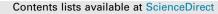
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# Alkali activation of recovered fuel-biofuel fly ash from fluidised-bed combustion: Stabilisation/solidification of heavy metals

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#### ABSTRACT

Recovered fuel-biofuel fly ash from a fluidized bed boiler was alkali-activated and granulated with a sodium-silicate solution in order to immobilise the heavy metals it contains. The effect of blast-furnace slag and metakaolin as co-binders were studied. Leaching standard EN 12457-3 was applied to evaluate the immobilisation potential. The results showed that Ba, Pb and Zn were effectively immobilised. However, there was increased leaching after alkali activation for As, Cu, Mo, Sb and V. The co-binders had minimal or even negative effect on the immobilisation. One exception was found for Cr, in which the slag decreased leaching, and one was found for Cu, in which the slag increased leaching. A sequential leaching procedure was utilized to gain a deeper understanding of the immobilisation mechanism. By using a sequential leaching procedure it is possible fractionate elements into watersoluble, acid-soluble, easily-reduced and oxidisable fractions, yielding a total 'bioavailable' amount that is potentially hazardous for the environment. It was found that the total bioavailable amount was lower following alkali activation for all heavy metals, although the water-soluble fraction was higher for some metals. Evidence from leaching tests suggests the immobilisation mechanism was chemical retention, or trapping inside the alkali activation reaction products, rather than physical retention, adsorption or precipitation as hydroxides.

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#### 1. Introduction

The EU's energy policy encourages the use of renewable biofuels and waste for energy production (Europe 2020, 2010). Recovered Fuel (REF) or Solid Recovered Fuel (SRF) is produced from municipal or industrial waste (SFS-EN 15359, 2011). By using REF for energy production, less waste ends up in landfills and the need for fossil fuels decreases.

Suitable methods for producing energy from REFs are combustion, gasification and pyrolysis (VTT Report, 2000). In Finland, REF is mostly co-combusted with biofuels or peat in fluidized bed boilers (FBB) in combined heat and power plants (PlasticsEurope Report, 2008). The total amount of FBB ash generated annually in Finland is 600,000 t, including ash from biomass, peat and REF combustion (Emilsson, 2006). The temperature in an FBB is 800– 900 °C, which creates a stable combustion environment for different solid fuels.

Because REF is produced from waste, it contains high levels of hazardous elements such as Pb, Zn and Sb. Hazardous elements

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http://dx.doi.org/10.1016/j.wasman.2015.05.019 0956-053X/© 2015 Elsevier Ltd. All rights reserved. are found in greater concentrations in fly ash (FA) generated from REF combustion. The high levels of heavy metals in REF FA prevent its use (FINLEX<sup>®</sup>, 2006). This forces energy producers to transport the FA to landfills, leading to greater cost and environmental risk. A workaround would be recovering heavy metals from FA (Ehsan et al., 2006; Isoyama and Wada, 2007; Moutsatsou et al., 2006; Mulligan et al., 2001; Schnoor, 1997). However, often, this is not technologically or economically feasible, so stabilization/solidification (S/S) is the next best option (Bobrowski et al., 1997; Glasser, 1997; Malviya and Chaudhary, 2006).

Recently alkali activation, also referred to as *geopolymerization*, has received attention as the S/S method of choice (Bankowski et al., 2004a, 2004b; Fernandez-Jimenez et al., 2005; Guo and Shi, 2012, 2013a; Jaarsveld et al., 1998; Komnitsas et al., 2013; Lancellotti et al., 2010; Luna Galiano et al., 2011; Luna et al., 2009; Nikolić et al., 2014; Ogundiran et al., 2013; Perera et al., 2005; Phair et al., 2004; Provis, 2009; Tzanakos et al., 2014; van Jaarsveld et al., 1999, 1997; Xu et al., 2006; Zhang et al., 2008a, 2008b; Zheng et al., 2011, 2010). In alkali activation, solid aluminosilicate precursors such as metakaolin, coal FA or blast furnace slag are dissolved in an alkaline solution, usually sodium hydroxide or sodium silicate, to produce a three-dimensional, aluminosilicate

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However, the precise S/S mechanism remains unknown. Possible mechanisms can be divided into physical and chemical immobilisation, although a clear-cut distinction is impractical because these mechanisms can operate jointly (Glasser, 1997). Physical immobilisation occurs on the micron scale. Zeolite-type aluminosilicate-structures could trap some atoms within their crystal structures. Other mechanisms by which physical immobilisation can occur include prevention of contact between the leaching medium and the heavy metals via a physical barrier. Chemical immobilisation, metals react with other elements and become part of the aluminosilicate structure, possibly by replacing silicon atoms (Schoenung, 2008). In addition, leaching could decrease because of adsorption forces or precipitation as hydroxides (Bernal et al., 2014).

This paper examines the S/S of FA from the co-combustion of REF and biofuels using alkali activation. To date, alkali activation of REF FA has not been studied. Fly ash from fluidized bed-combustion of coal has been studied recently, and promising results have been obtained with other binding materials (Chindaprasirt et al., 2011; Li et al., 2012a; Liu et al., 2014; Slavik et al., 2008; Tyni et al., 2014; Xu et al., 2010). However, S/S of FBB FA by alkali activation has not been studied. The combustion temperature in FBBs is lower than that in coal-burning facilities (800–900 °C vs. 1200–1300 °C). A lower combustion temperature yields lower glassy-phase material and, thus, potentially less reactive FA in alkali activation (Chindaprasirt and Rattanasak, 2010; Li et al., 2012b). In addition, biofuel and peat FA contain significant amounts of alkali, earth-alkali, and iron compounds which complicate alkali-activation reaction chemistry.

The method of choice in this study is to simultaneously granulate and alkali-activate REF FA with a sodium-silicate solution to produce spherical granules. If S/S is successful, these granules could be used in construction, civil engineering or as a substitute for sand and gravel in concrete. In addition to S/S capability, the physical properties and microstructure of the granules should be analysed to estimate their potential for use in civil engineering. These properties will be evaluated in further studies.

The aim of this work is to define the efficiency of the S/S of heavy metals by leaching standard (SFS-EN 12457-3, 2002) and by a sequential extraction procedure (Bruder-Hubscher et al., 2002). In the sequential extraction procedure, various types of chemical reagents are applied to the samples in series, and each successive treatment is more drastic than previous one. This way, it is possible to estimate the mobility (i.e. bioavailability) of heavy metals in environmental samples. Loosely bound metals such as those that are water-soluble and fraction leachable with ammonium acetate or acetic acid are much more mobile in the environment than those that are leachable only with strong acids such as hydrogen-fluoric acid (HF) and aqua regia. Thus, the loosely bound fractions are much more likely to be released in the environment and are, thus, potentially bioavailable (Filgueiras et al., 2002). Additionally, considering S/S by alkali activation, the sequential extraction procedure can reveal more information about heavy metal species before and after alkali activation, thus unveiling the immobilisation mechanism.

#### 2. Experimental

#### 2.1. Materials

The REF-biofuel FA used in this study was obtained from a heat and electricity power plant that uses a bubbling FBB to combust REF. The REF was made of packing material waste such as plastic (not PVC), cartons, paper and wood collected from industry and retail suppliers. The REF was of Class 1 quality according to the relevant standard (SFS-EN 15359, 2011). The fuel mixture used in the power plant comprised 50% REF and 50% biofuel (mainly wood bark). The FA sample was collected from electrostatic precipitators (ESP) into 10-L containers.

The effects of blast-furnace slag (S) (Finnsementti, KJ400) and metakaolin (M) (Metastar 402, Imerys Minerals) as co-binders were studied by adding them in 20 wt% and 40 wt%, respectively, to the FA. The samples were named FA100 (100% – FA), FA60S40 (60% – FA, 40% – blast-furnace slag), FA80S20 (80% – FA, 20% – blast-furnace slag), FA60M40 (60% – FA, 40% – metakaolin) and FA80M20 (80% – FA, 20% – metakaolin). Sodium-silicate solution (Zeopol<sup>®</sup> 25, Huber) (Na-Sil) was used as an alkali activator. Na-Sil had a SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 2.5, pH of 12.5 and water content of approximately 66 wt%.

#### 2.2. Methods

The chemical composition of the precursors was determined with X-ray fluorescence (XRF) (Omnian Pananalytics Axios<sup>max</sup>) from a melt-fused tablet. The particle-size distributions were measured with a Beckman Coulter LS 13320 and reported as volumetric-based sizes ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ). Specific surface area measurement was based on the physical adsorption of gas molecules on a solid surface using a physisorption analyzer (ASAP 2020, Micrometrics) and the results were reported in a form of a BET isotherm. Dry matter content and loss-of-ignition (LOI) at 525 °C and 950 °C were determined using thermo-gravimetric analysis equipment (PrepAsh, Precisa). A field emission scanning electron microscope (FESEM, Zeiss Ultra Plus) was used to analyse the FA particles. The sample distance was 7.3 mm, and the acceleration voltage was 3.0 kV.

The pseudo-total concentrations of elements in FA and alkali-activated granules were characterised by microwave-assisted wet digestion using a 3:1 mixture of HNO<sub>3</sub> and HCl for 0.5 g of FA and determination was made using a inductively coupled, plasma-optical emission spectrometer (ICP-OES) (Thermo Electron IRIS Intrepid II XDL Duo, Thermo Scientific). Duplicate measurements were made for each sample.

#### 2.3. Granulation

A high shear mixer (Eirich R-01) was used to granulate the precursors. A high-shear mixer was chosen for this study because it can spread viscous fluids and produce dense and strong granules with a narrow size distribution within a short period (Reynolds et al., 2007). The granulator has a 5-L drum rotating clockwise at a speed of 45 rpm. Inside the drum is an impeller measuring in 10 cm in diameter and spinning counter-clockwise at a speed of 900 rpm. The tilt angle of the drum is 10°. There is a scraping blade inside the drum to remove any material stuck to the drum wall and to compact the balled material. The granulation procedure employed in this study is as follows: (1) dry precursors were weighed, mixed and added to the drum; (2) before switching on the drum and the impeller, approximately 15 g of Na-Sil was sprayed on the precursors to prevent dusting; (3) drops of Na-Sil were added until the target granule size (2-4 mm diameter) was achieved. Each batch was sealed in air-tight plastic bags and stored at room temperature for 28 days before the granules were analysed.

#### 2.4. Leaching tests

#### 2.4.1. Standard EN 12457-3

The standard leaching method (SFS-EN 12457-3, 2002) was used in this study. This two-step extraction method uses water

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