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Electrodialytic remediation of fly ash from co-combustion of wood and straw

Wan Chen *, Pernille E. Jensen, Lisbeth M. Ottosen, Gunvor M. Kirkelund

Department of Civil Engineering, Technical University of Denmark, Denmark

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ABSTRACT

The heavy metal content in fly ash from biomass combustion, such as straw, wood and sludge, often needs reducing before the ash can be used as fertilizer for agricultural land or as a component in the production of construction materials. In this study, fly ash from a boiler fueled with wood chips and straw was treated either by electrodialytic remediation (EDR) directly or by a combination of EDR and pre-wash with distilled water to investigate the possibilities of reducing the heavy metal content and reusing nutrients as fertilizer and bulk material in construction materials. Different experimental set-ups were tested for EDR treatment primarily of Cd and Pb as well as of Cu and Zn. Elemental contents such as K, P and Ni were compared in ash samples before and after treatment. The results showed that pre-washing caused an increase in total concentrations of most heavy metals because the highly soluble fraction, mainly KCl and K_2SO_4, was removed. After EDR treatment, the Cd concentration was reduced to below 2 mg kg^{-1} in all ash samples with high and stable average removal of above 95%, no matter how high the initial concentration was. The amount of Pb removed varied from 12% to 67%. Even though Pb was extracted from the ash samples, its concentrations in the treated ash samples were elevated due to the ash dissolution, except in the case of pre-washed ash treated in a two-compartment EDR cell, where the mass of Pb removed was the highest with a final concentration of about 100 mg kg^{-1}. The two-compartment EDR cell probably performed better due to a fast acidification process. In addition, this process was less energy-consuming. However, the fast acidification did in turn affect the leaching property of the treated ash, such as As and Ni, exceeding the limiting concentrations. The EDR/pre-wash-EDR treated ash mainly contained quartz, and the X-ray diffraction (XRD) peaks of K salts had disappeared. This shows that the potassium fertilizer potential was lost in the treated ashes, but the quartz mineral is beneficial in construction materials, such as ceramics. The K fertilizer could be recovered from the water after pre-washing and also from the catholyte through chemical operations, including a separation step.

1. Introduction

The European Union's renewable energy target and climate and energy policies have driven the increasing use of renewable energy resources in heat and power production [1]. Field crop residues, such as straw, are one source of agricultural biomass fuels, which are generally cheap in price and abundant in quantity and are, therefore, increasingly being used for energy production. However, pure straw combustion has slagging and fouling problems in boilers because of the high ash content and the high content of chlorine and potassium. Co-combustion of straw with other fuels, such as coal and forest (woody) fuels, can ease the problem by diluting the elements that form straw ash [2]. The main ash-forming elements are: Al, Ca, Fe, K, Mg, Mn, Na, P, S, Si and Cl [3]. Straw has a high ash content in the range of 4–7%, whereas wood chips have a relatively low ash content of less than 2% [4]. By incorporating Ca-rich wood in straw combustion, Ca-rich particles can be deposited in the straw-based K-silicate melt to form silicates and oxides (e.g. CaO) of high melting points, thus changing the elemental composition of the bottom ash and reducing slagging propensity [2]. In Denmark, co-combustion of straw and wood chips has been implemented in some bio-fueled power plants.

The main by-products generated in the co-combustion of wood and straw are bottom and fly ashes. This type of bio-ash usually contains plant nutrients (K and P) which have value as fertilizers [5,6]. The bottom ash can normally be spread on agricultural fields, thus using the fertilizer value directly [7]. In Denmark, the fly ash

* Corresponding author. Tel.: +4545251816.
E-mail address: wach@byg.dtu.dk (W. Chen).

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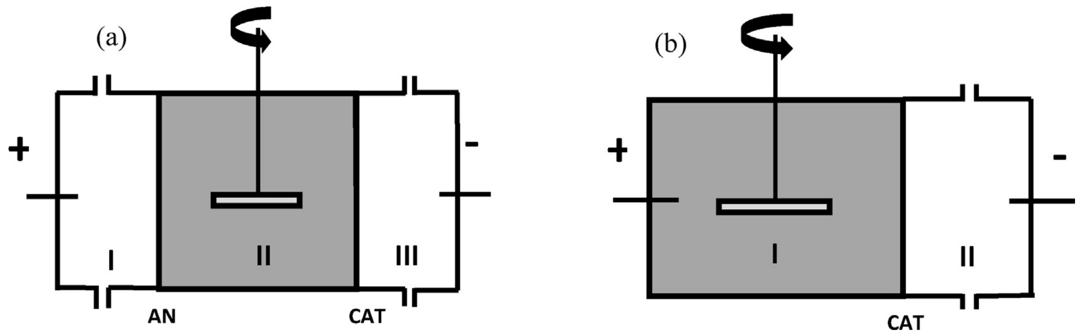

Fig. 1. The schematic drawing of the types of EDR cells used in the experiments. Anion exchange membrane = AN; cation exchange membrane = CAT.

cannot be used in this way because the heavy metal content (especially Cd [8]) often exceeds the maximum limit value of 5 mg Cd kg^{-1} TS (total solid) in the Danish regulation "Bioaskebekendtgørelsen" [9] for use of bio-ash on agricultural land. This study, therefore, focuses on using the resources in fly ash from wood and straw co-combustion.

EDR (electrodialytic remediation) is a method of removing heavy metals from particulate materials. It was originally developed for remediation of contaminated soils in a stationary, humid state [10], and later developed towards the treatment of fine particulate materials in suspension [11]. In the electric field, mobile ions in the suspension will electromigrate to electrode compartments through anionic or cationic ion exchange membranes, thus achieving a separation of ions from the suspension. The reduction and oxidation of water at the electrodes are the primary reactions occurring in the EDR system [12]. The half reactions are: (1) cathode reaction $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$, and (2) anode reaction $2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^-$. Removing Cd from biomass combustion fly ash in a three- or five-compartment EDR setup was reported in [5,10,13–15], and EDR turned out to be successful. Not only heavy metals but also other mobile element ions, such as K and P, are removed from ash suspensions during EDR. Later a two-compartment cell setup was developed for extraction of P from wastewater sludge. In the two-compartment cell, an ash-water suspension is directly acidified from the anode reaction as the anode is placed in the suspension. In this study, the focus is on the separation of nutrient elements and heavy metals for the recovery of the nutrients in an environmentally usable form. If the nutrients recovered can be used on agricultural fields, they will give additional economic value and replace a part of the commercial potash K fertilizer with a recently reported sale price of about US $310 per tonne [16]. The reuse of treated ash residue will also give an economic benefit, as disposal of the ashes is expensive in many countries. However, a few studies have reported results related to the possible management of EDR-treated ash residue according to the ash properties [17–19].

In this study, co-combustion fly ash from a boiler fueled with wood chips and straw was treated either by EDR or by a pre-wash/EDR combination to lower the heavy metal content in the ash. We tested a two-compartment EDR cell for the first time to treat such co-combustion ash and compared it with the three-compartment cell regarding heavy metal removal. We investigated the influence of the water pre-wash on EDR treatment. This is relevant to industries using water to wash out nutrients (mainly K) from bio-ashes, to offer an alternative technique to handle the ash residues by reducing the heavy metal content. In line with a zero-waste concept, a possible reuse of the detoxified fly ash residue for construction purposes was discussed. Since the fly ash studied contained plant nutrients, how the nutrients could be recovered during EDR or the pre-wash/EDR combination was discussed.

2. Experimental

2.1. Materials

Two straw/wood co-combustion fly ash (FA) samples from Enstedværket Power Plant (Denmark) were used in this study. The FAs were sampled on different days and were named EFA-1 and EFA-2. After being washed with distilled water in three stages at the total liquid-to-solid (L/S) ratio of 15 l/kg, i.e. 5 l/kg in each, the fly ash samples were named WEFA-1 and WEFA-2, respectively. The wet ash samples were dried at 105 °C for 24 h for further use in the experimental work. The dry mass recovered from the pre-washing step was directly used to calculate the content of soluble compounds.

2.2. Experiments

The EDR cells illustrated in Fig. 1 were used in this study. They were different in configuration, i.e. three-compartment (Fig. 1a) and two-compartment (Fig. 1b). In relation to conventional EDR for e.g. water treatment, compartment II in Fig. 1a and compartment I in Fig. 1b were demineralization compartments, where the ash-water suspension was placed. The remaining compartments where the electrodes were placed, were concentration compartments filled with circulating electrolytes (a 0.01 M $NaNO_3$ solution with a pH of 2 adjusted by HNO_3). In the setup illustrated in Fig. 1b, the anode was directly placed in the ash suspension. The cells were cylindrical with an inner diameter of 8 cm and made from polymethyl methacrylate. The compartment for ash suspension was 10 cm long and the length of the other compartments was 5 cm.

Table 1
EDR conditions.

Experiment no.	Sample	Current/mA	Compartment	Duration/d	Charge/C
E1	EFA-1	50	3	14	60480
E2	WEFA-1	50 (Day 1) to 10	3	~67	60480
E3	EFA-2	50	3	10	43200
E4	WEFA-2	10	3	70	60480
E5	WEFA-2	40	3	10	34560
E6	WEFA-2	40	2	10	34560