

# **Alkaline Activation as a Procedure for the Transformation of Fly Ash into New Materials.**

## **Part II - An Assessment of Mercury Immobilisation**

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KEYWORDS: coal fly ash, Mercury, immobilisation, leaching, TCLP, EN 12457

### 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 5000mg/kg Hg as HgCl<sub>2</sub>, was prepared. The ashes alone complied with Mercury leaching criteria according to the TCLP and EN 12457 tests. Control AAFA cement samples complied with TCLP criteria but exceeded acceptable limits for wastes according to the EN 12457 test by varying degrees. Fly ash activated cements doped with 5000mg/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. The results for Hg-doped cements contribute to the body of evidence showing that alkali-activation of fly ash can be considered as a useful process for immobilizing elevated concentrations of toxic and hazardous elements.

## 1 – INTRODUCTION

### 1.1 – Mercury

The combined characteristics of high toxicity, high environmental mobility and the ability to bio-accumulate in marine 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<sup>1,2</sup>.

In Sweden, from 2010 onwards, all wastes containing more than 0.1% (1000mg/kg) Hg are to be placed in a permanent bedrock repository<sup>3</sup>. In the standardised European leaching tests<sup>4</sup>, used to determine which landfill type is suitable for a particular waste, Hg is the most stringently regulated metal. Granular wastes leaching more than 2mg/kg and monolithic wastes leaching more than 0.4mg/m<sup>2</sup>/kg are considered unsuitable for disposal in hazardous waste landfill<sup>5</sup>. In the American toxicity characteristic leaching procedure<sup>6</sup>, the lowest acceptable limit for any soluble metal, by a factor of five, is 200µg/l for Hg. Furthermore, any waste exceeding this limit must then be treated and comply with a more stringent Hg limit of 25µg/l<sup>7</sup>.

### 1.2 – Coal fly ash and Mercury

Despite the fact that coal generally contains less than 1mg/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. Pacyna and Pacyna (2002)<sup>8</sup> stated that in 1995, some 75% of anthropogenic emissions were due to coal combustion.

Mercury can either be retained in bottom ashes, fly ashes, air pollution control sludge or pass to the atmosphere. Partitioning of Mercury will depend on coal type and combustion plant set-up. Above 600°C, the only stable form of Mercury is the elemental vapour. According to Mukherjee et al (2008)<sup>9</sup>, the presence of chlorine, sulphur and calcium in flue gases at temperatures of 400°C or lower favours the oxidation of elemental Hg vapour to Hg<sup>2+</sup>, facilitating its deposition on charged fly ash particles and subsequent removal by dust control equipment. It is generally regarded that Hg is preferentially absorbed onto unburned carbon surfaces in fly ash and is predominantly associated with the finer fraction of ash particles. Average fly ash partitioning percentages of Hg of 18%<sup>10</sup>, 27%<sup>11</sup> and 58%<sup>9</sup> have been reported in the literature. Generally less than 1% remains in bottom ash.

### 1.3 – Coal fly ash re-use

Regarding potential added value and scale, by far the most attractive re-use option for coal fly ash is as a cement substitute in the construction industry. Global cement production was estimated at 3 billion tonnes in 2009<sup>12</sup>. The elemental composition of fly ash is dominated by silicates and aluminosilicates with significant fractions present as disordered, XRD amorphous glassy phases. Such phases are responsible for the beneficial pozzolanic activity shown by coal fly ash in the presence of hydrating Portland cement matrices and for the cementitious behaviour observed when fly ashes are mixed with highly alkaline solutions. The latter behaviour has played a significant role in the development of a new generation of alkali activated cements<sup>13-16</sup>. However, while 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.

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<sup>17</sup>. 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.

### 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<sup>7</sup>. Chemical

interaction between Mercury and cement hydration reactions and products is regarded as minimal<sup>18</sup>.

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<sup>19,20</sup>. Palomo and Lopez de la Fuente (2003)<sup>21</sup> showed that alkali-activated fly ashes (AAFA) were better suited to Boron immobilisation (15,000mg/kg dosage) than Portland cement both due to 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  $Pb_3SiO_5$ <sup>22</sup>. However, the same authors also stated that AAFA systems were not suitable for Cr(VI) immobilisation at doses of 26,000mg/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 (2006)<sup>23</sup>, 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 1000mg/kg doses of Cd, Cu, Cr(III) and Pb. However with Arsenic, immobilisation efficiencies in AAFA cements doped with 10000mg/kg As were shown to be only around 50% by Fernández-Jiménez et al (2005)<sup>24</sup>.

With regards to Hg, the only work to date that the authors are aware of involving alkali-activated cements of is that of Qian et al (2003a and 2003b)<sup>25,26</sup>. These authors reported that an increase in Hg immobilisation occurred with alkali-activated slag (AAS) cured up to 28 days of age. The increase in immobilisation correlated well with the reduction in cement porosity with age, suggesting that physical encapsulation is important to comply with leaching criteria. The same authors, with supporting TGA/DTA data proposed that with the higher dosage of 20000mg/kg, Hg initially forms both HgO and an amorphous Hg-silicate precipitate due to endothermic peaks observed at 303°C and 486°C respectively.

Considering the promising results reported with AAS cements<sup>25</sup>, the aim of this paper is therefore to investigate the ability of AAFA cements 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 (Escucha, Slovakia and 1210), were all of the class F variety. The Escucha sample 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 45µm sieve. Reagent grade sodium hydroxide (Panreac) and distilled water were used to prepare the 8M NaOH activator solution. In the case of Mercury doped samples, reagent grade Mercuric Chloride ( $MgCl_2$  - Merck) was used as the external Mercury source.

### 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 80mA (Philips PW 1404/00/01).

### 2.3 – Elaboration of cement pastes

The minimum acceptable liquid to solid (L/S) ratio between each coal fly ash and the 8M NaOH activator solution to form a workable paste was determined in preliminary experiments and were found to be 0.37, 0.43 and 0.30 for Escucha, Slovakia and 1210 ashes respectively. Fly ashes were added to the activator solution and hand mixed for 2 minutes before being cast into 1x1x6 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 container maintained at 99% relative humidity and 85°C for a period of 20 hours. 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<sub>2</sub> 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 1x1x6 cm were tested for flexural (NETZSCH 6.111.2, GmbH) and compressive strength (Ibertest Autotest 200/10 SW) approximately 24 hours after being cast.

### 2.5 – Leaching tests

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

#### 2.5.1 – Adapted TCLP test

The procedure described in the method 1311 document published by the US EPA was followed with some slight variations. First of all 40g of sample was mixed with 800mL of leachate instead of 100g with 2L. Secondly, the speed of rotation of end over end shaker was 3rpm instead of 30rpm and finally, samples were filtered through a double layer of 3µm cellulose based filter paper instead of 0.6-0.8µm glass fibre filters. In the case of ash samples, it was not possible to use material in the size range of 4-9.5mm. Following filtration, leachate pH was measured and a known quantity of 5M HNO<sub>3</sub> was added to maintain a pH of <2 prior to ICP-OES analysis for regulated metals.

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

### 3 – RESULTS AND DISCUSSION

#### 3.1 – Ash characteristics

Major elements present in the fly ashes are shown in Table 1.

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

Element (as oxide)	Escucha	Slovakia	1210
SiO <sub>2</sub> (%)	51.07	56.51	53.78
Al <sub>2</sub> O <sub>3</sub> (%)	24.34	21.42	28.83
Fe <sub>2</sub> O <sub>3</sub> (%)	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 <sub>2</sub> O (%)	0.40	0.63	0.47
SO <sub>3</sub> (%)	0.62	0.99	0.35
K <sub>2</sub> O (%)	2.58	2.59	4.25
TiO <sub>2</sub> (%)	0.82	0.87	1.11
P <sub>2</sub> O <sub>5</sub> (%)	0.07	0.15	0.22
LOI (%)	1.26	2.21	1.80
<b>Sum total (%)</b>	<b>99.83</b>	<b>99.99</b>	<b>99.72</b>

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 Escucha ash, which is most likely due to the inclusion of bottom ash in this sample.

#### 3.2 – Soluble Hg levels and immobilisation efficiency

Leachable Hg concentrations for the three fly ashes and AAFA cements (with and without Hg addition) are shown in Table 2. For ease of comparison with EN 12457 data, TCLP results and relevant limits (normally expressed as mg/L of leachate) were converted to mg/kg of ash/cement paste by multiplying by the liquid to solid ratio of 20 used in this test.

Table 2 – Soluble Hg in fly ashes and AAFA cements relative to TCLP and EU landfill directive limits (expressed as mg/kg) and total Hg contents.

EN 12457 limits (mg/kg)*	Escucha			Slovakia			1210				
	Inert	No-haz	Haz	ash	AAFA	AAFA+Hg	Ash	AAFA	AAFA+Hg	ash	AAFA
0.01	0.2	2.0	0.001	0.016	61.86	0.005	0.765	131.8	0.01	3.444	63.07
% Hg immobilisation**			??	??	98.8	??	??	97.4	??	??	98.7
Final pH			9.1	11.4	11.8	10.9	11.8	11.8	10.0	11.8	11.9
TCLP limits (mg/kg)	Escucha			Slovakia			1210				
	UTS†	ash		ash	AAFA	AAFA+Hg	Ash	AAFA	AAFA+Hg	ash	AAFA
0.5	4.0		<0.42	<0.42	58.2	<0.42	<0.42	18.0	<0.42	<0.42	35.2
% Hg immobilisation**			??	??	98.8	??	??	99.6	??	??	99.3
Final pH			4.8	4.5	4.6	4.9	4.6	4.5	4.9	4.9	4.7

\* To qualify for disposal to inert landfill, non-hazardous and hazardous landfill, soluble Hg must be <0.01, 0.01<0.20 and 0.20<2.0mg/kg respectively. Concentrations above 2.0mg/kg are not deemed suitable for landfill disposal.

\*\* % immobilisation calculated as (soluble Hg / total Hg) x 100. Total Hg content for Hg-doped AAFA samples was assumed to be 5000mg/kg with any contribution from fly ash being negligible.

† A stricter TCLP limit (Universal Treatment Standard) for Hg exists for treated wastes that originally exceeded the 4.0mg/kg limit.

In the case of EN 12457 tests, there was a 10 fold difference in soluble Hg levels between the ashes. Of particular interest is that Hg solubility in control AAFA cements showed an increase by factors of 16, 153 and 344 respectively compared to untreated ashes. In Hg-doped samples, despite high levels of Hg solubility relative to landfill waste acceptance criteria limits,  $\geq 97.4\%$  of all Hg is present in a non-soluble form. Therefore it can be concluded that in an alkaline environment (pH 9-12) the majority ( $\geq 97\%$ ) of total Hg present in the AAFA matrices is in a water insoluble form.

With regards to TCLP tests, all ash samples and control AAFA cements complied with the stricter universal treatment standard although it was not possible to comment on the ease of compliance since the limit of detection of the ICPOES instrument was only slightly below the UTS limit. With the Hg-doped cements, immobilisation efficiencies of  $\geq 98.8\%$  were noted. Even though the pH was much more acidic than in EN 12457 leachates (4.5-4.9 versus 9.1-11.9), the vast majority of Hg remained insoluble in Hg-doped cements.

The TCLP results are similar to the 99.6% Hg immobilisation of 5000mg/kg Hg-doped AAS cements at ages of 3 days<sup>25</sup>. 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 with 2000mg/kg Hg-doped Portland cements<sup>27</sup> and could be significant with AAFA cements, particularly due to the use of elevated temperature curing.

### 3.3 – 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 Figure 1. Escucha ash clearly performs best with regards 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 the Slovakia and 1210 ashes despite the large difference in L/S ratios employed (0.43 and 0.30). The effect of adding 0.5% Hg as HgCl<sub>2</sub> appears to have little or no detrimental effect on the strengths of the Slovakia and 1210 cements but does seem to negatively affect the compressive strengths of the Escucha samples.

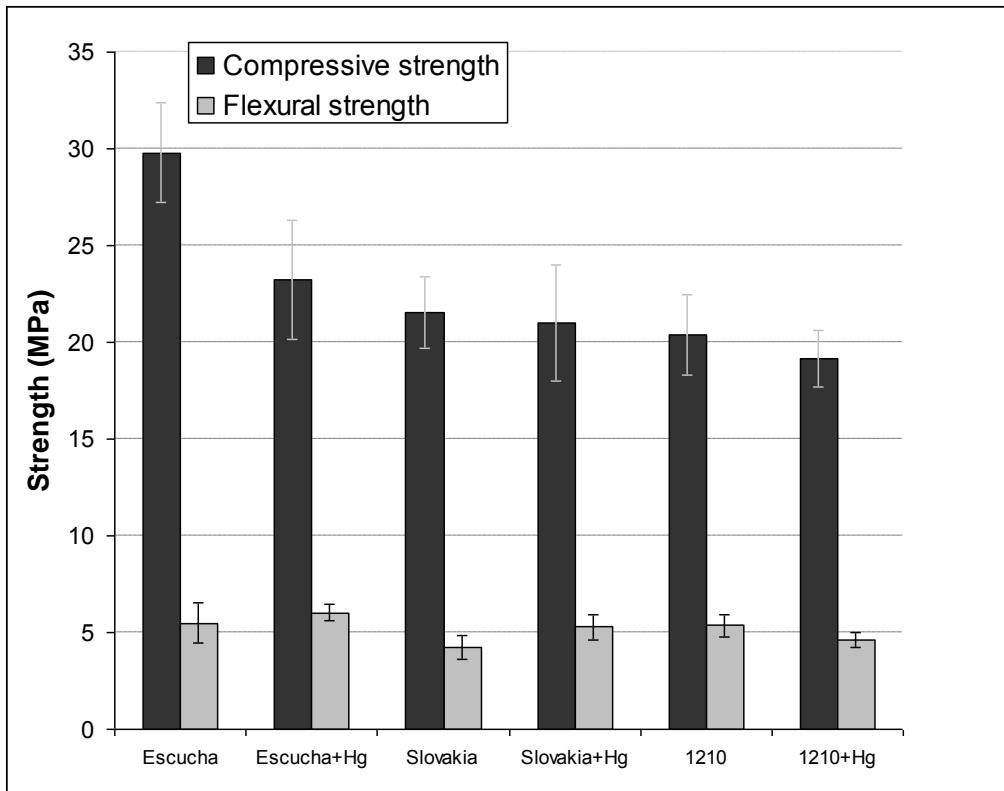


Figure 1 – Compressive and flexural strengths of AAFA samples at 1 day of age. Values are averages of 12 and 6 measurements respectively. Errors bars shown are +/- 1 standard deviation.

#### 4 – CONCLUSIONS

The work presented represents a primary study investigating the relative solubility of Hg in fly ashes and AAFA pastes. From the work carried out, the following conclusions can be drawn:

- According to EN 12457 and TCLP tests, all ashes complied with the strictest standards for soluble Hg.
- All AAFA control cements complied with the strictest TCLP standard for soluble Hg, with levels below the ICPOES detection limit.
- 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 Hg increased by factors of 16, 153 and 344, which could be a concern regarding the potential use of AAFA cement as construction materials.
- Between 97 and 99% of soluble  $\text{HgCl}_2$  was converted to an unknown form in the AAFA matrix shown to be insoluble at pH's of 4-5 and 9-12.
- AAFA pastes develop good 1 day compressive (20-30MPa) and flexural strengths (5MPa) and the effect of Hg addition at 5000mg/kg, with one exception, appears to be negligible.

Further work is underway with regards to the Hg already present in fly ashes, the evolution of Hg-immobilisation efficiency with samples cured for longer periods, the

possibility of loss of HG vapours during curing and the speciation of Hg that exists in Hg-doped AAFA pastes.

## REFERENCES

- [1] Camargo, J.A. Chemosphere, 2002, 48, p. 51.
- [2] Hylander, L.D. and Meili, M. The Science of the Total Environment, 2003, 304, p. 13.
- [3] English translation of Swedish Government Official Report “A safe Mercury Repository” SOU 2001:58 by the Swedish Environmental Protection Agency.
- [4] BS EN 12457-2 : 2002. Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges. British Standards Institute.
- [5] UK Environment Agency document, Guidance on sampling and testing of wastes to meet landfill waste acceptance procedures, Version 1, April 2005.
- [6] USEPA Test Method 1311-1 – TCLP, Toxicity Characteristic Leaching Procedure – 1992 revision.
- [7] Randall, P. and Chattopadhyay, S. Journal of Hazardous Materials, 2004, B114, p. 211.
- [8] Pacyna, E.G. and Pacyna, J.M. Water, Air, and Soil Pollution, 2002, 137, p. 149.
- [9] Mukherjee, A.B., Zevenhoven, R., Bhattacharya, P., Sajwan, K.S. and Kikuchi, R. Resources, Conservation and Recycling, 2008, 52, p. 571.
- [10] Wang, Q., Shen, W. and Ma, Z. Environmental Science and Technology, 2000, 34, p. 2711.
- [11] Meij, R. and Winkel, H. Science of the Total Environment, 2006, 368, p. 393.
- [12] CEMBUREAU The European Cement Association website. <http://www.cembureau.be/about-cement/key-facts-figures> accessed March 2011.
- [13] Palomo, A., Grutzeck, M.W. and Blanco, M.T. Cement and Concrete Research, 1999, 29, p. 1323.
- [14] Van Jaarsveld J.G.S. and Van Deventer, J.S.J. Industrial and Engineering Chemistry Research, 1999, 38, p. 3832.
- [15] Palomo, A., Alonso, S., Fernández-Jiménez, A., Sobrados, I. and Sanz, J. Journal of the American Ceramic Society, 2004, 87 (6), p. 1141.
- [16] Hu, M., Zhu, X. and Long, F. Cement and Concrete Composites, 2009, 31, p. 762.
- [17] US Environmental Protection Agency, Federal Register, 2010, 75 (118) p.35128.
- [18] Poon, C.S., Peters, C.J. and Perry, R. The Science of the Total Environment, 1985, 41, p. 55.
- [19] Van Jaarseveld, J.G.S., Van Deventer, J.S.J. and Schwartzman, A. Minerals Engineering, 1999, 12, p. 75.
- [20] Shi, C. and Fernández-Jiménez, A. Journal of Hazardous Materials, 2006, B137, p. 1656.
- [21] Palomo, A. and Lopez de la Fuente, J.I. Cement and Concrete Research, 2003, 33, p. 281.
- [22] Palomo, A. and Palacios, M. Cement and Concrete Research, 2003, p. 289.
- [23] Xu, J.Z., Zhou, Y.L., Chang, Q. and Qu, H.Q. Materials Letters, 2006, p. 820.
- [24] Fernández-Jiménez, A., Palomo, A., MacPhee, D.E. and Lachowski, E.E. Journal of the American Ceramic Society, 2005, 88 (5), p. 1122.
- [25] Qian, G., Sun, D.D. and Tay, J.H. Journal of Hazardous Materials, 2003a, B101, p. 65.

- [26] Qian, G., Sun, D.D. and Tay, J.H. Cement and Concrete Research, 2003b, 33, p. 1251.
- [27] Hamilton, W.P. and Bowers, A.R. Waste Management, 1997, 17, p. 25.