Extraction of Co, Sb, Sr, and V from MSWI fly ash by electrodialysis – a screening of experimental setups

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Introduction

MSWI fly ashes contain valuable elemental resources and can be regarded as urban mines if technologies are developed for the recovery. In this work, we focus on recovery of Co, Sb, Sr and V, which are all chemical elements listed in the EU 2020 list of critical raw materials. Electrodialysis (ED) could potentially be a method used as basis for extraction of these elements from MSWI fly ash, and if so the hazardous MSWI fly ashes could be regarded as urban ores. ED is based on application of an electric DC field in combination with ion exchange membranes. When based on green energy sources, the major input to the extraction process is not eroding finite global resources, which is an advantage of the method. ED has previously been applied to remediate MSWI fly ash (e.g. Kirkelund et al. 2015) where the aim was to obtain a stable residue which was not leaching heavy metals and chlorides above limiting values for reuse of waste in constructions. ED has also been developed for recovery P from sewage sludge ash while simultaneously separating P and heavy metals (e.g. Ottosen et al. 2016). In the present work, a screening of three different ED setups was conducted. The three setups differed in placement of ion exchange membranes and electrodes in relation to suspended ash. The objective was to see, which of the setups was best suited for further development of ED when aiming at extraction of Co, Sb, Sr and V.

Material and methods

The MSWI fly ash was from the Danish state-of-the-art waste incineration plant CopenHill. Prior to the ED experiments, the ash was washed to remove the major part of the soluble salts. The procedure for water washing: 400 g ash suspended in 2 L distilled water and the liquid phase was decanted. This was repeated three times and subsequently the ash was filtered and dried at 105 °C. The pH and concentrations of Co, Sb, Sr, and V were measured in both raw ash and washed ash.

One ED experiment was carried out with washed ash in each of the three cells in Fig. 1. The ED cells had an internal diameter of 8 cm, and a suspension compartment length of 10 cm. All experiments were made with a suspension of 35 g washed MSWI fly ash in 350 mL of distilled water and an applied constant current of 50 mA. The experiments lasted for 7 days (experiment a) or 8 days (experiments b and c)

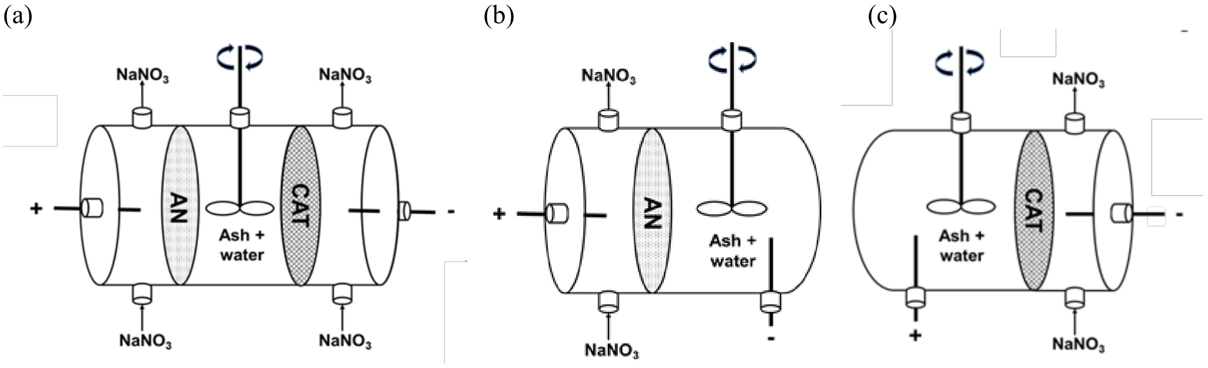

Figure 1. The ED cells used in the screening: (a) three-compartment (3C), (b) two-compartment with anion exchange membrane (2C-AN), and (c) two-compartment with cation exchange membrane (2C-CAT)

Results and discussion

From the washing procedure about 40% of mass was determined to be water soluble. The pH and concentrations of Co, Sb, Sr and V in the investigated ash before and after water washing is in Table 1. The high pH shows that when the ash is suspended in water, hydroxides are leached or formed. The increase in concentrations for Co, Sr and V after washing shows that these elements remain in the ash during the washing out of the soluble salts. The Sb concentration, on the other hand, decreased slightly, which shows that the ash had Sb containing compounds, which were soluble in water, and (more than 40% of the Sb) was extracted during the water washing.

Table 1. pH and concentrations of Co, Sb, Sr and V (mg/kg) in raw (as received) and washed MSWI fly ash

	pH	Co	Sb	Sr	V
Raw ash	11.6 ± 0.2	8.5 ± 0.4	705 ± 18	26.2 ± 0.7	31.2 ± 1.0
Washed ash	11.0 ± 0.1	13.0 ± 0.3	677 ± 8	34.9 ± 0.6	49.4 ± 0.2

The pH of the ED treated ashes were 6.0, 10.8 and 4.1 in experiments a, b and c, respectively. The differences in pH are due to the differences in the placement of membranes and electrodes in the three setups. In cell b, the cathode was placed in the ash suspension, and hydroxyl ions were continuously supplied from the half-cell reaction at the cathode $2H_2O + 2e^- \rightarrow 2OH^- + H_2$. Oppositely, the anode was placed in the ash suspension in cell c, which result in acidification from the half-cell reaction at the anode ($H_2O \rightarrow 2H^+ + \frac{1}{2}O_2$ (g) + $2e^-$). In cell a, the electrodes were both placed in separate compartments, and the acidification here was due to water splitting at the AN and exchange of protons from catholyte with other ions in the ash suspension.

Figure 2 shows that the ED extraction of the four critical elements differs both between elements and cells. The distribution of Co, Sb, Sr and V by the end of the experiments are shown as: in the ash, in the solution of the suspension, in the anode end (+) in cells a and b (sum of anolyte, AN and at anode), and in the cathode end in cells a and c (sum of catholyte, Cat and on cathode). The extraction of the four elements in the three cells differed clearly. It was low in cell c, where almost all Co, Sb and V and 85% Sr remained in the ash, showing that these elements are not extracted in alkaline and reducing environments. The ash was acidified in both cell a and c. The lowest pH was reached in experiment c, where also the highest extraction was found. The extraction of Co approached 100% in both cells, 52 and 53 % Sr was found in the (-) end of the cells showing that this element was extracted in cationic form. More Sr (17%) was in the solution in experiment c than in experiment a (3%), showing that the lower pH supported higher extraction. The Sb and V were extracted in cell a to a very low extent, and in cell c, 26% Sb and 24% V were extracted. In the next step of the development of ED, the focus will be on increasing the extraction of these two elements, possibly by longer duration or higher current to reach a lower ash pH.

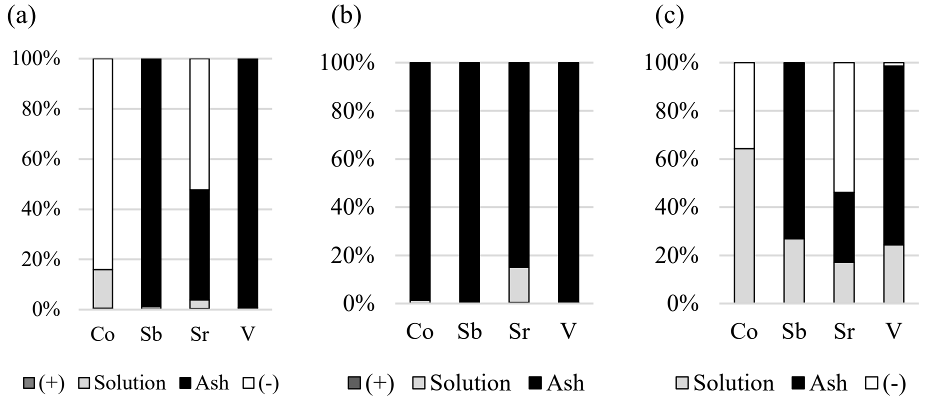

Figure 2: The distribution of Co, Sb, Sr and V in the three ED cells at the end of the experiments a, b and c.

Conclusions

Of the three ED cells tested in this screening, the best extraction results were obtained in the 2C-CAT cell, where ~100% Co, 71% Sr, 26% Sb and 24% V were extracted from the investigated MSWI fly ash. The ED process needs optimization, but the potential for extraction of these critical elements with green energy as major input was illustrated.

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