Conference paper

Shirley, R and Black, L *Chloride and sulphate release from alkali activated s/s of APC using co-fired PFA.* In: 30th Cement and Concrete Science Conference, 13-14 September 2010, Birmingham.

Cement & Concrete Science Conference: Birmingham, 2010

Chloride and sulphate release from alkali activated S/S of APC using Co-Fired PFA

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Abstract: An increasingly favoured alternative to landfill is energy from waste (EfW) incineration. However, the leach behaviour and heavy metal content of the solid air pollution control (APC) residue collected when cleaning the gas stream to meet stringent air pollution limits, results in an absolutely hazardous classification in the European Waste Catalogue (EWC). Current methods for handling this waste stream are unsatisfactory, unsustainable or economically inefficient. Work presented here examines the possibility of solidification / stabilisation (s/s) of these residues using other waste streams, including a co-fired PFA and a waste caustic solution, with the primary objective of meeting the waste acceptance criteria (WAC) for stable non-reactive (SNR) hazardous waste. In this way a resource- and economically-efficient treatment may be realised. This paper presents results strength, workability and setting time, plus chloride and sulphate leach data using a monolithic and granular leach test. The extent of sulphate immobilisation is strongly dependent on chloride leaching, in part due to higher sulphate solubility in a chloride solution.

1. Introduction

There are many potential treatment methods for APC residues (1). Amongst these treatment options is solidification/stabilisation. This is the process of mixing the waste with supplementary materials in order to form a solid monolith in which waste elements may be immobilised chemically and physically by the reaction products (2,3). A considerable amount of work has been performed on the solidification/stabilisation of APC residues, including work which utilises cement, blast furnace slag, coal fly ash or a blend of these materials (4-9).

In this work the potential of s/s using other waste materials destined for disposal or treatment and disposal is examined. These include a PFA from a co-fired (coal and biomass) power station which is deemed unsuitable for construction purposes due to high LOI and sulphur content (EN 450) and is therefore subject to disposal. With increasing use of co-firing of power stations in the UK, PFA with similar compositions to the one utilised in this work may become more regularly produced. The use of low grade, high carbon 'rejected' fly ash, has shown potential for s/s of synthetic heavy metal sludge (10). Also utilised is an aluminium-containing caustic solution from an industrial cleaning process The potential for the use of alkali activated cementitious systems as a waste binder has been discussed previously (11,12). There is indication that alkali activated cements results in a less porous, more durable matrix which is beneficial for waste encapsulation (11-13). Similarly, a study of alkali activation of PFA/GGBS blends (without waste addition) using NaOH solutions showed that PFA/GGBS, caustic strength and curing temperature all played a role in determining the mechanical behaviour (14). The success of this treatment is judged against the WAC for SNR sites and recent literature (15). Criteria examined include workability, setting time, UCS, and leach performance. The effects of varying conditions including l/s, APC/PFA, duration of curing and curing temperature are shown.

2. Materials and Methods

The composition of the materials used in this work is shown in table 1. Samples were cast as 50mm cubes and compacted on a vibrating table or by hand tamping as necessary, mix compositions are summarised in table 2 whilst the test methods used are summarised in table 3. Samples were also submerged in water for 7 days prior to testing 28 day UCS.

Element	Ca	Cl	Si	Al	Na	K	Pb	Zn	S	LOI
APC	46	20	0.24	0.08	1.4	0.5	0.17	0.19	0.65	5.4
PFA	3.07	0.04	24.06	10.22	0.83	1.94	0.00	0.21	3.75	10.4
WC				2.65	7.96					

Table 1: %w/w composition of reactants as determined by XRF and acid digestion

Mix	APC (g)	PFA (g)	NaOH (g)	l/s	Curing Temp (°C)
1:4 l/s=0.55	12.9	51.6	35.5	0.55	40
1:4 l/s=0.75	11.4	45.6	43	0.75	40
1:4	10	40	50	1	40
2:3	20	30	50	1	20/40/80
3:2	30	20	50	1	40

Table 2: Mix compositions per 100g

Test	Standard	Deviation
Workability	BS EN 13395-1:2002	None
Setting time	EN 480-2:2006	Standard Consistence not used
UCS	BS EN 12390-3:2009	50mm Cubes
Granular Leach	BS EN 12457-2:2002	20g samples and rotating table used.
Monolithic Leach	EA NEN 7375: 2004	None

Table 3: Test methods used.

3. Results and Discussion

Mix	Flow Value (mm)	Setting Time (HH:MM)	7d UCS (MPa)	28d UCS (MPa)	%UCS loss (7d sub)
1:4 (0.55)	146	<16:45	6.1	13.4	8.4
1:4 (0.75)	213	22:00	5.4	10.1	18.7
1:4	>testable	31:45	5.2	4.6	56.3
2:3 (20)	180	<7 days	0	3.0	0
2:3	180	31:15	3.8	8.7	14.2
2:3 (80)	180	05:45	7.4	7.89	46.5
3:2	135	49:00	3.9	6.5	3.8

Table 4: Workability, Setting Time and UCS Data

Table 4 presents the engineering data for the different mixes. Many of the results are as would be expected. There was a decrease in workability with increasing APC content, attributed to the hygroscopic nature of the residues. Higher curing temperatures rapidly decreased setting time. Higher APC content increases setting time (4,5) although this is offset by the increased consistence of 1:4 compared to 2:3. UCS decreased upon immersion in water due to significant TDS. Strength loss upon washing could be altered by APC content, l/s and curing temperature.

Mix	**Diffusion Controlled Increment**	ε_{64}	pD_e	**Cumulative % Released**	**12457-2 (mg/kg)**
1:4 (0.55)	None	243,458*	n/a	90	26,300
1:4 (0.75)	None	276,104*	n/a	100	27,700
1:4	None	234,825	n/a	90	21,200
2:3 (20C)	1-4	718,467	10.8	100	49,500
2:3	1-4	746,924	10.7	100	45,900
2:3 (80C)	None	455,625*	n/a	100	43,700
3:2	2-7	434,567	11.6	55	70,900

Table 5: Cl release during EA NEN 7375:2004 and BS EN 12457-2:2002
*after 7/8 fractions

Mix	**Diffusion Controlled Increment**	ε_{64}	pD_e	**Cumulative % Released**	**12457-2 (mg/kg)**
1:4 (0.55)	None	35,283*	n/a	17	4900
1:4 (0.75)	None	35,470*	n/a	17	4350
1:4	None	22,892	n/a	11	2850
2:3 (20C)	1-7	17,733	13.0	13.5	5800
2:3	1-4	48,736	12.1	10.5	2259
2:3 (80C)	None	37,996*	n/a	20	2163
3:2	2-7	34,670	12.2	22	5420

Table 6: sulphate release during EA NEN 7375:2004 and BS EN 12457-2:2002

As is consistent with previous work on s/s of APC residues without additional treatment, Cl greatly exceeds the WAC limits for monolithic (10,000mg/m²) and granular (15,000mg/kg) tests (Table 5). Percentage release suggests very little or no chemical fixation of Cl and its release is entirely dependent on physical encapsulation, and therefore on the microstructure of the monoliths. Results for UCS loss upon submersion and monolithic leach results suggest lower porosity at higher APC contents, lower l/s, and lower curing temperatures. Similar behaviour was seen for sulphate release although the percentage release suggests some chemical fixation. WAC for sulphate (monolithic-10,000mg/m², granular-20,000mg/kg) was met during the granular leach test but exceeded during the monolithic leach tests which may suggest sulphate release to be highly time dependent.

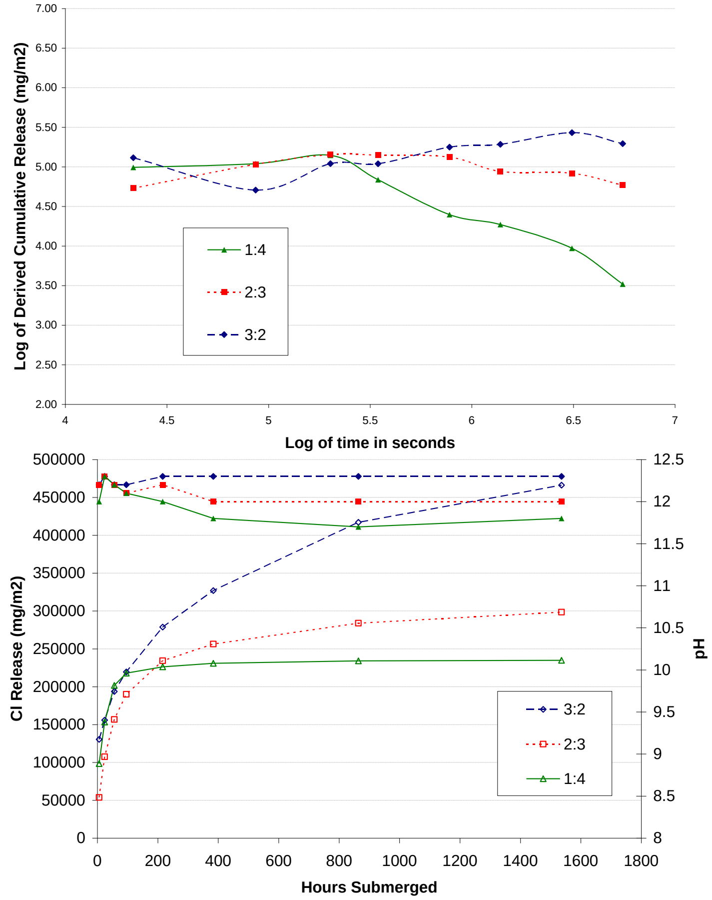

Figure 1: Cl Release (EA NEN 7375:2004)

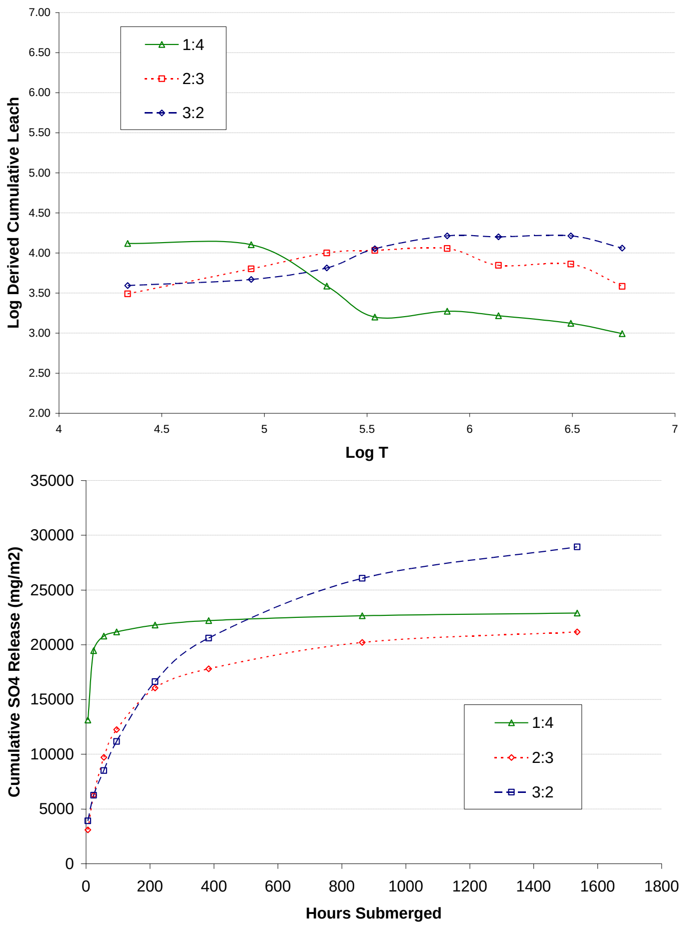

Figure 2: SO_4 Release (EA NEN 7375:2004)

Despite sample 3:2 containing less sulphate than 1:4 (tables 1&2), release was higher. This is due to the greater sulphate solubility in Cl rich solutions (with higher ionic strength). This is also suggested by the slowed release of sulphates in the monolithic test for 2:3 following Cl depletion, whilst sulphate release from 3:2 continues nearly unabated with similarly high continued Cl release. The relationship is also evident in the behaviour of 1:4 which demonstrates higher sulphate release before Cl is depleted, at which point it is greatly reduced despite a relatively small fraction of total sulphate content leached.

Conclusions

APC residues undergo pozzolanic reactions with waste pfa to form solid blocks. However, chlorides and, to a lesser extent, sulphates are not immobilised. Leached ions form part of the leach environment and via interaction with solute ions can have significant implication on the solubility of other species. Thus, high Cl concentration in leachates from APC residues can increase SO_4 release from s/s matrices. This can result in failed SNR WAC when using some co-fired (non-EN 450) PFAs.

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