

Elemental analysis of ash residue from combustion of CCA treated wood waste before and after electro dialytic extraction

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Abstract

Element distribution in a combined fly ash and bottom ash from combustion of copper chromate arsenate (CCA) treated wood waste was investigated by scanning electron microscopy (SEM/EDX) before and after electro dialytic extraction. The untreated ash contained various particles, including pieces of incompletely combusted wood rich in Cr and Ca, and irregular particles rich in Si, Al and K. Cr was also found incorporated in silica-based matrix particles. As was associated with Ca in porous (char) particles, indicating that Ca-arsenates had been formed during combustion. Cu was associated with Cr in the incompletely combusted wood pieces and was also found in almost pure form in a surface layer of some matrix particles – indicating surface condensation of volatile Cu species. In treated ash, Ca and As were no longer found together, indicating that Ca-arsenates had been dissolved due to the electro dialytic treatment. Instead particles rich in Ca and S were now found, indicating precipitation of Ca-sulphates due to addition of sulphuric acid in connection with the electro dialytic treatment. Cu and Cr were still found associated with incompletely combusted wood particles and incorporated in matrix particles. Chemical analyses of untreated and treated ash confirmed that most As, but only smaller amounts of Cu and Cr was removed due to the electro dialytic extraction. Overall metal contents in the original ash residue were: 1.4 g As, 2.76 g Cu and 2.48 g Cr, after electro dialytic extraction these amounts were reduced by 86% for As, 15% for Cu and 33% for Cr.

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1. Introduction

When copper chromate arsenate (CCA) treated wood waste is burned, Cu, Cr and As, and other inorganic (ash forming) elements are converted into new compounds. More volatile species (as for instance many As compounds) may initially volatilise due to the hot temperatures in the furnace, whereas less volatile elements/compounds will remain as solids, forming the residual ash fraction. The volatilised species may subsequently condense on the surface of fly ash particles when the flue gas temperature decreases downstream of the boiler, leading to enrichment in the fly ash fraction. Combustion of CCA treated wood together with municipal solid waste is problematic. To

avoid emission of As it is necessary to install special flue gas cleaning systems at the plants. Furthermore the result will be a very large amount of ash residues enriched with Cu, Cr and As compared to the ash composition of today. Thus it is beneficial or even necessary to sort the impregnated wood from other waste, which is already done in, e.g. Denmark and Finland, and treat the impregnated wood separately. Handling of the ash after combustion of CCA treated wood is an important issue, since such ashes are highly toxic due to the high concentration of Cu, Cr and As and furthermore As is easily extractable from the ashes under acidic conditions and thus danger of As-leaching from the ash, if land-filled without special precautions, is severe.

After a chemical extraction, separation of ash material and solution with the unwanted components is difficult. A separation method that may be used for extraction of these

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components from the suspension of ash could be the electro-dialytic extraction method. This method was first developed for removal of heavy metals from soils (Ottosen et al., 1997), and the method is based on applying an electric DC field to the soil to be decontaminated. A combination of ion exchange membranes is used to separate the processing solutions around the electrodes from the soil. The method has also shown potential to remove heavy metals from different ashes as municipal solid waste incineration fly ash and bio ashes (Pedersen et al., 2003; Pedersen, 2003; Ferreira et al., 2005) and it has been found that it is beneficial to treat the ashes in a stirred suspension (Pedersen, 2003). The primary objective of this present work is to evaluate changes in chemical composition due to electro-dialytic extraction of an ash originating from combustion of CCA treated wood. The methods used include chemical analysis and scanning electron microscopy/energy dispersive X-ray (SEM/EDX). The electro-dialytic extraction experiment was originally performed to remove the most mobile parts of Cu, Cr and As and thus to ease land-filling of the ash.

2. Experimental

2.1. Experimental ash

A combined fly ash and bottom ash sample from combustion of CCA treated wood waste was used for the investigations. The ash was obtained from a combustion experiment performed in Ås, Norway, in August 2000. A total of 378.1 kg wood waste was burned, and from this 6.1 kg ash was produced, corresponding to a weight reduction of 98%. The cyclone temperature was 800–900 °C during the combustion experiment. The ash was characterised, and the result can be found in Ottosen et al. (2005). In summary the ash contain very high concentrations of Cu, Cr and As: 35 ± 4 g As kg⁻¹, 69 ± 2 g Cu kg⁻¹, 62 ± 1 g Cr kg⁻¹.

A loss on ignition of 2.9% represents the organic residue in the ash and reveals that the wood is not completely incinerated. The pH was found to 11.5. Such a high pH value is typical for a wood combustion ash (e.g., Hansen et al., 2001) and it is presumably caused by a high content of Ca-oxides and hydroxides.

For the present investigation also the concentrations of Mn, Mg, Ca and K were measured in acid digested ash samples. The concentrations were 3.4 ± 0.3 g Mn kg⁻¹, 6.7 ± 0.6 g Mg kg⁻¹, 16 ± 1 g K kg⁻¹ and 79 ± 8 g Ca kg⁻¹.

2.2. Chemical extraction in HNO₃ and H₂SO₄

In an earlier investigation (Ottosen et al., 2005), it was seen that As was often associated with Ca in the present ash, probably as As-carbonates. It was decided to conduct comparable extraction experiments in HNO₃ and H₂SO₄ to see if it was possible to precipitate Ca as gypsum without co-precipitation of As, Cu and Cr. If successful the idea was to suspend the ash in H₂SO₄ during electro-dialytic extraction to avoid wasting current on Ca-removal.

Extraction experiments were made with 5.0 g dry ash and 25 ml HNO₃ or H₂SO₄ of different concentrations. The concentrations of HNO₃ were 0.75 M and 1.0 M, and the concentrations of H₂SO₄ were 0.5 M and 0.75 M. The extractions were made in duplicates. Cu, Cr, Mn, Mg, Ca and K were measured in all samples using atomic absorption spectrometry. As analyses were made by an external laboratory, thus the As concentrations were only measured in the extractions in 0.75 M HNO₃ and 0.5 M H₂SO₄.

3. Electro-dialytic extraction experiment

The principle of a laboratory cell for electro-dialytic extraction is shown in Fig. 1. It consists of three compartments. In the central cell compartment the suspension of ash is placed and stirred during the experiment. The electrodes are placed in the outer compartments and ion exchange membranes separate the cell compartments. When the DC voltage is applied across the cell the ions in the ash suspension will be transported into the electrode compartments with the electrode of opposite sign as the ion itself.

A laboratory experiment was made with electro-dialytic treatment of the mixed bottom and fly ash from combustion of impregnated wood in a cell as shown in Fig. 1. The cell had an internal diameter of 8 cm and the length of the central cell compartment was 10 cm. In each of the electrode compartments 500 ml 0.05 M H₂SO₄ was circulated. In the central compartment a suspension of 40 g ash and 235 ml 0.5 M H₂SO₄ was placed and a stirrer was placed in the compartment from the top of the compartment. The current density was kept constant at 0.8 mA cm⁻² throughout the five d the experiment lasted and the voltage varied between 3.6 V and 2.7 V. At the end of the experiment the concentrations of Cu, Cr and As was measured in the different parts of the cell: in the ash, the solution of the central compartment, in the membranes, in the solutions in the electrode compartments and at the electrodes.

4. SEM/EDX analysis

SEM/EDX analyses were performed on the ash both prior to and after the electro-dialytic extraction. For

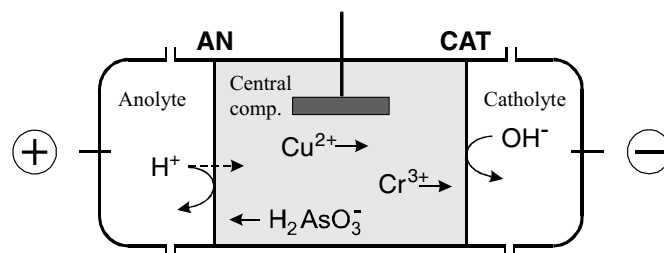


Fig. 1. Principle of a laboratory cell for electro-dialytic extraction (AN = anion exchange membrane, CAT = cation exchange membrane).

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