13 form calcium hydroxyzincate $(CaZn_2(OH)_6.H_2O)$, which coat CEMI grains and inhibit further hydration.

100% APC residue specimens exhibited no strength increase between 7 and 28 days curing. This observation, combined with the conduction calorimetry data and the low amounts of Si and Al present in the APC residues, indicate that pozzolanic reactions are not a major contributor to strength development when no binder is added. The 1 MPa strength of the 100% APC sample with w/s = 0.4 is attributed to the hydration of lime, i.e., essentially due to drying, without formation of a durable matrix.

Strengths after water immersion indicate that it is difficult for specimens with high APC residue addition to maintain structural integrity when exposed to water. Dissolution of salts present in APC residues severely affects matrix durability. Specimens prepared with high APC/low CEMI additions had significant strength loss or totally disintegrated when immersed in water. Higher water content samples had inferior mechanical properties, due to their increased porosities. High porosity and high water content also resulted in increased leaching from solidified products. The marginal strength increase after immersion for 50 wt % CEMI mixes may be due to the inherent variability in compressive strength measurement rather than a real effect, but does indicate that addition of 50 wt % of CEMI by total dry mass produced specimens that retain compressive strength when tested after immersion. However, conventional cement and concrete specimens for UCS testing are cured under water, and their UCS values are greater than those of specimens cured in a humid environment.

The chloride concentrations in the ANC extracts indicate that chemical stabilisation of chloride was poor. The granular leaching values determined for s/s products containing 0, 10 and 20% total dry mass of CEMI were far greater than the EU WAC limit for hazardous waste landfills

(Department of Environment, Food and Rural Affairs, 2002). Initial leachate pH values (i.e. 0 acid additions) are consistent with the presence of excess lime, while the partly-neutralised pH values could indicate the presence of alkaline phases characteristic of hydrated cement-based matrices. This is not likely, given the results from calorimetry and UCS measurement.

Comparing the measured and estimated leaching values with the monolithic WAC limit for 64 day release of 20×10^3 mg/m^2 (Hall et al.., 2005) suggests that chloride mobility was high for the CEMI systems investigated, as all mixes surpassed the WAC limit in the first 2 days of the test. Table 5 includes estimated 64-day emissions from similar studies on chloride leaching from CEMI solidified APC residues. The influence of aggregates on the leaching of chloride from CEMI solidified APC residues has been studied (Stegemann et. al., 2005). The values reported for 50% APC addition were from specimens without aggregate addition, and are similar to the values obtained in this study for the same mix. Although a direct comparison to the results in this study is not possible due to the addition of aggregates to the other mixes, it should be noted that leaching values obtained by Stegemann et. al. were similar regardless of the amount of APC residue, and hence chloride, added. In contrast, chloride leaching observed by Hall et al. (2005) was three orders of magnitude lower.

The potential mechanism for immobilisation of chloride in CEMI is the binding to the C_3A phases in the form of the chloro-complex Friedel's salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) (Suryavanshi et al., 1996). This depends on the amount of C_3A and also the presence of other anions such as SO_4^- which affect the immobilisation efficiency (Dehwah, 2006). Determination of whether chloro-aluminate phases formed in these samples requires further investigation, but the leaching results show they have a minor effect in the samples tested in this research.

5.   Conclusions

s/s treatment of APC residues using water without any CEMI addition does not result in products with sound physical properties, as the amounts of silica and alumina in the APC residues are insufficient for APC residues to be pozzolanic. Apparent strength development is caused by hydration of lime, rather than hydration to form a durable cement-based matrix.

Up to 30% APC residue additions accelerate CEMI hydration reactions, but total heat evolved during initial curing is reduced. CEMI hydration is severely inhibited, probably by the presence of heavy metals, in high APC residue/low CEMI samples. APC residues solidified using 10 and 20% CEMI have UCS values that exceed 1.0 MPa after 28 days. However, these samples show a significant decrease in UCS when tested after immersion in water. In addition to inhibition of binder hydration, leaching of soluble salts from the APC residues adversely affects the structural integrity of the s/s samples.

Water demand of CEMI mixes containing APC is high, and increasing the water addition improves sample workability and consistence, but increases porosity and has a detrimental effect on product mechanical properties.

Performance criteria for UCS, consistence and setting time were satisfied by mixes with CEMI additions of 10, 20 and 50 %wt at w/s ratios of 0.65, 0.65 and 0.55 respectively.

Chloride is not effectively immobilised in the CEMI-s/s APC residues at binder additions of 50% or lower. Monolithic tests show chloride leaching from all formulations in excess of relevant WAC limits. The commercial feasibility of using higher binder additions is questionable, and it is unlikely that immobilisation would be significantly improved in other binders that result in a matrix with similar hydration products.

Acknowledgements

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Table

Table 1
Granular waste UK WAC limits (Environment Agency, 2006) and APC residue composition data and range of concentrations typically leached using the L/S=10 EU compliance leaching test for granular wastes BS EN 12457-3 (Resource Recovery Forum, 2004).Units in mg kg^{-1} unless specified.

APC composition data	Aqua regia total metals/water soluble ions	Leachable metals/ions at L/S10	WAC Limits		
			Inert Waste Landfill	Non-reactive waste at non hazardous waste landfill	Hazardous Waste Landfill
Total organic carbon (w/w %)	1 – 2.5	130 mg/kg DOC as C	3%	5%	6% [*]
LOI (%)	1.5 – 3.0	n/d			10% [*]
free lime %w/w CaO	15 - 20	n/d			
pH	12.0-12.6	11.6-12.8		> 6	
Al	10000-24000	<5			
As	10-210	<0.0005 – 4	0.5	2	25
Ba	70-400	10 – 45	20	100	300
Ca	250000-300000	50000 - 90000			
Cd	100-260	<0.5	0.04	1	5
Co	9-18	<0.05 - 0.15			
Cr	12-200	0.5 - 2.5	0.5	10	70
Cu	350-920	1.3 - 3	2	50	100
Fe	3000-7200	0.5 - 2.5			
Hg	<1-34	0.04 - 0.5	0.01	0.2	2
K	9000-24000	16000 - 22000			
Mg	4000-6000	0.3 - 1.5			
Mn	350-560	0.01 - 0.25			
Mo	2-16	<1 - 4	0.5	10	30
Na	13500-22500	11000 - 18000			
Ni	15-45	0.2 - 45	0.4	10	40
P	1500-3000	<5			
Pb	2500-5500	300 - 700	0.5	10	50
Sb	200-500	<0.0001 - 0.2	0.06	0.7	5
Se	0.1-6	<0.0005 - 9	0.1	0.5	7
Sn	200-800	<4			
Ti	900-4000	<0.9			
Tl	0.5-0.8	<0.06			
V	<30	0.09 - 0.6			
Zn	4000-18500	40-85	4	50	200
Water extractions					
Br	1000-2000	900 - 1700			
F	100-1500	1 - 45	10	150	500
Cl	130000-220000	140000 - 170000	800	15,000	25,000
water soluble SO$_4$ [#]	8000-38000	7000 - 12000	1000	20,000	50,000
CO$_3$ as CaCO$_3$	10000 - 45000	1500 - 8500			
water soluble alkalinity as CaCO$_3$	-	23000 - 32000			
TDS [+]			4,000	60,000	100,000
*Trace Organics (*ug/kg = ng/kg*)*					
Total phenols (9)	< 1-30	n/d			
Total PCBs (7)	<=20	n/d	1		
Total PAHs (16)	70-300	n/d	100		
PCDD/DF (ITEQ)	0.5 – 2.6	n/d			

[*]   Either TOC or LOI must be used for hazardous wastes

[+]   The values for TDS can be used instead of the values for Cl and SO$_4$

[#]   If an inert waste does not meet the SO$_4$ L/S 10 limit, alternative limit values of 1500 mg l^{-1} SO$_4$ at C$_2$ (initial eluate from the percolation test (prCEN/TS 14405:2003)) and 6000 mgkg^{-1} SO$_4$ at L/S10 (either from percolation test or batch test BS EN 12457 -3), can be used to demonstrate compliance with the acceptance criteria for inert wastes

Table 2
Conduction calorimetry data for CEMI/APC mixes.

Sample (w/s = 0.5)	Max. rate of heat evolution (W/kg)	Time of max. rate of heat evolution (hours)	Total heat evolved during 98 hour test (kJ/kg)	Total heat expected* (kJ/kg)
CEMI	2.42	8.9	205.4	N/A
10% APC	3.05	5.2	186.2	189.6
30% APC	3.30	3.3	132.5	157.8
50% APC	4.56	0.6	103.5	126.1
70% APC	8.05	0.6	85.5	94.0
100% APC	13.69	0.6	46.7	N/A

* Heat calculated based on the heat evolved from the 100% APC and CEMI mixes and the relative amounts of each component in the different mixes.

Table 3
Chloride leaching and pH results

CEMI Addition	Liquid-to-solids (mL/g)	[Cl⁻] (mg/kg)	pH - 0 meq/g acid addition	pH - 1 meq/g acid addition	pH - 2 meq/g acid addition
0%	0.4	144,500	12.2	12.3	12.2
	0.6	143,500	12.1	12.2	12.2
	0.7	137,000	12.1	12.2	12.2
	0.8	137,000	12.1	12.2	12.2
10%	0.5	113,200	12.3	12.1	11.9
	0.55	121,200	12.3	12.1	12.0
	0.6	113,500	12.3	12.0	11.9
	0.65	119,000	12.3	12.1	11.9
20%	0.45	93,500	12.4	12.0	12.1
	0.5	93,700	12.3	12.1	12.0
	0.6	90,700	12.4	12.0	12.0
	0.65	88,000	12.4	12.1	12.1
50%	0.4	55,700	12.6	12.3	12.1
	0.5	47,500	12.6	12.2	12.2
	0.55	46,500	12.6	12.2	12.0
	0.6	52,700	12.6	12.1	12.1

Table 4
Measured cumulative chloride 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.

CEMI addition	Water-to-solids (mL/g)	ε_n^* (mg/m^2)	Diffusion Controlled Increment	$\Delta\log\varepsilon_n/\Delta\log t$ of diffusion controlled increment
10%	0.5	1,167,000	1-3	0.45
20%	0.45	1,027,000	1-3	0.45
	0.5	997,000	1-3	0.46
	0.6	875,000	1-3	0.44
50%	0.4	615,000	1-4	0.40
	0.5	590,000	1-4	0.43
	0.55	573,000	1-2	0.48
	0.6	580,000	1-2	0.43

Table 5
Estimated 64 day emission based on diffusion controlled increments. Mixes presented are at a w/s of 0.5.

Study	% w/w APC	Cl (mg/kg)	Estimated 64 day chloride emission (mg/m^2)
Lampris et. al. (present work)	50.0	80,000	1,420,000
	80.0	128,000	3,100,000
	90.0	144,000	4,310,000
Stegemann et. al. (2005)	15.5	25,000	1,500,000
	20.1	32,000	1,200,000
	25.1	40,000	1,500,000
	30.6	49,000	1,900,000
	36.5	58,000	1,900,000
	50.0	80,000	1,800,000
Hall et al. (2005)	0.25-5	400-9,000	2,044

Figure
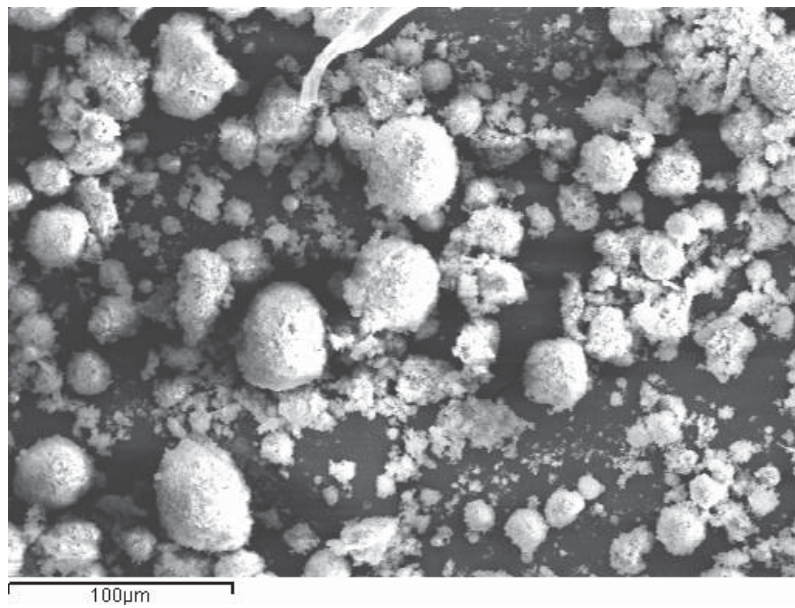
Fig. 1. SEM image of as-received APC residues.
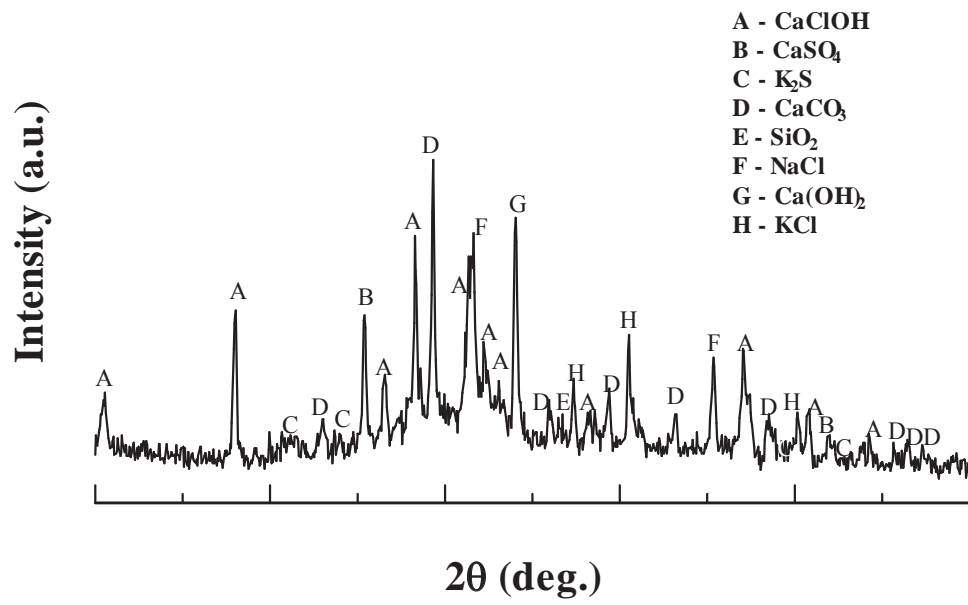
Fig. 2. XRD data for as-received APC residues.
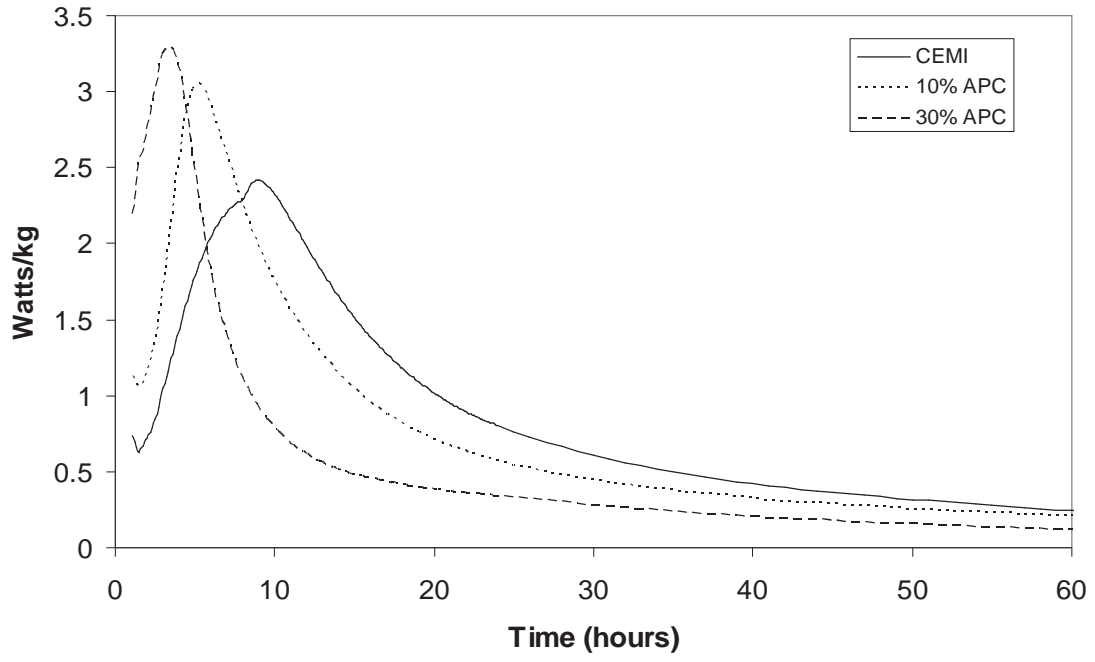
Fig. 3. Heat evolution during hydration of high CEMI/low APC residues mixes.
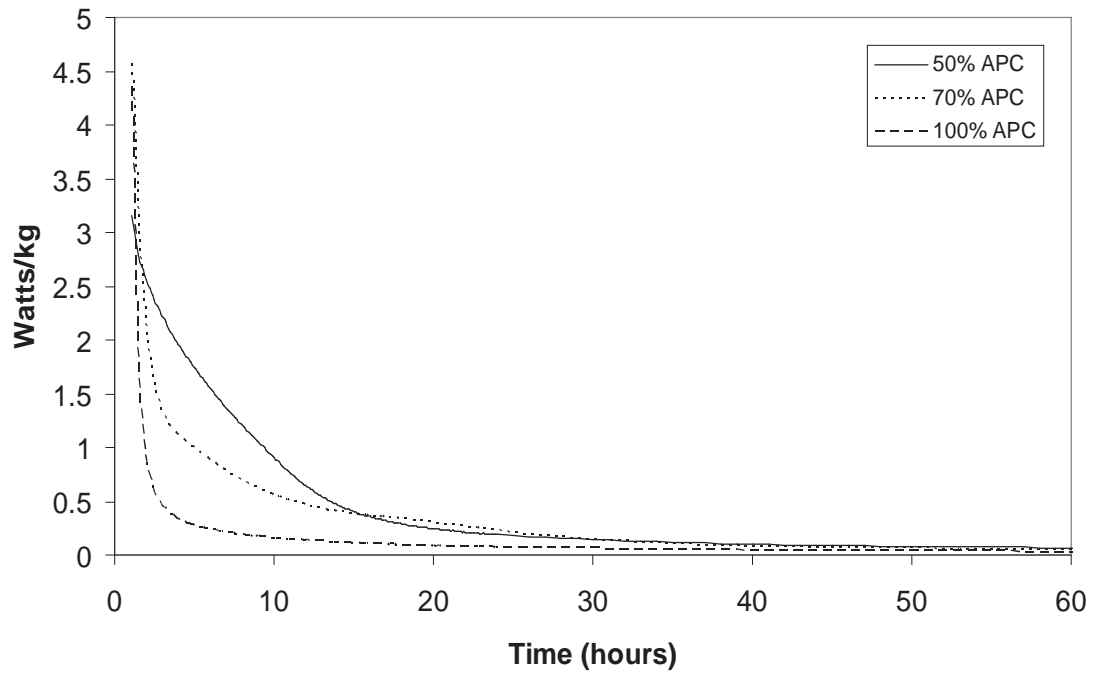
Fig. 4. Heat evolution during hydration of low CEMI/high APC residues mixes.

a)

b)

c)

d)
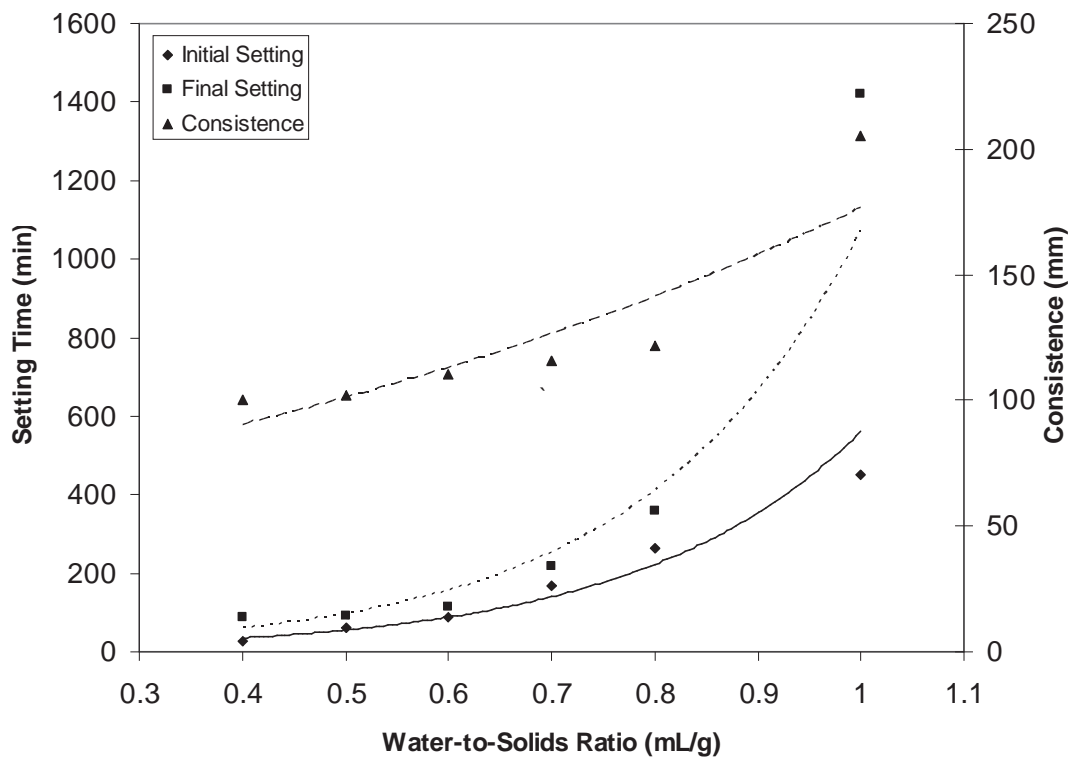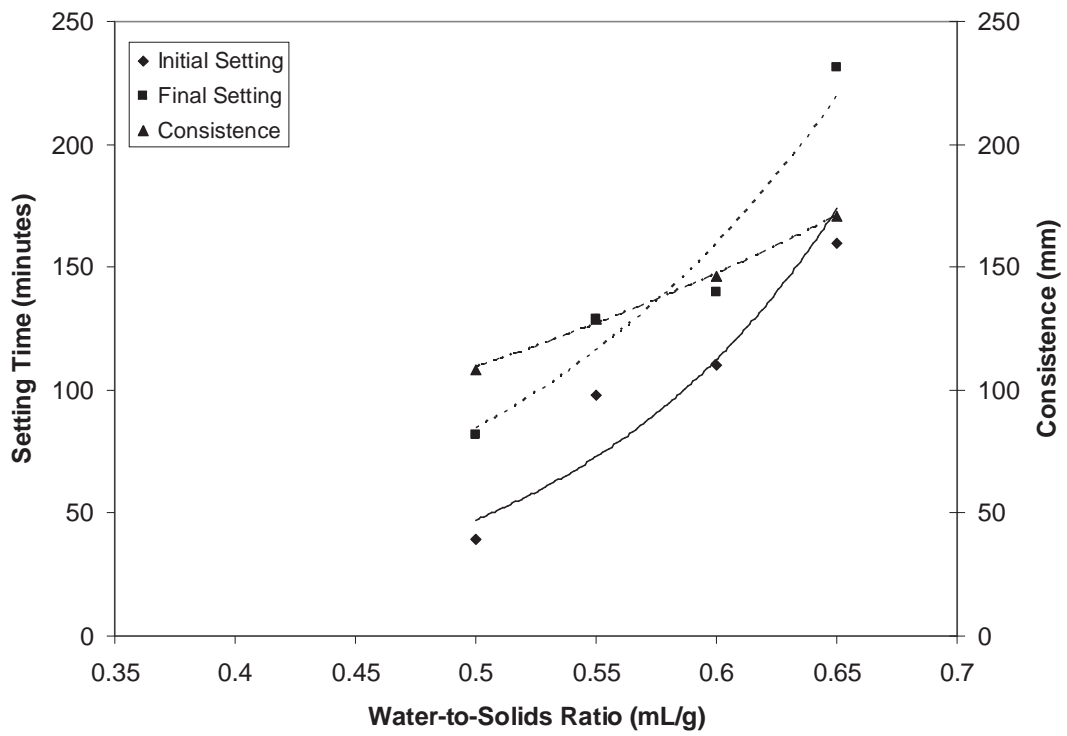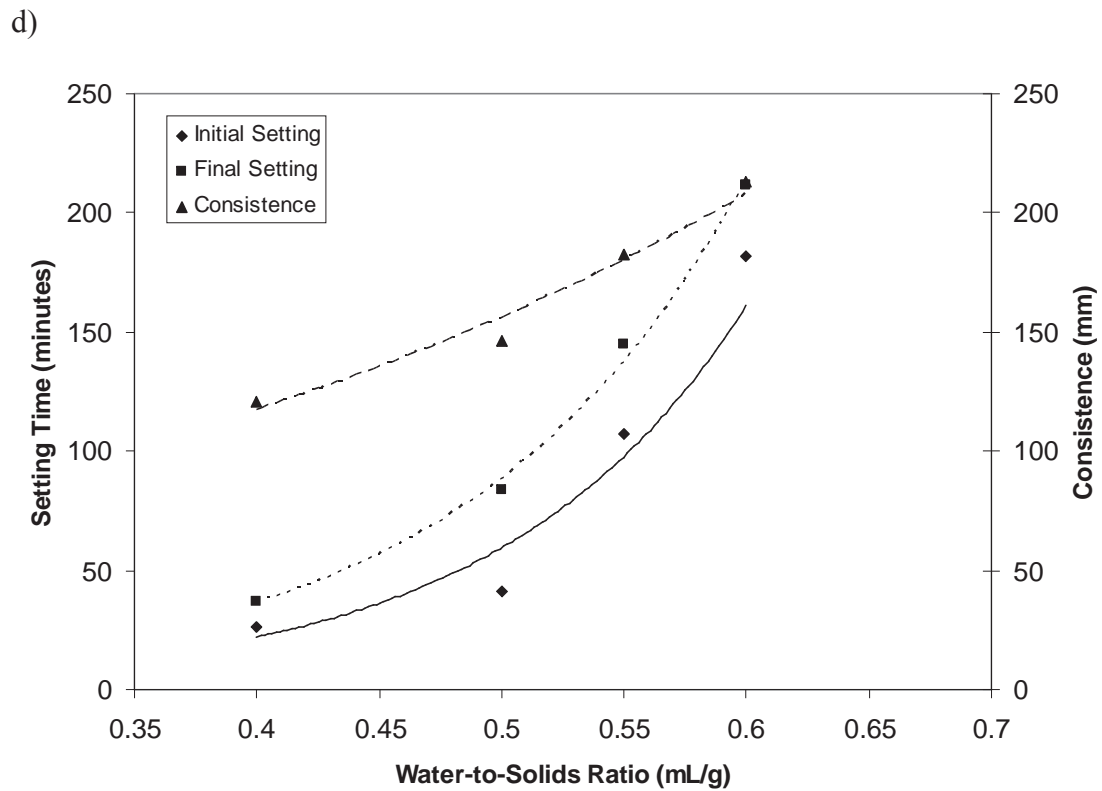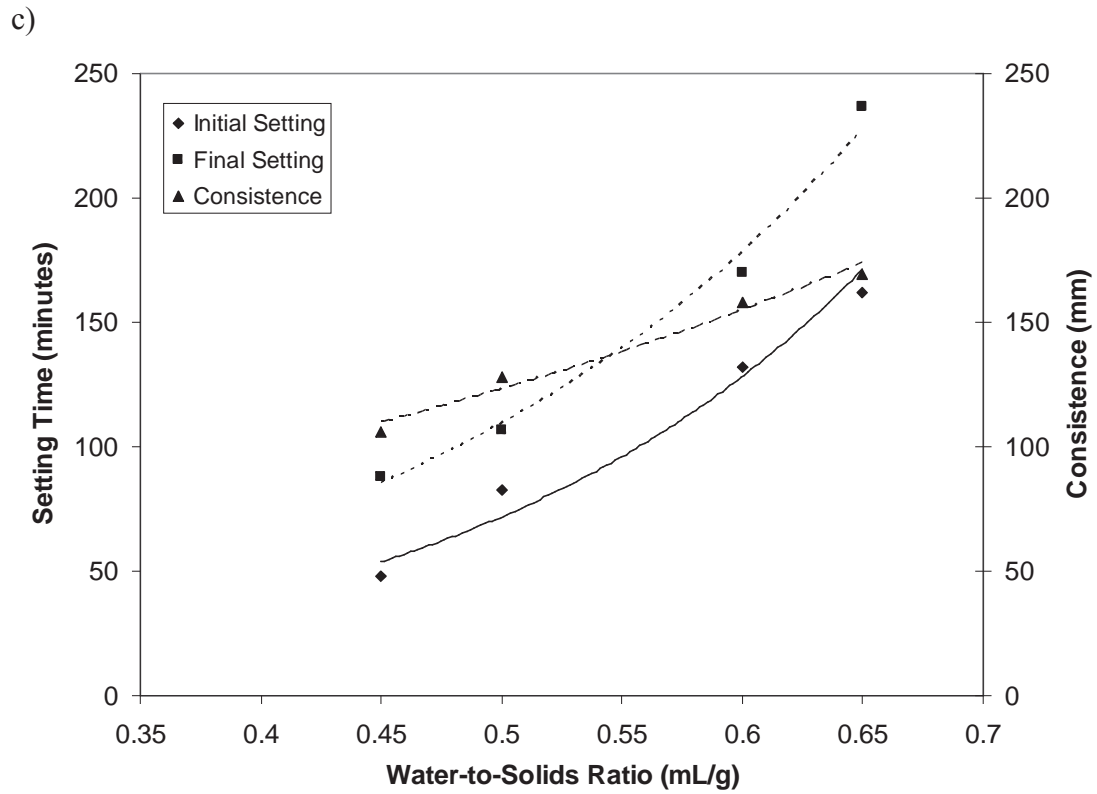
Fig. 5a-d. Setting time and consistence of APC residues with: a) 0% CEMI addition, b) 10% CEMI addition, c) 20% CEMI addition and d) 50% CEMI addition
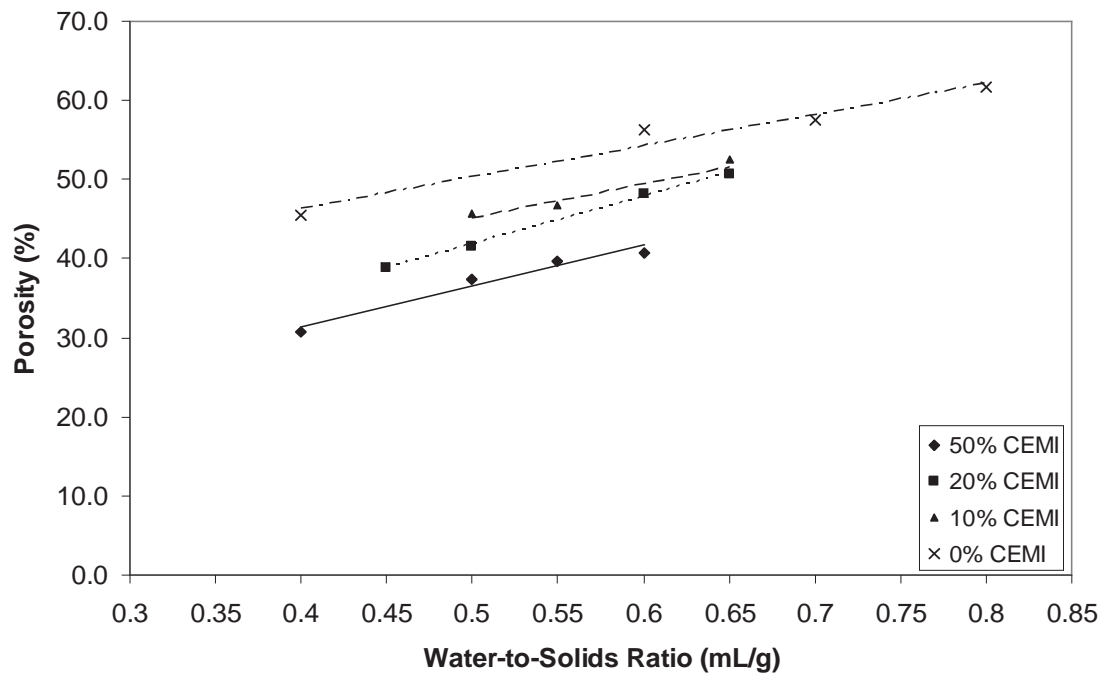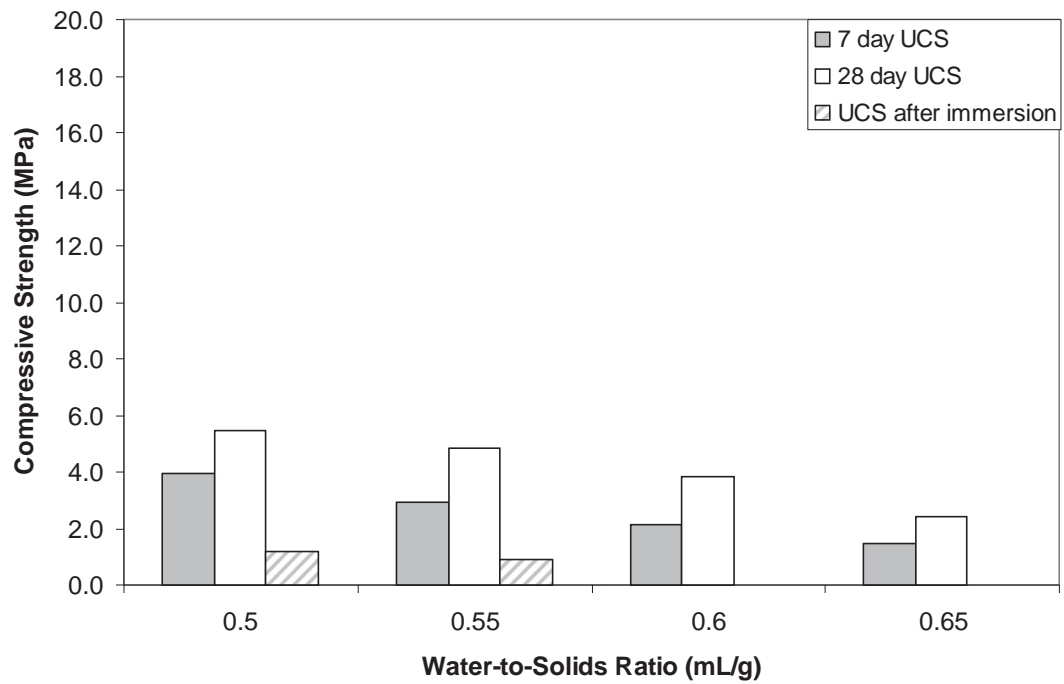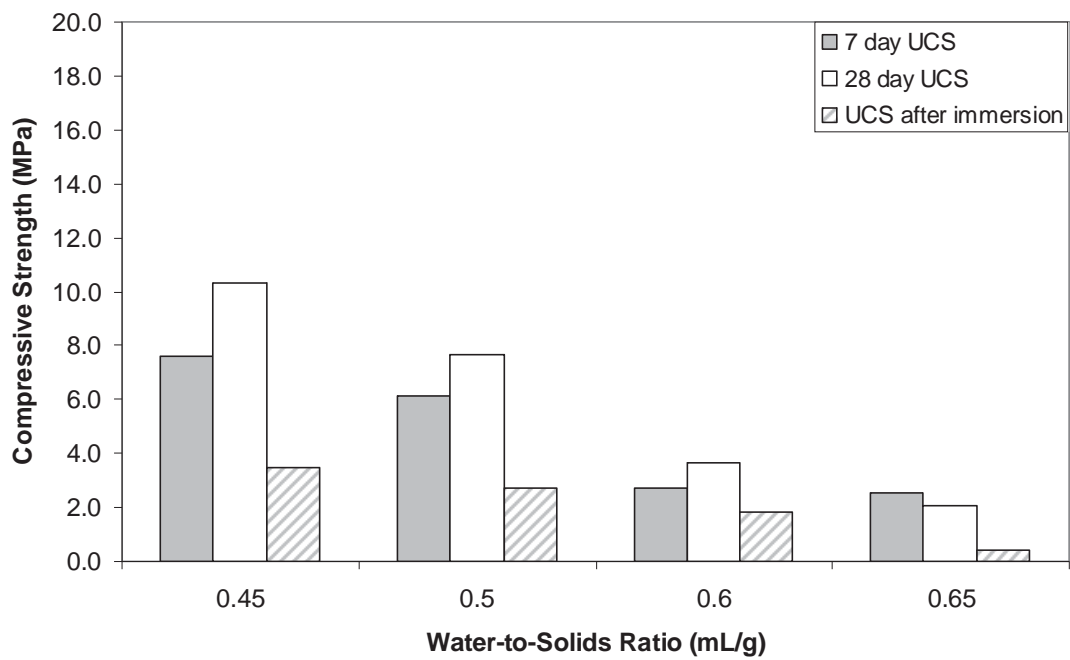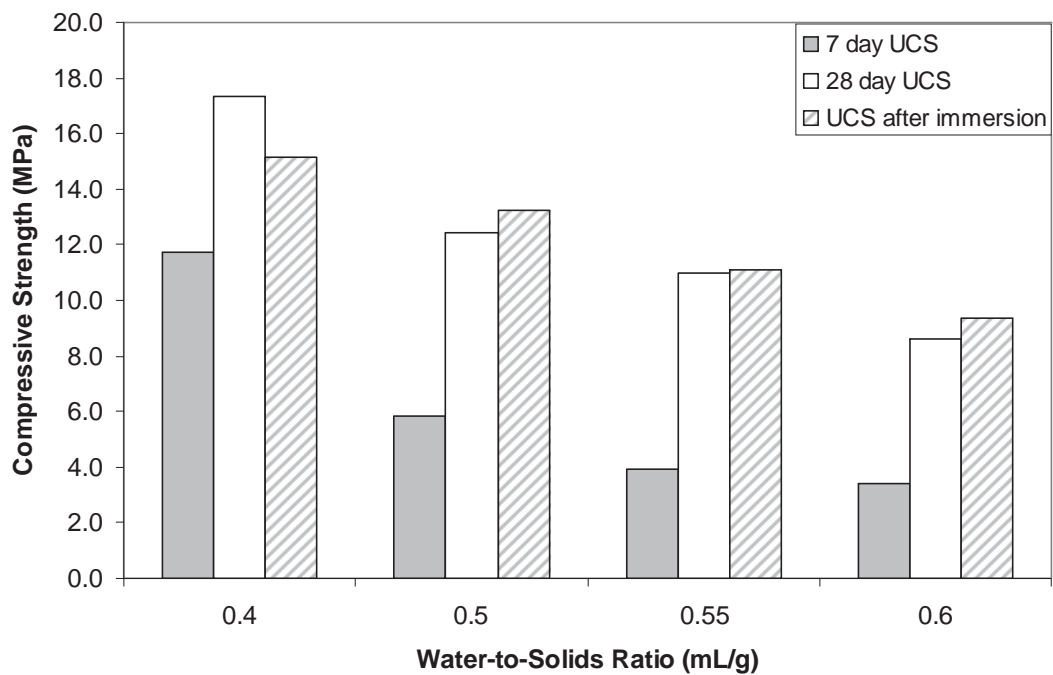
Fig. 6. Porosity at 28 days of mixes investigated

a)
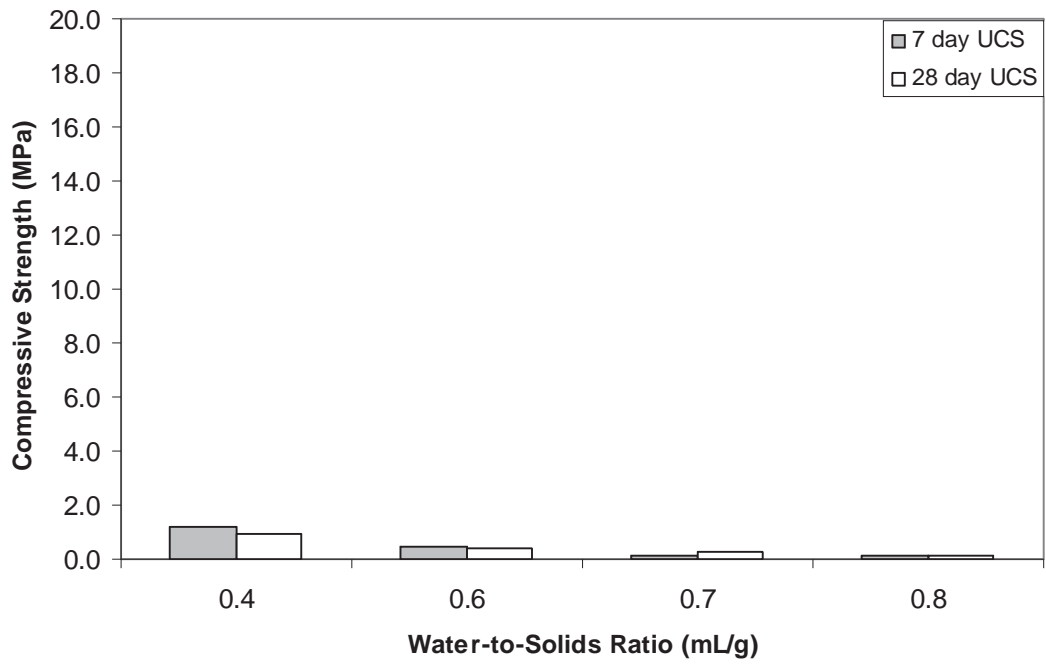
b)

c)

d)

Fig. 7a-d. Compressive of APC residues with: a) 0% CEMI addition, b) 10% CEMI addition, c) 20% CEMI addition and d) 50% CEMI addition
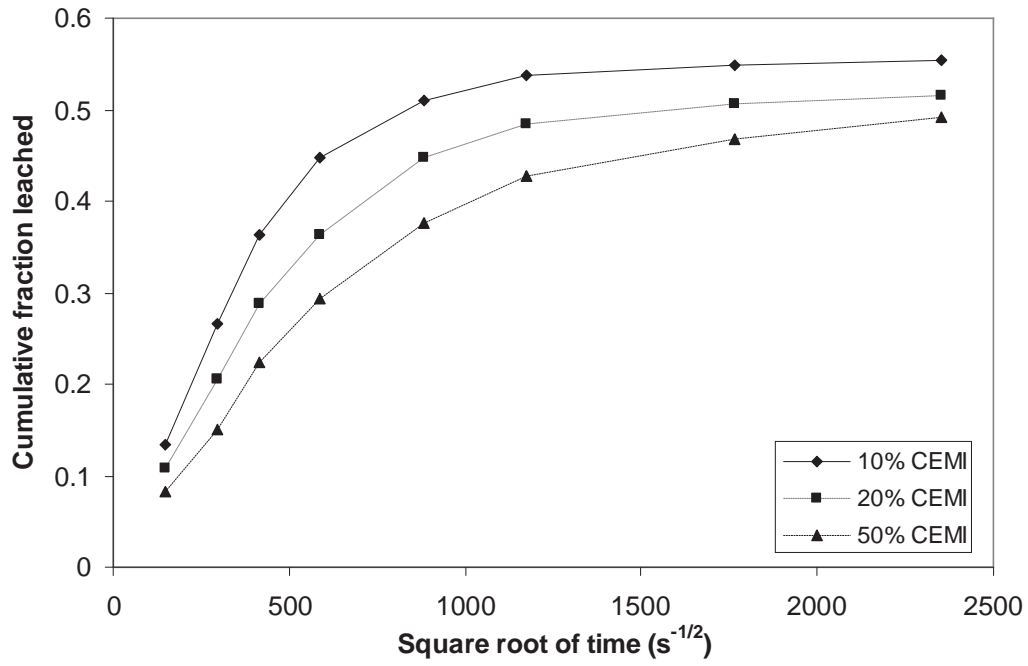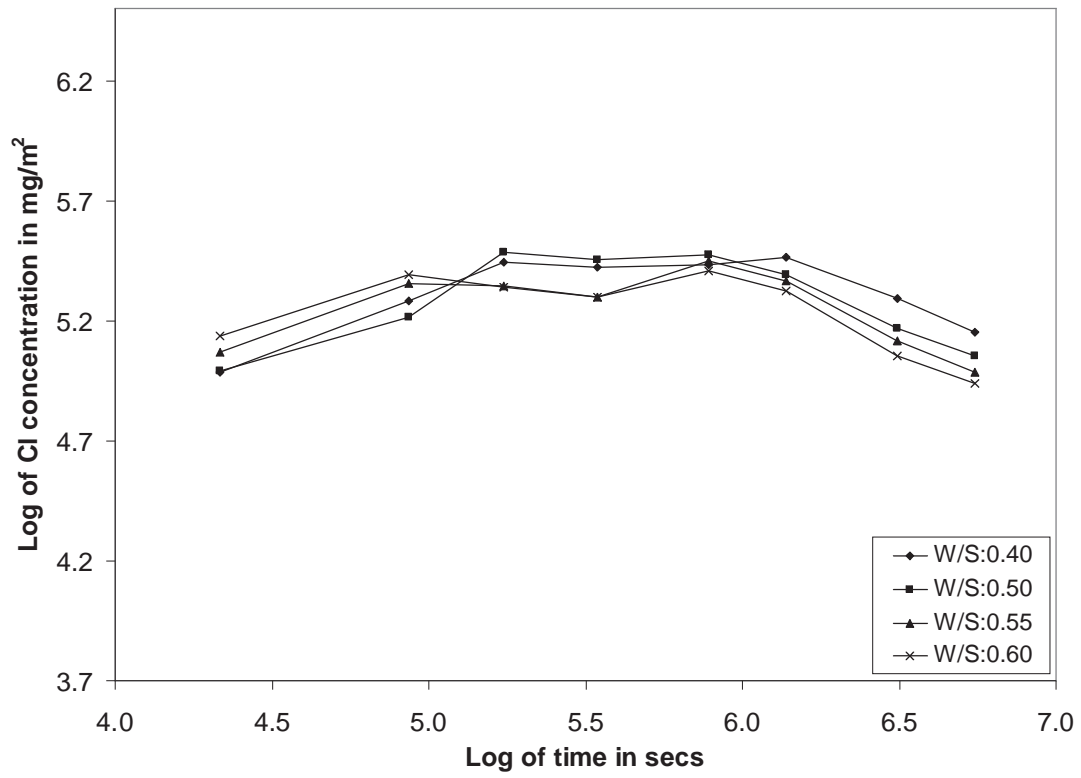
Fig. 8. Cumulative fraction of chloride released from 10%, 20% and 50% CEMI mixes at a w/s ratio of 0.5.
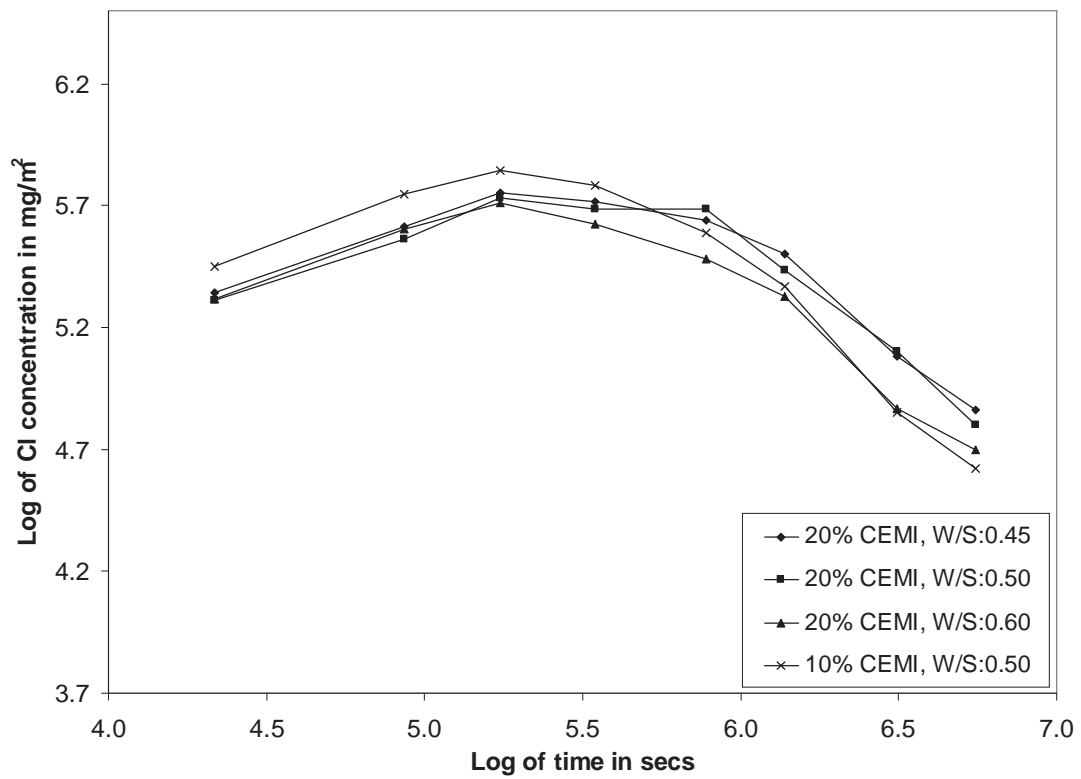
a)

b)

Fig. 9. Cumulative derived leaching plots of: **a.** 50% CEMI mixes and **b.** 20% and 10% CEMI mixes tested according to NEN 7375:2004.