An assessment of Mercury immobilisation in alkali activated fly ash (AAFA) cements

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ABSTRACT

This paper presents total and soluble Mercury contents for three coal fly ashes and alkali-activated fly ash (AAFA) cements consisting of 100% fly ash as starting material. To evaluate the potential of the AAFA cement matrix to immobilise Hg from an external source, another batch of cements, doped with 5000 mg/kg Hg as highly soluble $HgCl_2$, was prepared. The ashes and control AAFA cements complied with Mercury leaching criteria for non-hazardous wastes according to both TCLP and EN 12457 tests. Fly ash activated cements doped with 5000 mg/kg Hg and aged for 2 days immobilised 98.8–99.6% and 97.3–98.8% of Hg according to TCLP and EN 12457 tests respectively. Evidence from SEM-EDX suggests that Hg was immobilised by precipitation as highly insoluble HgS or Hg_2S, although partial precipitation as less insoluble HgO or Hg silicates could not be entirely ruled out based on data presented. The results for Hg-doped cements contribute to the growing body of evidence that shows AAFA cement as a useful material for immobilizing elevated concentrations of toxic and hazardous elements.

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1. Introduction

1.1. Mercury

The combined characteristics of high toxicity, high environmental mobility and the ability to bio-accumulate in aquatic fauna has led to Mercury being identified as a priority pollutant worldwide. Efforts to find alternatives to Mercury have resulted in industrial demand declining by around 80% between the years 1960 and 2000 [1,2].

Regulations regarding Mercury-containing wastes in developed countries are becoming increasingly stringent. For example, from 2010 onwards in Sweden, all wastes containing more than 0.1% (1000 mg/kg) Hg are to be placed in a permanent bedrock repository [3]. In the standardised European leaching tests [4], used to determine which landfill type is suitable for a particular waste, Hg is the most stringently regulated metal. Granular wastes leaching more than 2 mg/kg and monolithic wastes leaching more than 0.4 mg/m²/kg Hg are considered unsuitable for disposal even in hazardous waste landfill sites in the UK [5]. In the American toxicity characteristic leaching procedure [6], the lowest acceptable limit for any soluble metal, by a factor of five, is 200 µg/L for Hg. Furthermore, any waste exceeding this limit must then be treated

to comply with a more stringent soluble Hg limit of 25 µg/L prior to landfilling [7].

1.2. Coal fly ash and Mercury

Despite the fact that coal generally contains less than 1 mg/kg Hg, the massive scale of the coal combustion industry and the fact that Hg is highly volatile has resulted in anthropogenic Mercury emissions being dominated by coal combustion [8].

Mercury normally exists in coal as HgS impurities in pyrite (FeS), which rapidly (in <1 s) oxidises to hematite (Fe_2O_3) and/or magnetite (Fe_3O_4) under typical coal combustion conditions [9]. The vapourised Mercury can either be retained in bottom ashes, fly ashes, air pollution control sludge or pass to the atmosphere as vapours in exhaust gases. The precise partitioning of Mercury will depend on coal type and combustion plant set-up and is extremely difficult to predict. Temperatures in the coal combustion zone can be 1200–1600 °C. Above 600 °C, the only stable form of Mercury is the elemental vapour. Following combustion, fly ashes leave the furnace in the exhaust gas stream. Heat is recovered from the exhaust gases and when flue gas temperatures are low enough, typically 150–420 °C, fly ashes can be recovered using electrostatic precipitators. The addition of ammonia or sulphur oxides to exhaust gases to improve particle removal efficiencies at this stage will also affect the behaviour of Hg. According to Mukherjee et al. [10], the presence of chlorine and sulphur in flue gases at temperatures of 400 °C or lower favours the oxidation of elemental Hg vapour to Hg^{2+}, facilitating its deposition on charged fly ash particles and

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subsequent removal by dust control equipment. It is generally regarded that Hg is preferentially absorbed onto unburned carbon surfaces present in the fly ash which are predominantly associated with the finer fraction of ash particles [11]. Average partitioning percentages of Hg present in the original coal to separated fly ashes of 18% [12], 27% [13] and 58% [10] have been reported in the literature. Less than 1% of Hg typically remains in bottom ash.

1.3. Coal fly ash re-use and alkali activation

Coal fly ash is generally considered as a non-hazardous waste and millions of tonnes of this material are beneficially re-used each year as partial substitutes for ordinary Portland cement. Furthermore, pure fly ash cements, consisting of 100% by mass fly ash, have been developed within the last decade via an alkali activation process at moderately elevated temperatures [14–16]. Such cements can be considered as low CO_2/embodied energy equivalents to ordinary Portland cement.

The alkali activation of fly ash (AAFA) in the absence of Portland cement (PC) and lime is a chemical process in which the ash is mixed with certain alkaline activators and cured at a mild temperature to generate a material with good cementitious properties. The main reaction product formed is a XRD amorphous alkaline aluminosilicate hydrated gel, often termed as N-A-S-H due to its chemical structure [17,18]. In this gel, tetrahedrally coordinated Si and Al combine to form three-dimensional structures, with the Al tetrahedral imparting a negative charge which is balanced by Na^+ cations provided by the alkali activator solution. Zeolites can also be formed as secondary reaction products.

However, in the aftermath of the massive spill of coal fly ash slurry in Tennessee in 2008, the US EPA is currently considering changes to the existing exemption of coal fly ash to the Resource Conservation and Recovery Act [19]. These changes, if implemented, would require coal fly ash that is not beneficially reused, to be subject to the same disposal restrictions as municipal waste or hazardous waste. One of the main environmental concerns with fly ash is Mercury contamination.

Although the environmental benefits of construction products containing high proportions of waste materials has been rightly lauded, such materials may present an increased risk of leaching of heavy metals to the environment. Therefore the first objective of this work was to quantify the soluble Hg levels present in fly ash and AAFA cements according to EU and US standard leaching methods.

1.4. Heavy metal stabilisation/solidification

Physical and chemical immobilisation of heavy metal bearing wastes in Portland cement based blocks prior to landfill disposal has been widely employed in order to comply with landfill leaching criteria. The cement matrix presents both a physical barrier and a highly alkaline environment in which metals will exist predominantly as highly insoluble hydroxide salts.

However, this is not the case with Mercury, whose ability to exist in solid, liquid, dissolved aqueous and gaseous forms under normal environmental conditions, causes problems with normal cement stabilisation/solidification processes [7]. Chemical interaction between Mercury (II) and Portland cement hydration reactions and products is regarded as minimal [20]. An X-ray photoelectron spectroscopy (XPS) and SEM/EDX study of Portland cement (PC) doped with 100,000 mg/kg (10%) $Hg(NO_3)_2$ indicated the localised formation of HgO in the cement matrix and these areas being associated with the presence of elevated levels of calcium carbonate

and the absence of silicate [21]. These authors proposed the precipitation reaction in an alkaline environment as:

$$Hg^{2+} + 2OH^- \rightarrow HgO + H_2O \tag{1}$$

Alkali-activated cements have been the subject of considerable research interest during the last decade and may represent a feasible and more environmentally friendly alternative to Portland cement for stabilisation/solidification of a number of heavy metal bearing wastes [22,23]. Palomo and Lopez de la Fuente [24] showed that alkali-activated fly ashes (AAFA) were better suited to Boron immobilisation (15,000 mg/kg dosage) than Portland cement due to both a higher degree of immobilisation and a lack of interference during setting and hardening. In another paper, excellent Pb immobilisation in the AAFA matrix has been attributed to the formation of highly insoluble Pb_3SiO_5 [25].

However, the same authors also stated that AAFA systems were not suitable for Cr(VI) immobilisation at doses of 26,000 mg/kg due to the formation of soluble $Na_2CrO_4 \cdot 4H_2O$, which severely inhibited the solidification process. Such problems were not experienced by Xu et al. [26], when working with Cr(III) at lower doses. These authors reported extremely low TCLP leachate metal concentrations from mixed metakaolin/fly ash alkali-activated cements containing 1000 mg/kg doses of Cd, Cu, Cr(III) and Pb. However with Arsenic, immobilisation efficiencies in AAFA cements doped with 10,000 mg/kg As were shown to be only around 50% by Fernández-Jiménez et al. [27].

With regard to Hg, the only work to date that the authors are aware of involving alkali-activated cements of is that of Qian et al. [28,29], who used alkali activated slag (AAS) cured at room temperature as the cementitious matrix. These authors reported immobilisation efficiencies of 99.4% and 99.99% of Hg added as 5000 mg/kg $HgNO_3 \cdot H_2O$ after 1 day and 28 days of curing respectively. The increase in immobilisation correlated well with the reduction in cement porosity with age, suggesting that physical encapsulation is an important factor. The same authors proposed that with a higher dosage of 20,000 mg/kg, Hg initially forms both HgO and an amorphous Hg–silicate precipitate due to endothermic peaks observed at 303 °C and 486 °C respectively in TGA/DTA analysis.

Considering the promising results reported with AAS cements, the second objective of this paper is therefore to investigate the ability of alkali activated fly ash (AAFA) cements cured at moderately elevated temperatures to immobilise Hg both present in the original fly ash and added as an external source.

2. Materials and methods

2.1. Materials

The three different coal fly ashes used in this work (labelled as A, B and C), were all of the class F variety. Ash A was a combination of bottom ash and fly ash whereas the other two were pure fly ash samples. Prior to the experiments, each ash was milled until at least 95% of the ash mass passed a 45 μm sieve. Reagent grade sodium hydroxide (Panreac) and distilled water were used to prepare the 8M NaOH activator solution and reagent grade Mercuric Chloride ($HgCl_2$ – Merck), which possesses a high degree of aqueous solubility and is much more stable than equivalent nitrate salts at the moderately elevated curing temperature of 85 °C, was used as the external Mercury source where appropriate.

2.2. Ash characterisation

Major elements present in the ashes were determined by X-ray fluorescence (XRF) using radiation at an acceleration voltage of 100 kV and current of 80 mA (Philips PW 1404/00/01). Crystalline

phases in ashes were measured by X-ray diffraction (XRD) using a Cu anode and CuKα radiation generated at a voltage of 40 kV and current of 50 mA (Bruker D8 Advance). Total Mercury contents were determined by cold vapour atomic absorption spectroscopy in an external laboratory.

2.3. Elaboration of cement pastes

The minimum acceptable liquid to solid (L/S) ratios between each coal fly ash and the 8M NaOH activator solution to achieve a suitably flowable paste consistency to allow for proper casting into moulds was determined in preliminary experiments and were found to be 0.37, 0.43 and 0.30 for ashes A, B and C respectively. Fly ashes were added to the activator solution and hand mixed for 3 min before being cast into 1 cm × 1 cm × 6 cm stainless steel moulds with the aid of a jolting apparatus. The moulds were then sealed in a plastic bag and the bag placed in a sealed container maintained at 99% relative humidity and 85 °C for a period of 20 h. Samples were then removed and allowed to cool to room temperature before being opened and demoulded.

In the case of Mercury doped cement pastes, the appropriate quantity of $HgCl_2$ was accurately weighed out along with the fly ash and thoroughly mixed before being added to the activator solution and cast as described above with the reference pastes.

2.4. Cement paste analysis

Specimens of 1 cm × 1 cm × 6 cm were tested for flexural (NET-ZSCH 6.111.2, GmbH) and compressive strength (Ibertest Autotest 200/10 SW) approximately 24 h after being cast. During mixing of the 5000 mg/kg Hg-doped samples, very occasionally some small orange precipitates were visible in the paste. A section of hardened paste displaying this orange precipitate was carbon coated and analysed by Field Emission SEM with an EDX mapping analysis using a Hitachi S-4800 instrument with a cold cathode field emitter and operating voltage up to 20 kV.

2.5. Leaching tests

Additional cement samples were broken with a hammer and combined with broken pieces from strength tests before passing through a 9.5 mm and 4 mm sieve. Pieces with diameters between 4 and 9.5 mm were used for the TCLP leaching test and pieces passing a 4 mm sieve were used for the EN 12457 leaching test. Leaching tests were started within 24 h of demoulding (paste age ≤2 days).

2.5.1. Adapted TCLP test
The procedure described in the method 1311 document published by the USEPA was followed with some slight variations due to the specific characteristics of the rotation device used. First of all 40 g of sample was mixed with 800 mL of 0.1 M CH_3COOH leachant instead of 100 g with 2 L. Secondly, the speed of rotation of end over end shaker was 3 rpm instead of 30 rpm and finally, samples were filtered through a double layer of 3 μm cellulose based filter paper instead of 0.6–0.8 μm glass fibre filters. We believe that by maintaining the same liquid to solid ratio, contact time and leachant, results should not deviate greatly from those expected from a standard TCLP test procedure. In the case of ash samples, it was not possible to use material in the size range of 4–9.5 mm. Following filtration, leachate pH was measured and a known volume of 5M HNO_3 was added to maintain a pH of <2 prior to ICP-OES analysis for Hg.

2.5.2. EN 12457-2 test
These leaching tests were carried out in an external laboratory according to standard EN 12457-2, which uses deionised water as

Table 1
Coal fly ash XRF data and total Hg contents.

Element (as oxide)	A	B	C
SiO$_2$ (%)	51.07	56.51	53.78
Al$_2$O$_3$ (%)	24.34	21.42	28.83
Fe$_2$O$_3$ (%)	15.09	8.57	5.81
MnO (%)	0.04	0.08	0.05
MgO (%)	0.96	2.19	1.27
CaO (%)	2.58	3.78	1.78
Na$_2$O (%)	0.40	0.63	0.47
SO$_3$ (%)	0.62	0.99	0.35
K$_2$O (%)	2.58	2.59	4.25
TiO$_2$ (%)	0.82	0.87	1.11
P$_2$O$_5$ (%)	0.07	0.15	0.22
LOI (%)	1.26	2.21	1.80
Sum total (%)	99.83	99.99	99.72
Total Hg[a] (mg/kg)	0.007	0.045	0.36

[a] Determined by cold vapour atomic absorption.

the leachant at a liquid to solid ratio of 10, with the mixture being rotated end over end for 24 h at 5–10 rpm. Leachate conductivity and pH were recorded after filtration and then the leachate was acidified prior to Hg analysis by ICP-MS.

3. Results

3.1. Ash characteristics

Major elements, loss on ignition after 1 h at 950 °C and total Hg contents of the fly ashes are shown in Table 1. The low CaO contents (<4% by mass) are typical of class-F type ashes produced by bituminous coal combustion. The ashes are similar in major elemental composition with the exception of the elevated Fe content apparent in ash A, which is most likely due to the inclusion of bottom ash in this sample.

The data in Fig. 1 show that all three ashes contain significant quantities of crystalline quartz (SiO_2) and hematite (Fe_2O_3). Mullite ($3Al_2O_3 \cdot 2SiO_2$) content differed greatly between the ashes (C > A ≫ B) as did Maghemite (Fe_2O_3) content (A ≫ B > C). Furthermore, ash A also showed traces of crystalline Iron, again most likely due to the inclusion of bottom ash with this sample. The only sample shown to contain anorthite ($CaAl_2Si_2O_8$) crystal phases in significant quantities was ash B.

3.2. AAFA cement mechanical strengths

The compressive and flexural strengths of the three alkali-activated fly ashes at 1 day of age, both with and without Mercury addition, are shown in Fig. 2. Paste A clearly performs best with regard to compressive strength development and is slightly better than the other two ashes with respect to flexural strengths. There is no significant difference in compressive strength development between pastes formed with ashes B and C, despite the large difference in L/S ratios employed (0.43 and 0.30). The effect of adding 0.5% Hg as $HgCl_2$ had little or no detrimental effect on the strengths of pastes B and C but did seem to negatively affect the compressive strengths of the paste A samples.

3.3. Soluble Hg levels

Leachable Hg concentrations for the three fly ashes, control AAFA cements and Hg-doped AAFA cements are compared with the limits specified in EN 12457 and TCLP tests in Figs. 3 and 4.

Fig. 3 shows that all untreated fly ashes complied with the EU limits for inert wastes and all control AAFA cements complied with relevant limits for non-hazardous wastes. However, it is also clear that EN 12457 soluble Hg is consistently higher in control AAFA
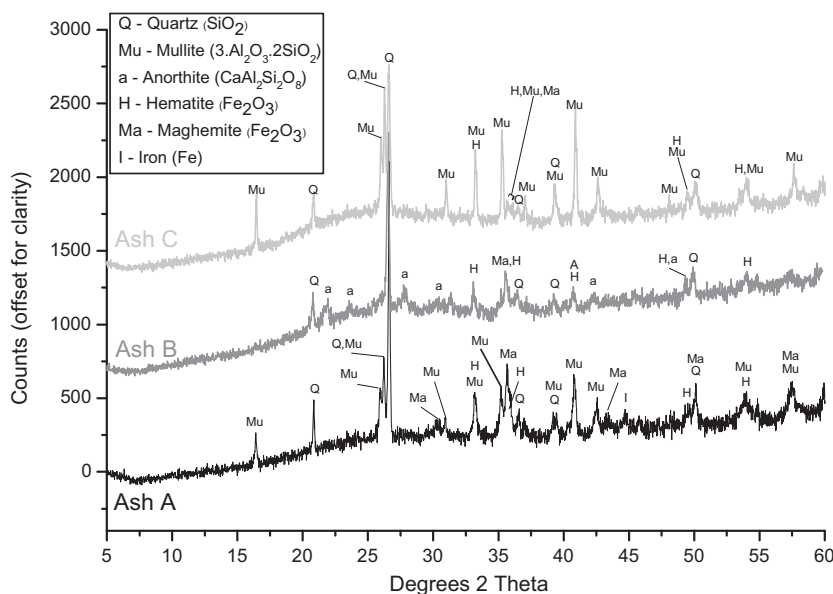
Fig. 1. XRD data for ashes A, B and C.

pastes than the equivalent untreated ashes. This suggests that the physicochemical environment created during the alkali activation process causes a slight but consistent increase in the solubility of native Hg species already present in coal fly ashes. Contributing factors are likely to be the moderately elevated curing temperature employed, the inherent high pH environment and possibly the large excess of Na^+ ions present. Fig. 3 also shows that with Hg-doped AAFA cements, all samples exceeded the EN 12457 limits for hazardous wastes by at least a factor of 30.

With TCLP results it was not possible to comment on the change in Hg solubility in untreated and alkali activated fly ashes since all leachates had Hg concentrations below the limit of detection. However, as the ICP-OES detection limit was slightly below the stricter universal treatment standard limit of 0.025 mg/L, (see Fig. 4), it can be concluded that all ashes and control AAFA cements comply with the soluble Hg requirements for non-regulated wastes. However, all Hg-doped cements failed to comply with the upper limit for TCLP soluble Hg by at least a factor of 4.
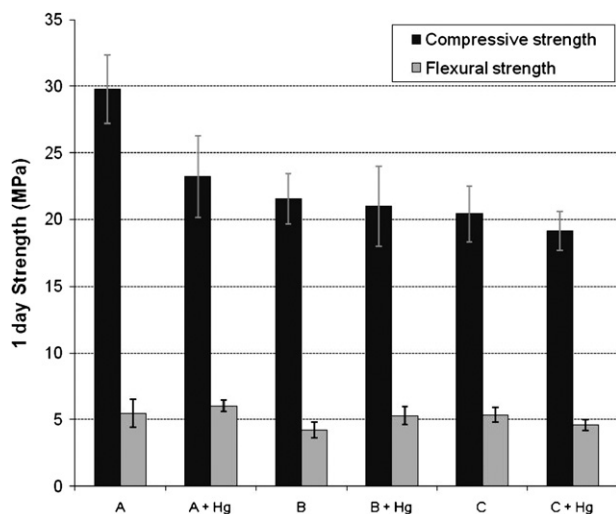

Fig. 2. Compressive and flexural strengths of control and 5000 mg/kg Hg doped AAFA cements at 1 day of age. Values are averages of 11 and 6 measurements respectively. Error bars shown are ±1 standard deviation.

3.4. SEM/EDX analysis of Hg-doped AAFA pastes

Mercury was added as $HgCl_2$, a highly soluble grey/white salt which, after dry premixing, was not distinguishable from the rest of the mixture. However, upon contact with 8M NaOH solution, yellow/orange coloured precipitates occasionally became visible. It was thought that this could be HgO, as reported by Qian et al. [28,29] in Hg-doped AAS cements since HgO exists in yellow or red coloured allotropes. To gather further information about the chemical make-up of this precipitate, parts of broken Hg-doped cement pastes showing the orange precipitates on the surface of the sample were analysed by SEM/EDX as shown in Fig. 5.

The mapping data in Fig. 5 confirms that the orange precipitate is a Mercury containing compound. There is a very strong correlation between the occurrence of Sulphur and Mercury, indicating that the precipitate is; HgS, Hg_2S, $HgSO_4$ or Hg_2SO_4. Cinnabar (HgS) is a well known naturally occurring mineral that is stable at room temperature and exhibits a characteristic red colour. The low concentration of Oxygen atoms in the Hg-containing region, relative to the surrounding N-A-S-H type gel that is characteristic of AAFA cements, implies that $HgSO_4$ cannot be the main Hg precipitate. Chlorine atoms were ubiquitously present in the sample, including the Hg-precipitate region, thus the possibility of traces of $HgCl_2$ remaining in the paste could not be ruled out. The orange colour of the precipitate fits well with that of HgO, which was the originally expected product, since red and yellow allotropes of this compound exist [30]. This would have been in agreement with the observations of McWhinney et al. [21] in Portland cement and Qian et al. [28,29] in AAS cement.

Results of EDX analysis (given in Table 2) show atomic ratios of Hg:S of between 0.7 and 3.3. It is likely that the excess Hg atoms are present as HgO precipitates or perhaps as Hg-silicates as suggested by Qian et al. [29]. Even though Oxygen atom concentrations were much lower in the area of the Hg precipitate than the surrounding gel according to mapping data, the EDX data in Table 2 shows significant levels of Oxygen atoms being present. However, with EDX data it is difficult to determine to what extent the underlying aluminosilicate gel contributes to readings, this will vary as a function of the depth of precipitate, which cannot be controlled or accurately estimated. Regardless, the possible existence of HgO and Hg-silicates cannot be completely ruled out.
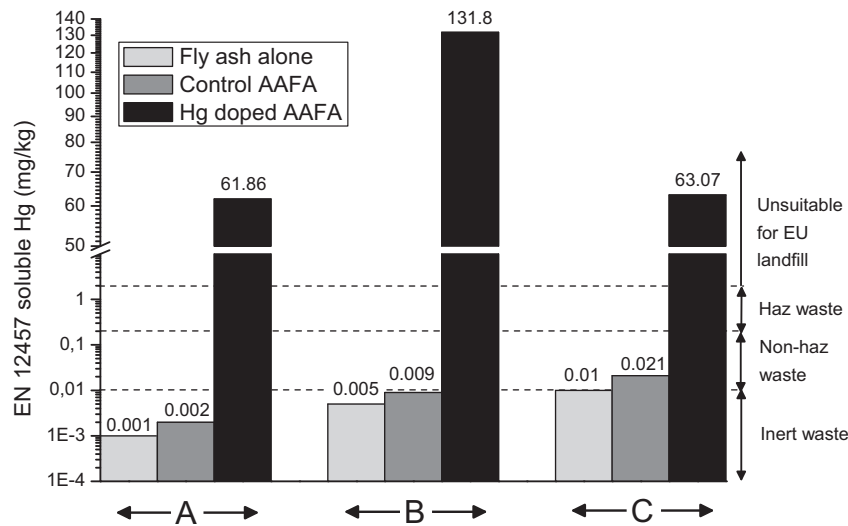
Fig. 3. EN 12457 soluble Hg results for ashes, 2 day old control AAFA cements and 2 day old Hg-doped AAFA cements. Results are compared with the relevant EU landfill waste acceptance limits of; <0.01 mg/kg for inert wastes, 0.01–0.2 mg/kg for non-hazardous wastes and 0.2–2.0 mg/kg for hazardous wastes.
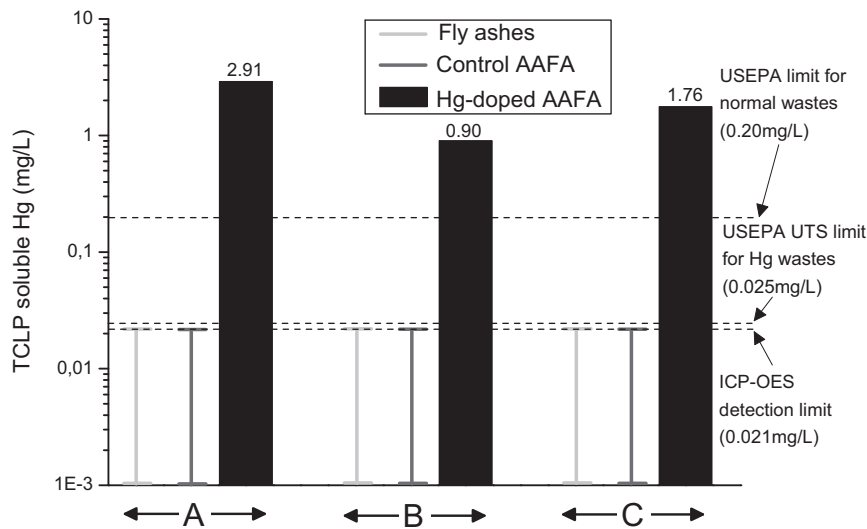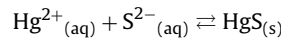

Fig. 4. TCLP leachate Hg concentrations for ashes, 2 day old control AAFA cements and 2 day old Hg-doped AAFA cements compared to TCLP limits for soluble Hg.

Of the three most likely Hg precipitates considered to form in AAFA matrices, two (HgS and Hg_2S) are extremely insoluble and one (HgO) is only very slightly soluble in water. The solubility products (K_{sp}) of HgS, Hg_2S and HgO are of the orders of 10^{-52}, 10^{-47} and 10^{-8} respectively. Eq. (2) shows the solubility product

of HgS, which, when in equilibrium with water at standard conditions, would equate to a dissolved Hg concentration of around 2.5×10^{-24} g/L. In general, efforts to stabilise Mercury containing wastes have focussed on the formation of HgS [31–34].

$$Hg^{2+}_{(aq)} + S^{2-}_{(aq)} \rightleftarrows HgS_{(s)}$$

$$K_{sp} = \frac{[Hg^{2+}_{(aq)}][S^{2-}_{(aq)}]}{[HgS_{(s)}]} = 1.6 \times 10^{-52} \tag{2}$$

3.5. Mercury immobilisation efficiency

Despite the failure of Hg-doped cements to comply with EU and US leaching criteria, it is still of interest to note that the vast majority ($\geq$97%) of the 5000 mg/kg Hg added remained in an insoluble form. The immobilisation efficiencies for all Hg-doped cements are shown in Fig. 6.

Despite variation between ashes, Fig. 6 shows that Hg in Hg-doped AAFA cements was always less soluble in TCLP tests than EN 12457 tests. This was surprising since the TCLP test is considered more aggressive with regards to heavy metal leaching and
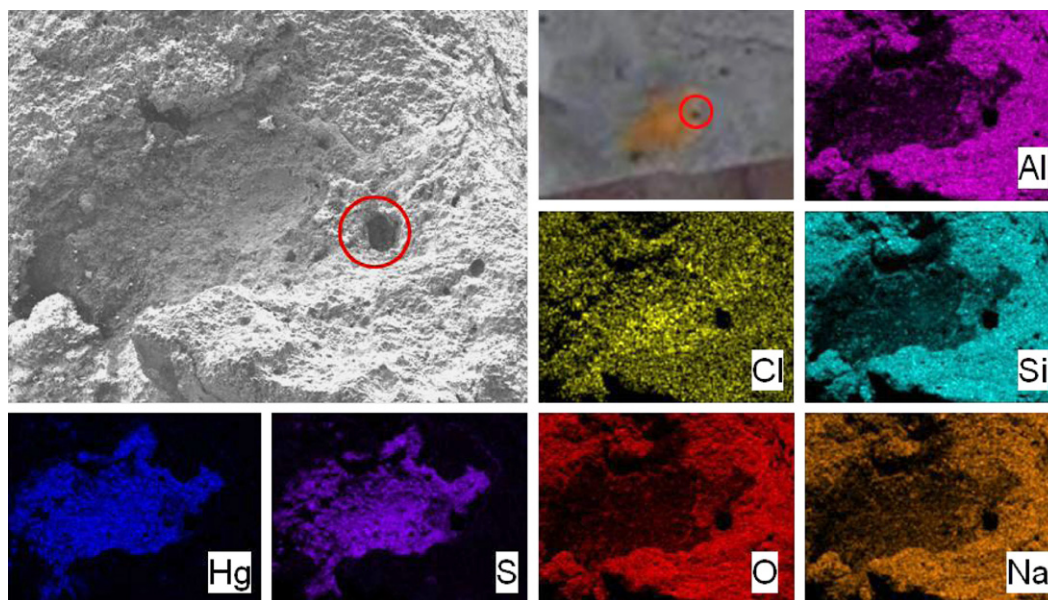
Table 2
EDX data from microanalysis of the Hg precipitate region in Fig. 5.

	1	2	3	4	5	6	7	8	Mean
S	7.1	5.0	1.3	1.1	4.2	2.6	7.0	1.8	3.8
Al	1.1	1.7	11.2	1.6	2.5	4.4	1.5	0.7	3.1
Si	5.3	5.7	15.3	2.3	3.6	3.7	3.8	14.2	6.7
Na	7.8	14.2	2.4	14.7	15.0	14.8	9.4	12.5	11.4
Mg	0.9	1.1	0.0	0.0	0.1	1.8	0.2	0.0	0.5
K	0.1	0.6	1.1	0.0	0.1	0.4	0.3	0.6	0.4
Ca	2.7	4.2	1.9	2.5	3.9	4.3	5.8	7.6	4.1
Fe	0.7	0.0	2.1	0.7	0.4	6.4	0.1	0.2	1.3
Cl	12.3	13.1	4.7	54.0	20.9	7.9	11.8	12.2	17.1
O	42.2	41.7	58.3	21.2	35.6	45.2	41.7	49.1	41.9
Hg	19.7	12.6	1.6	1.9	13.7	8.5	18.4	1.3	9.7
Hg:S ratio	2.8	2.5	1.2	1.7	3.3	3.3	2.6	0.7	2.3

Fig. 5. SEM with elemental EDX mapping analysis of orange precipitates as observed in 5000 mg/kg Hg-doped alkali activated ash cement pastes using ash A. (For interpretation of references to colour in this figure legend, the reader is referred to the web version of this article.)

consistently produced more acidic leachates than the EN 12457 test. One contributing factor is likely to be that the sample particle sizes specified in the TCLP are much larger (4.5–9.5 mm) than those specified in EN 12457 (<4 mm). The larger particle sizes in the TCLP test would present a much smaller surface area to the leachant and therefore limit any diffusion controlled solubility. Furthermore, in the case of HgS, solubility is said to increase with increasing pH and in the presence of excess sulphide due to the formation of soluble mercuric bisulphide complexes (HgS_2^{2-}) [34,35]. With regard to HgO, it has also been shown that Hg solubility increases moderately in increasingly alkaline solutions [30]. These two factors, paste fragment size and leachate pH, are most likely to be responsible for the higher Hg immobilisations observed in TCLP tests.

The TCLP results are similar to the 99.4% Hg immobilisation of 5000 mg/kg Hg-doped alkali activated slag (AAS) cements after 1 day curing reported by Qian et al. [28]. It is possible that immobilisation efficiencies were overestimated in both works since experiments were carried out in such a manner that did not detect nor quantify any possible emissions of Hg vapour to the atmosphere
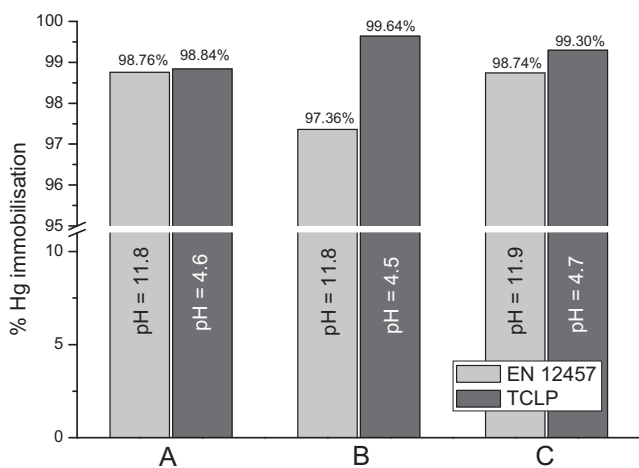
during mixing, casting, curing and demoulding. Such Hg losses have been reported before by Hamilton and Bowers [36] with 2000 mg/kg Hg-doped Portland cements and could be significant with AAFA cements, particularly due to the use of elevated temperature curing.

4. Discussion

From the results presented, there are some points that clearly merit further discussion:

4.1. Why does the solubility of "native" Hg present in the fly ashes increase slightly following alkali activation but the solubility of $HgCl_2$ dramatically decrease during the same process?

This behaviour can be explained if it is considered that the "native" Hg and the $HgCl_2$ added are considered as distinct species. The characteristics of $HgCl_2$ are well known; the Hg exists in the 2+ oxidation state and is highly mobile in an aqueous environment. During paste mixing, the added Hg^{2+} cations are relatively free to move along concentration gradients and encounter suitable sulphur or sulphide species to form insoluble precipitates. However, little is known about the nature of "native" Hg on fly ash particles. It could exist in the 0, 1+ or 2+ oxidation states and vary significantly between ash samples. A general consensus in the literature is that elemental Hg vapour does interact with other gaseous constituents in the flue gas and can be catalytically oxidised to the 2+ state and remain in the gaseous state, or be adsorbed to particle surfaces, as depicted in Fig. 7.

Direct Hg^0 vapour condensation on fly ash particles is possible where temperatures fall below the boiling point of Hg (357 °C). Unfortunately, as far as the authors are aware, no analytical technique is yet available that is capable of deducing the oxidation state or speciation of metals on particle surfaces at such low concentrations as Hg exists in fly ash (ppb). The broad correlation between carbon content and fly ash Hg concentration reported by Hower et al. [11] implies that adsorption on activated carbon surfaces present from unburned coal char particles can be a significant factor controlling Hg behaviour. We therefore tentatively postulate that during mixing of the paste, the inherent physicochemical
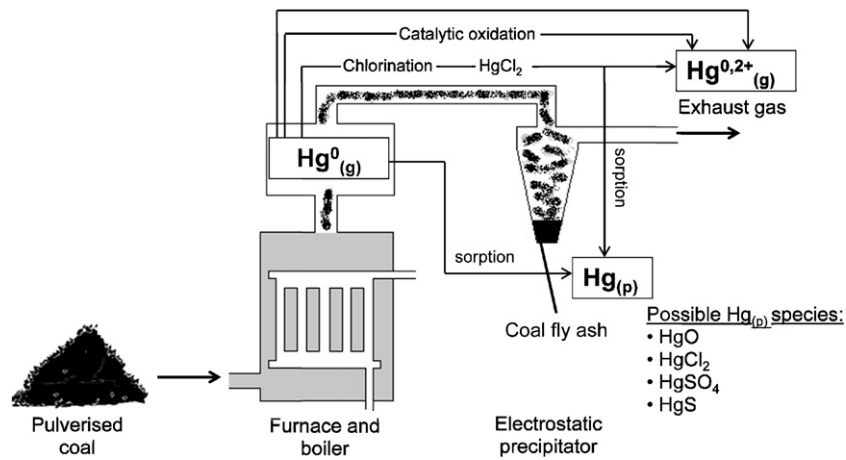

Fig. 6. Comparison of Hg immobilisation efficiencies in Hg-doped AAFA cements according to both EN 12457 and TCLP tests. The pH values given for each sample were measured in the filtered leachate following the relevant leaching test.

Fig. 7. Possible fates of Mercury during coal combustion.

Adapted from Galbreath and Zygarlicke [37].

conditions facilitate the desorption of a significant fraction of this native Hg. The form of desorbed Hg must be much less mobile and/or less liable to react with sulphur/sulphide to form HgS than the added $HgCl_2$. With this being the case, the desorbed Hg then becomes physically immobilised as the paste hardens, but is distant from the original surface it was absorbed to and thus is more prone to leaching than before.

4.2. Is the formation of HgS the principal mechanism of Hg immobilisation in Hg-doped AAFA?

This is a valid question because if all Hg were converted to HgS or Hg_2S, then Hg immobilisation levels should have been much higher than the 97–99% recorded by leaching test results. First, we should consider if sufficient Sulphur in the fly ashes was present to react with all of the Mercury added. Reaction stoichiometry dictates that the formation of 1 mol of HgS would require 200.6 g of Hg and 32 g of S. To convert 5000 mg of Hg into HgS would therefore require slightly less than 800 mg of S from 1 kg of fly ash. According to XRF

data shown in Table 1, and converting mass as SO_3 to mass as S, total Sulphur contents were 2500, 4000 and 1400 mg/kg for the ashes A, B and C respectively. Although XRF data does not specify the form of Sulphur present, it is at least theoretically possible that sufficient elemental Sulphur or sulphide is supplied by the three fly ashes used in this study.

Considering HgS precipitates, one factor that clearly supports the relatively high Hg solubility in doped AAFA samples is the effect of Cl^- ion interference. In a study examining the influence of interfering anions on the TCLP solubility of sulphide stabilised Mercury, it was reported that chloride ions strongly interfered with the HgS formation process and increased the solubility of Hg by a factor of around 100 compared to control samples without Cl^- [34]. The EDX mapping data shown in Fig. 5 clearly show that Cl^- ions were present in the same site as the HgS precipitate. Chloride ion interference, along with the possible formation of soluble $Na_2(HgS_2)$ complexes could well explain the higher than expected HgS solubility observed in the Hg-doped AAFA samples.

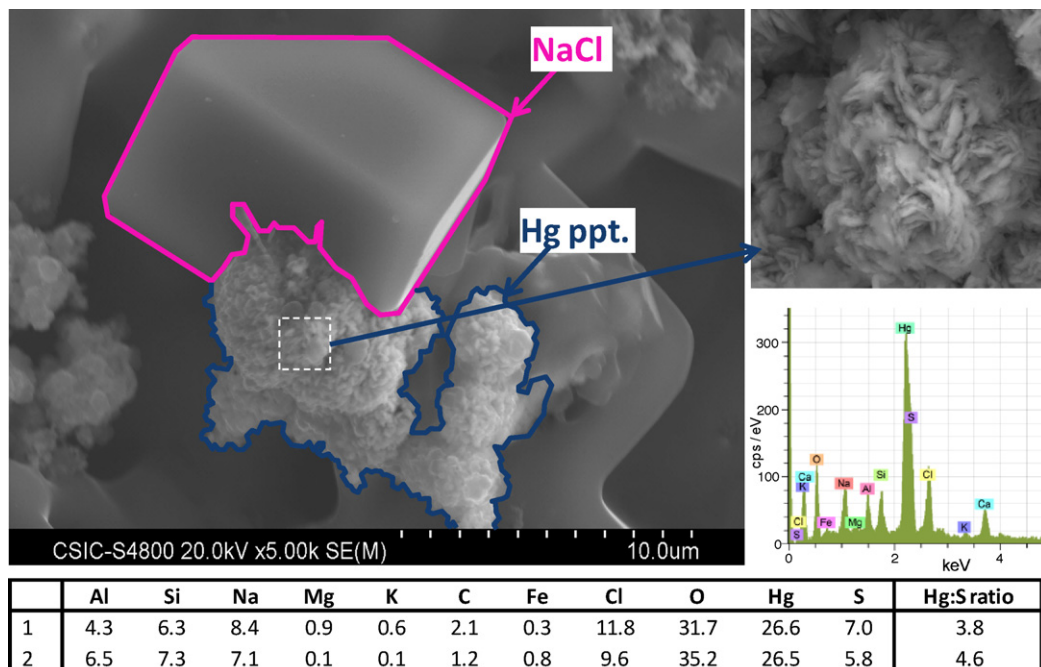|	Al	Si	Na	Mg	K	C	Fe	Cl	O	Hg	S	Hg:S ratio
1	4.3	6.3	8.4	0.9	0.6	2.1	0.3	11.8	31.7	26.6	7.0	3.8
2	6.5	7.3	7.1	0.1	0.1	1.2	0.8	9.6	35.2	26.5	5.8	4.6

Fig. 8. SEM/EDX analysis of 2 day old 5% Hg doped AAFA paste using ash B. Similar images were apparent for equivalent samples with both ashes A and C.

Unfortunately, XRD, FTIR and TGA data (not included) failed to show the presence of any well defined Hg species. To this end, a series of paste samples doped with 5% Hg were prepared and the hydrated paste examined by SEM/EDX (see Fig. 8).

From Fig. 8, new cubic phases are evident with 5% Hg when compared with 0.5% Hg samples. The cubic structures were actually NaCl, formed by reaction of Cl^- from the $HgCl_2$ and Na from the NaOH activator solution. However, as with the 0.5% Hg pastes, a poorly crystalline precipitate consisting predominantly of Hg and S was also noted. In all regions with an elevated Hg concentration, S was also present at elevated levels, despite the fact that in 5% Hg samples a clear stoichiometric excess of Hg was present relative to S. If part of the excess Hg was indeed converted to HgO or Hg-silicates, which is suggested by the EDX data in Fig. 8, then it did not result in massive precipitation of stand-alone crystal structures, but instead amorphous precipitated species, which could be Hg-sulphides co-precipitated with HgO and Hg-silicates or simply Hg-sulphides co-precipitating with gel which contains absorbed Hg. Examination of the 5% Hg pastes by XRD, FTIR and TGA (data not included) did not reveal evidence of any new crystalline or well ordered Hg species, only NaCl.

Despite the fact that other authors have reported the stabilisation of Hg as HgO in alkaline environments [21,28], our SEM/EDX data suggests that the formation of poorly crystalline sulphides is the predominant stabilisation mechanism in AAFA cement. In particular it is surprising that sulphide stabilisation was not noted in AAS cements since blast furnace slag will typically contain higher sulphide contents than coal fly ashes.

However, the effect of the different experimental variables such as the starting material (blast furnace slag vs coal fly ash), the choice of Hg salt to add ($HgNO_3.H_2O$ vs $HgCl_2$), the alkali activator used (NaOH + Na-silicate vs 8 M NaOH) and the curing temperature (25 °C vs 85 °C) will undoubtedly contribute to these differences in Hg stabilisation. The curing temperature may be of particular importance if a minimum energy of activation has to be provided to form Hg sulphides.

5. Conclusions and further work

The work presented is an initial study investigating the relative solubility of Hg in fly ashes, AAFA pastes and Hg-doped AAFA pastes. From the work carried out, the following conclusions can be drawn:

- AAFA pastes develop good 1 day compressive (20–30 MPa) and flexural strengths (5 MPa) and the effect of 5000 mg/kg $HgCl_2$ addition as Hg on strengths was, with one exception, negligible.
- According to EN 12457 and TCLP tests, all ashes complied with the strictest standards for soluble Hg.
- All AAFA control cements complied with non-hazardous waste criteria for soluble Hg according to both EN 12457 and TCLP standards.
- The more stringent EN 12457 limits require leachates to be analysed by the more sensitive ICPMS equipment. These results revealed that following alkali activation, the solubility of native Hg in fly ashes increased by a factor of 2, which could be a concern regarding the potential use of fly ashes containing high contents of Hg in AAFA cements.
- The formation of highly amorphous HgS or Hg_2S precipitates was at least partly responsible for Hg immobilisation efficiencies of 97.6–99.3% in Hg-doped samples with both TCLP and EN 12457 tests.
- Mercury immobilisation efficiencies were consistently higher in TCLP tests than EN 12457 tests. This can be explained by the fact that TCLP tests use coarser test material and that the higher

final leachate pH value in EN 12457 tests actually increases the solubility of HgS.
- Chloride ion interference from the original $HgCl_2$ added is likely to be responsible for higher Hg solubility than would be expected with pure HgS or Hg_2S precipitates.
- When increasing the Hg dosage to 50,000 mg/kg, distributions of Hg and S atoms in the paste continued to be virtually identical, indicating HgS or Hg_2S formation, despite the large stoichiometric excess of Hg, continuing to be important. Formation of other Hg precipitates free of Sulphur such as HgO or Hg-silicate was not evident from SEM/EDX analysis. Instead it appears that the precipitates represent a mixture of HgS and HgO/Hg-silicate or HgS and N-A-S-H type cementitious gel with Hg absorbed to it.

Further work investigating the immobilisation efficiencies using elemental Hg and/or $Hg(NO_3)_2$ as the Hg source, and in pastes cured for longer periods, is recommended to better understand the mechanisms of HgS formation and the factors controlling its solubility in the AAFA matrix. Furthermore, optimisation studies varying the dosage of Hg and the possible effect of Na_2S additions to the mixture would be of great relevance to this work.

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