Improving metal extraction from MSWI fly ash through different experimental conditions for the electrodialytic treatment method

G.M. Kirkelund[1]*, B.A.R.Ebert[1], L.M. Ottosen[1]

[1]Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Keywords: electrokinetic, waste incineration, heavy metals, metal extraction, circular economy.

*Presenting author email: gunki@byg.dtu.dk

Abstract

Municipal solid waste incineration (MSWI) results in fly ash as one of the residues. MSWI fly ash is classified as hazardous waste due to the high concentrations of leachable inorganic elements and has to be disposed of in hazardous waste disposal sites. However, MSWI fly ash can also be regarded as a potential secondary raw material containing valuable resources, and several methods are under development for recovering the resources from MSWI fly ash instead of landfilling, which also supports the transition to a circular economy. Recovery of metals form the MSWI fly ash is one strategy of valorization of resources, and here the electrodialytic treatment method has shown potential. In this study, it was investigated if metal extraction rates could be improved by optimizing experimental conditions by performing 12 different electrodialytic experiments in laboratory scale. High extraction efficiencies between 80 - 95 % were obtained for Cd, Cu and Zn from two MSWI fly ash samples. Pre-washing the ash had the most significant influence on the metal extraction compared to experimental set-ups. The results of this study show potential for the electrodialytic method to recover high amounts of some metals from MSWI fly ash and be a method that can contribute to valorization of MSWI fly ash.

INTRODUCTION

Population growth and improved worldwide economy increases the demand for resources. The implementation of a circular economy is promoting reuse and upgrading of materials for a circular material loop, including waste materials. Hazardous fly ash is one residue after municipal solid waste incineration (MSWI). Due to the leachable heavy metals and salts, MSWI fly ash is being disposed of in hazardous waste disposal sites (typically in old mines) or stabilized before disposal, both which do not promote circular economy of the resources in the ash. MSWI fly ash contain elements, including base metals for industry (for instance Cu, Pb, Zn), critical elements [1] such as Sb and Ti and ash particles containing Al, Si, Fe and Ca which are eligible in construction materials. Some of these elements could have declining natural reserves or the natural reserves are more difficult to exploit, which means higher exploration costs.

Strategies to promote resource use from MSWI fly ash is recovery of metals or other elements from the ash, or using the MSWI fly ash itself after decontaminating/detoxificating the fly ash by manufacturing products from the treated [2].

Electrodialytic extraction of elements from different ashes and reusing the treated ash have shown potential as a combination of the strategies of element extraction and material reuse. Results with sewage sludge ash showed that P can be extracted for agricultural use and the treated ash as cement replacement in concrete [3] or clay replacement in bricks [4] and for MSWI fly ash metals were extracted before the ash was used as clay replacement in bricks [5] or as precursor in geopolymers [6].

MSWI fly ash is a highly alkaline material and extraction of elements from the ash requires lowering the pH. In electrodialytic treatment a direct current is applied to the MSWI fly ash and the induced electrokinetic processes reduces pH of the MSWI fly ash by water-splitting ($H_2O \rightarrow H^+ + OH^-$) at the cation exchange membrane in a three compartment set-up and by the anodic reaction ($2H_2O \rightarrow 4H^+ + O_2 + 4e^-$) in a two compartment set-up [7]. The acidification enables the release of metals from the ash into the liquid phase of the suspension and then metals on ionic form can electromigrate in the electrodialytic cell and collected in the electrolytes. Previous results have shown that after 14 days of electrodialytic treatment extraction percentages of 61 % Cd, 1 % Cr, 3 % Cu and Pb and 53 % Zn were achieved for one sample of MSWI fly ash [8] and after 28 days 98% Cd, 80% Cu, 84% Zn, 36 % Cr and 12 % Pb could be extracted [6]. In this study, it was investigated how metal extraction rates would be influenced by pre-washing the ash, using three- and two compartment set-ups in combination and by reusing process liquids.

MATERIALS AND METHODS

Experimental materials

The experimental MSWI fly ashes originated from two different incineration plants: 1) grate-fired plant Argo in Roskilde, Denmark (sample named ARGO), the fly ash sample was collected after bagfilters before the addition of air pollution control products, 2) grate fired plant Copen Hill in Copenhagen, Denmark (sample named ARC), the fly ash sample was collected after the electrostatic precipitator before the addition of air pollution control products. The fly ash samples were collected on a day with normal incineration conditions. The fly ash samples were stored at ambient temperature in sealed containers until the experimental work was carried out.

Analytical methods

The pH was measured in distilled water at a liquid-to-solid ratio (L/S) of 2.5 and after 1 hour of agitation, pH was measured by a Radiometer Analytical pH electrode. Total concentrations of Cd, Cr, Cu, Pb, Sb, Ti, Zn in the fly ash were measured by induced coupled plasma- optical emission spectrometry (ICP-OES, type Varian 720-ES) after digestion. Five digestions of each fly ash were made after the Danish Standard DS259 where 1 g of fly ash and 20 ml 7.3 M HNO3 were heated at 200 kPa (120°C) for 30 min. The liquid was thereafter separated by vacuum filtration through a 45 µm filter and diluted to 100 mL. Soluble Cl^- and SO_4^{2-} were determined by mixing 10.0 g fly ash with 25.0 mL distilled water. The suspension was agitated for 15 minutes before the liquid was separated through a 45 µm filter and analyzed for Cl^- and SO_4^{2-} by Ion Chromatography.

Washing of fly ash

To remove easily soluble salts and metals, the fly ash was washed as a pre-treatment to electrodialytic extraction. The ARGO fly ash was used to find the optimum liquid to solid (L/S) ratio between fly ash and distilled water before the electrodialytic experiments. Water washing of the ARGO fly ash was performed at L/S 5, 15 and 50. In a plastic container, 300 g fly ash was mixed with either 1.5 L. 4.5 L or 15 L distilled water. The fly ash and water was mixed thoroughly for 2-3 minutes. The suspension was thereafter filtered through Frisenette 1125 filters. Metal concentrations were measured in the washing water by ICP-OES. All filters and fly ash were dried at 105°C for three days, before the fly ash was crushed in a mortar and used in the electrodialytic extraction experiments. For the ARC fly ash, all fly ash was washed at L/S 15 before the electrodialytic experiments.

Electrodialytic extraction experiments

The electrodialytic experiments were performed with the two fly ashes and in three different experimental series: *washing*, *set-up* and *reuse.*

- The *washing* experimental series were made with ARGO fly ash pre-washed at different L/S ratios (L/S 5, 15 or 50), which was compared to raw (non-washed) fly ash, to determine the best washing procedure for the fly ash to be used in the electrodialytic experiments to remove chlorides and also to have stable experimental conditions. Only the three-compartment cell (Fig. 1a) were used for these experiments.
- The *set-up* experimental series was made with washed ARC fly ash to test the best conditions of experimental set-up between the two- (Fig. 1b) and three-compartment (Fig. 1 a) electrodialytic cell and a combination of the two (Fig. 1c). Tests with the combined two- and three-compartment cell are exploring the possible advantage of the faster acidification by the anodic reaction in the two-compartment cell and the full separation of both cationic and anionic species in the three-compartment cell.
- In the *reuse* experimental series, pre-washed ARC fly ash (L/S 15) was used and three experiments with the three-compartment set-up (Fig. 1a) were made and the processing liquids (washing water, electrolytes and suspension liquid) were reused between the experiments.

Experimental information is shown in Table 1. Duration for all experiments was 28 days and the applied current strength was 50 mA, corresponding to 1.0 mA/cm^2 current density per membrane area. The fly ash suspension consisted of 100 g fly ash (raw or washed) and 350 ml distilled water.

Series	Experiment name	Pre-washing, L/S ratio	Experimental cell
Washing (ARGO fly ash)	Raw	0	3C (Fig. 1a)
	L/S 5	5	3C (Fig. 1a)
	L/S 15	15	3C (Fig. 1a)
	L/S 50	50	3C (Fig. 1a)
Set-up (ARC fly ash)	3C	15	3C (Fig. 1a)
	2C	15	2C (Fig. 1b)
	3/2C 1 min	15	3/2C (Fig. 1c)–change every minute
	3/2C 1 h	15	3/2C (Fig. 1c)–change every hour
	3/2C 1d	15	3/2C (Fig. 1c)–change every day
Reuse (ARC fly ash)	R1	15	3C (Fig. 1a)
	R2	15	3C (Fig. 1a), process liquids form R1
	R3	15	3C (Fig. 1a), process liquid form R2

Table 1: Experimental conditions for electrodialytic experimental series *washing, set-up* and *reuse*

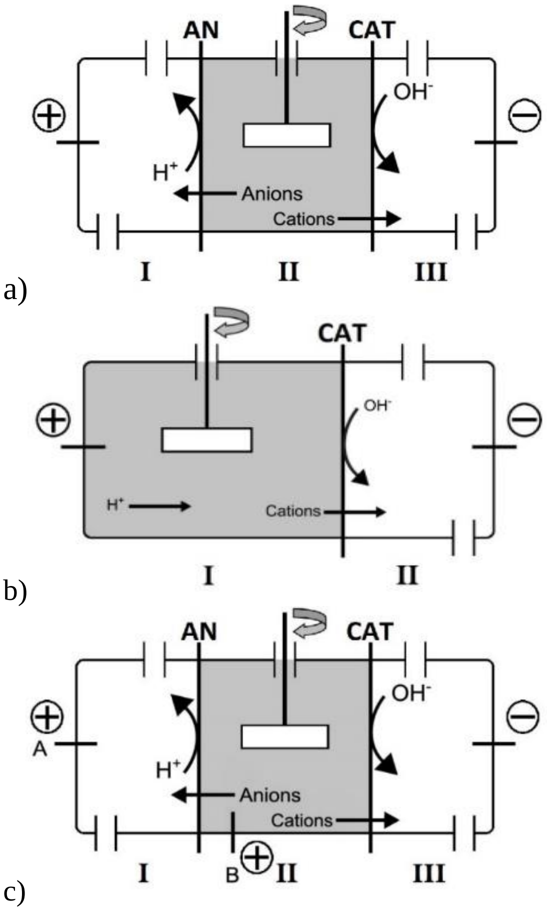

Fig. 1 Electrodialytic cell configurations a) three-compartment cell, b) two-compartment cell, c) combined three- and two-compartment cell. AN – anion exchange membrane, CAT – cation exchange membrane, A and B - anodes

The experimental cells made of Plexiglas were cylindrical with an internal diameter of cm. The compartment with ash suspension was 10 cm long. The suspensions were stirred by an overhead stirrer and the stirrer was made of a flexible plastic flap fastened to a glass rod. The electrodes were made of platinum coated titanium wire (diameter 3 mm) from Permascand. A Hewlett Packard E3612A power supply was used to maintain a constant electric DC current and a switch device was used to alternate the current between the anodes A and B in the experiments with alternating cell configuration (Fig. 1c). The ion exchange membranes were from Ionics (anion exchange membrane 20 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). During the electrodialytic experiments, pH and electrical conductivity (EC) were measured daily by Radiometer electrodes in the suspensions and the voltage over the cell noted. In the catholyte and the anolyte (only for the three-compartment experiments) 500 mL of 0.01 M $NaNO_3$, pH < 2 adjusted with HNO_3 were circulated. The pH in the catholyte was adjusted daily during the experiments to pH~2 with 7 M HNO_3.

After the experiments, the suspension was filtered through a 45 µm filter and the treated material dried at 105ºC before further digestion and metal analysis. The membranes and stirrer were placed in 1 M HNO_3 and the electrodes in 5 M HNO_3. All liquid samples including suspension liquid and electrolytes were kept for metal analysis by ICP-OES. In the experiments in the *reuse* series, a 20 mL sample was taken from the electrolytes and suspension liquids after experiments R1 and R2 and the remaining liquids reused in the next experiment. The process liquids in experiments R2 and R3 were replenished with distilled water (suspension liquid) or 0.01 M $NaNO_3$ to achieve similar staring volumes in all experiments. Clean stirrer, electrodes and ion exchange membranes were used in all the *reuse* experiments.

The percentage of metals extracted in the electrodialytic experiments was defined as the amount of metal not found in the ash compared to the total amount of metal, including in the ash, after the experiments.

RESULTS AND DISCUSSION

Fly ash characteristics

The characteristics of the two raw experimental fly ash samples are shown in Table 2. The metal concentrations in the fly ashes are compared to typical ore concentrations and active mines in Fennoscandia in 2013 [9]. All metals except Cd were found in concentrations that are similar to the lower ends of the mine and ore concentrations and the fly ashes can thus be considered an eligible urban mine for metals. The main difference between the two fly ashes were the SO_4 and Cl content.

Characteristic	ARGO	ARC	Ore concentrations [9] mg/kg	Active mines Fennoscandia 2013 (from [9]) mg/kg
pH_{H2O}	11.0 ± 0.1	12 ± 0.1		
Cl (%)	18	8.7		
SO_4 (mg/kg)	15,000	75,000		
Cd (mg/kg)	196 ± 5	279 ± 6	1,000-10,000	n.a.
Cr (mg/kg)	189 ± 4	126 ± 2,3	310,000	200,000
Cu (mg/kg)	2,270 ± 42	1,070 ± 19	5,000-20,000	1,000-26,700
Pb (mg/kg)	6,820 ± 295	6,250 ± 260	300,000-400,000	4,000-70,000
Sb (mg/kg)	915 ± 15	678 ± 43	27,000	1,000-25,000
Ti (mg/kg)	2,750 ± 70	2,320 ± 131	1,000 [10] 4,000-60000 [11]	n.a.
Zn (mg/kg)	38,300 ± 1,150	34,700 ± 1,500	50,000-150,000	4,400-110,000

Table 3: Characteristics of experimental fly ashes, n.a. – data not available

Pre-washing of fly ash

The results of the pre-washing of the fly ash is shown in Table 4.

	ARGO L/S 5	ARGO L/S15	ARGO L/S50	ARC L/S15
Dissolved fly ash (%)	28	37	43	39
Cd (%)	61	42	36	51
Cu (%)	-	-	-	-
Cr (%)	-	-	-	-
Pb (%)	2.3	0.5	-	1.7
Sb (%)	-	-	-	n.a.
Ti (%)	-	-	-	n.a.
Zn (%)	2.9	0.8	0.6	8.1
Cl^- (%)	97	100	100	84
SO_4^{2-} (g/kg)	29	53	87	151

Table 4. Fly ash dissolution and elements released by the washing pre-treatment, - not detected, n.a. – not analysed

The percentage of dissolved fly ash increased with increasing liquid to solid ratio for the ARGO fly ash sample. Between 84-100 % Cl was removed in the washing pre-treatment. A high percentage of 36-61 % Cd was also removed from by washing the ARGO fly ash. Lower percentages of Pb and Zn were also released from the ARGO fly ash by washing. The released percentages of Cd, Pb and Zn decreased with increasing L/S ratio and at the same time, the SO_4^{2-} in the washing water amount increased significantly. For the ARC fly ash at L/S15 the release of the heavy metals were 51% Cd, 8 % Zn and 2 % Pb, which are higher percentages than from the ARGO fly ash at the same L/S. From the washing step, it is desirable that mainly Cl is removed and not the metals, for the potential of recovering Cl products for reuse from the washing water. It has previously been shown that Cl extraction is independent of mixing time and L/S ratio, whereas sulfate extraction is dependent on L/S ratio [12], however for the ARGO fly ash, the Cl removal was found slightly dependent on L/S ratio.

Performance of electrodialytic experiments

The initial and final pH in the fly ash suspensions after electrodialytic extraction are shown in Table 5.

Series	Experiment	Initial pH	Final pH
Washing (ARGO Fly ash)	Raw	11.4	5.1
	L/S 5	9.6	2.8
	L/S 15	9.6	2.9
	L/S 50	9.9	3.6
Set-up (ARC fly ash)	3C	10.5	1.2
	2C	10.8	1.0
	3/2C 1 min	10.7	1.5
	3/2C 1 h	10.7	1.4
	3/2C 1d	10.8	0.9
Reuse (ARC fly ash)	R1	10.6	1.4
	R2	6.0	2.4
	R3	6.3	1.0

Table 5: Initial and final pH in the fly ash suspensions for the electrodialytic experiments.

The experiment with raw ARGO fly ash (exp. Raw) had to be terminated after 18 days because of very instable hydraulic flows in the electrodialytic cell and the final pH in the fly ash suspension of this experiment was pH 5.1 and a significantly lower metal extraction is expected for this experiment. The final pH in the fly ash suspension of the *set-up* and *reuse* experimental series was generally lower (pH 0.9-2.4) than in the *washing* experimental series (pH 2.8-5.1) and a higher metal extraction could be expected in the *set-up* and *reuse* experiments.

Typically, the voltage over the electrodialytic cells was below 5 V and the lower the voltage, the lower the overall energy use for the experiments. However in the exp. L/S 50 the voltage was around 10 V and some days over 50 V, due to a very low electrical conductivity in the fly ash suspension and this increased the overall energy use in the experiment and indicate that pre-washing at L/S 50 results in a fly ash that is more costly to treat electrodialytically. In the experiment R2, the anode had to be replaced during the experiment, and the voltage and pH in the suspension was higher in this experiment.

Electrodialytic metal extraction

The metal extraction during the electrodialytic experiments is seen in Figs. 2-4. The overall metal extraction order for the ARGO fly ash (*washing)* was Cd > Zn > Cu >>

Sb > Pb > Cr > Ti and for the ARC fly ash (*set-up* and *reuse)* Cd > Zn > Cu > Pb > Cr > Sb > Ti.

Washing experimental series

The main influence of pre-washing the fly ash before the experiments, was as mentioned above, that the exp. Raw was not hydraulically stable and lasted therefore only 18 days. Regardless of this, the Cd, Sb and Zn extraction was almost at the same level in this experiment as for the remaining experiments lasting 28 days. There was little difference in the metal extraction by the electrodialytic experiments if the fly ash was pre-washed by L/S 5 or L/S 15, even if the Cu, Pb, Sb and Ti extraction was slightly higher in the exp. L/S 5 compared to L/S 15. Contrarily, the metal extraction was lower when the fly ash was pre-washed by L/S 50. The distribution of the three metals with highest extractions (Cd, Cu and Zn) showed that these metals were mainly removed as cations and found in the cathode side of the experimental cells. The most significant difference between exp. L/S 5 and exp. L/S 15, was that in exp. L/S 5, the metals were also found removed to the anode side of the cell. This shows extraction as anions and indicates extraction as metal chloride complexes, although 97 % Cl was removed in the pre-washing step. In the Raw experiment metal extraction was also seen towards the anode. Metal extraction toward the anode is unwanted mainly because that indicates the presence of chlorides, as metals at this acidic pH is usually cations, and chloride which could form toxic Cl_2-gas at the anode.

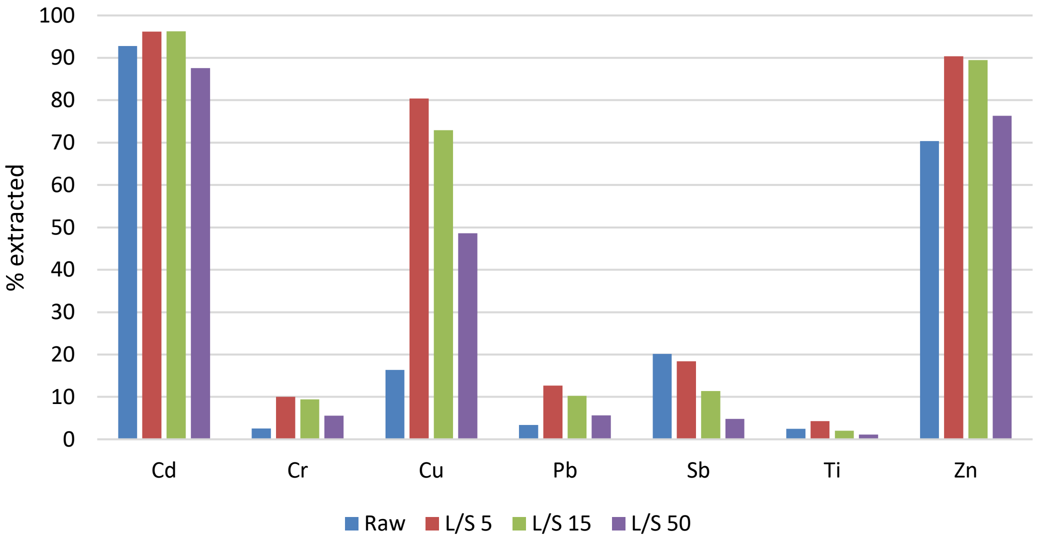

Fig. 2 Metal extraction efficiencies in the *washing* experimental series

Based on the results from the *washing* experimental series which showed i) 100 % Cl could be removed from the ARGO fly ash by water-washing, ii) high metal extraction and stable experimental conditions in the electrodialytic experiment of pre-washed fly ash and iii) metal extraction mainly as cations, it was chosen to pre-wash the fly ash for the *set-up* and *reuse* experimental series at L/S 15.

Set-up experimental series

In the *set-up* experimental series, Sb and Ti were only measured in two of the experiments (exp. 3/2C 1 h and exp. 3/2C 1 d). The experiments showed that there were some difference in the extraction by changing the set-ups. The set-ups with the three-compartment cells resulted in an overall high metal extraction, although the two-compartment cell resulted in higher Pb extraction than the three-compartment cell. There was a slightly higher metal extraction in the exp. 3/2 1 h compared to exp. 3 C and the extraction from these two experiments was higher than from exp. 3/2 1 min and exp. 3/2 1 day. As 87 % Cl was removed by the pre-washing of the ARC fly ash, metal extraction was seen to the anode side of the cells, but mainly towards the cathode side.

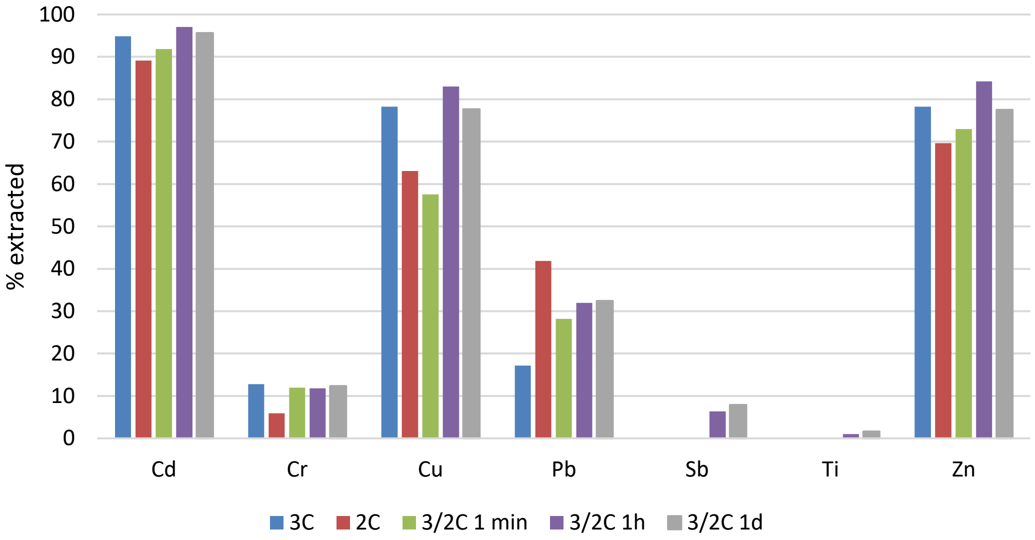

Fig. 3 Metal extraction efficiencies in the *set-up* experimental series

Reuse series

The metal extraction in the *reuse* experimental series is shown in Fig. 4. The initial and final pH in the fly ash suspensions were pH 10.4 and 1.4 in exp. R1, pH 6.0 and 2.4 in R2 and pH 6.3 and 1.0 in R3. Reusing the suspension liquid from exp. R1 lowered the initial suspension pH in exp. R2 and following exp. R3. One day into the exps. R2 and R3, an increase in the pH in the fly ash suspensions were seen, which is probably caused by the dissolution of hydroxides and hydrolysis of oxides in the fly ash, which releases OH^- to the suspension. The higher final pH in the fly ash suspension in exp. R2 was clearly linked to a lower metal extraction in this experiment. In this experiment, the voltage was high, due to a defect anode that had to be replaced mid-way in the experiment. However, the results from *reuse* experiments showed that it is possible to reuse the process liquids in the electrodialytic experiments and that the amount of processing liquids can be reduced in the process, which is important for upscaling of the process.

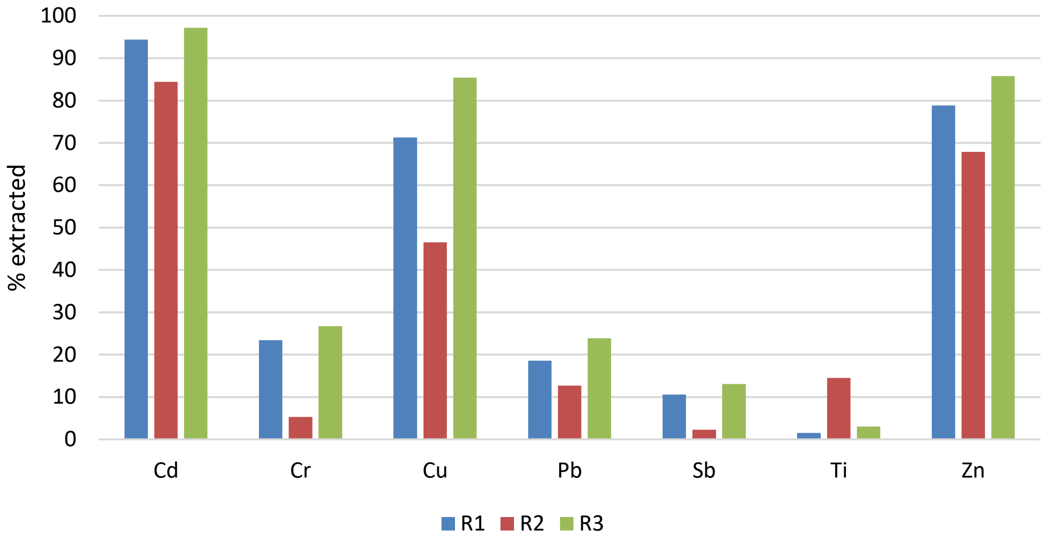

Fig. 4 Metal extraction efficiencies in the *reuse* experimental series

Comparing the metal extraction results for the two similar experiments for the ARGO (exp. L/S15) and ARC (exp. 3C) fly ashes (Fig. 5), similar metal extractions can be seen. This was even observed if the final pH in the fly ash suspension was different in these two experiments; pH 2.9 (exp. L/S 15) and pH 1.2 (exp. 3C) and from pH alone, higher extraction percentages was expected from exp. 3C.

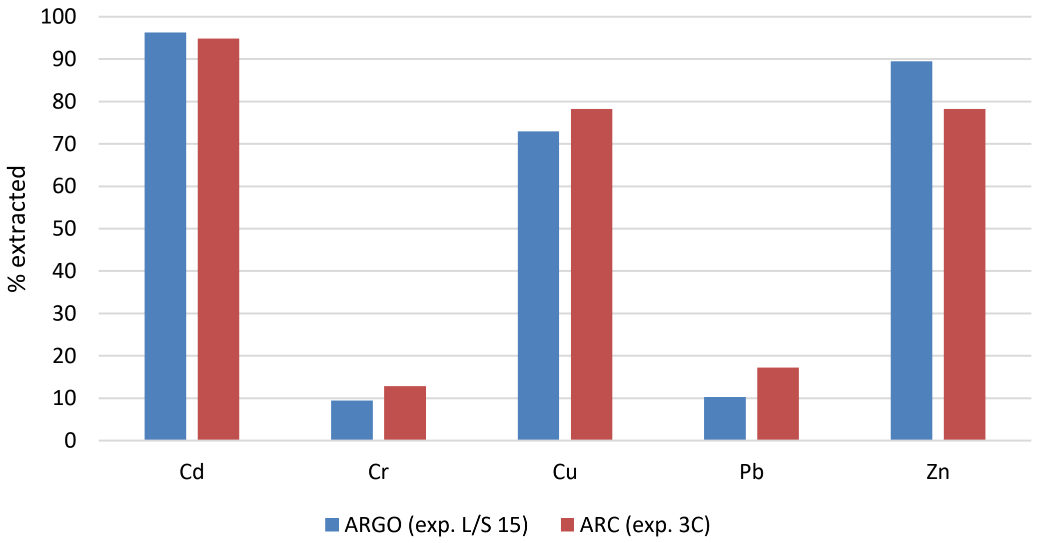

Fig. 5 Metal extraction efficiencies for ARGO and ARC fly ash for fly ash pre-washed L/S 15 and using 3 compartment cell

CONCLUSIONS

- Pre-washing the fly ash was necessary to obtain stable experimental conditions in the electrodialytic experiments, however the pre-washing should not be done at too high L/S ratio, which also resulted in unstable electrodialytic experiments. The pre-washing removed mainly Cl, but also parts of Cd, Pb and Zn from the fly ashes.

- Maximum electrodialytic extraction of the metals Cd, Cu and Zn were in the range between 80 – 97 %, 27- 40 % for Cr and Pb whereas the critical elements Sb and Ti were not easily extracted (maximum 13 and 14 %, respectively). The potential of mining MSWI fly ash for elements by the electrodialytic treatment method therefore depends on the element.
- The experimental set-up had a small influence on the metal extraction, however the three-compartment set-up and the combinations between three- and two-compartment set-ups resulted in higher extraction than the two-compartment set-up.
- Using the same experimental conditions on two different fly ash samples led to similar metal extraction percentages.
- Reuse of processing liquids between electrodialytic experiments were possible without influencing the metal extraction efficiencies.

Overall, the study showed that many different experimental conditions can be used to achieve high metal extractions and that the electrodialytic treatment is a method that can play an important role in supporting the circular economy for MSWI fly ash. To be able to demonstrate significant robustness of the electrodialytic extraction method for MSWI fly ash, future studies should include both replicability experiments with fly ash samples from several different plants and repetitiveness experiments with the same fly ash samples.

REFERENCES

1. European Commission, Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability 1, Brussels, 2020. https://ec.europa.eu/docsroom/documents/42849 (accessed May 10, 2021).
2. Quina MJ, Bontempi E, Bogush A, Schlumberger S, Weibel G, Braga R, et al. Technologies for the management of MSW incineration ashes from gas cleaning: New perspectives on recovery of secondary raw materials and circular economy. Sci Total Environ [Internet]. 2018;635:526–42. Available from: https://doi.org/10.1016/j.scitotenv.2018.04.150
3. Kappel A, Viader RP, Kowalski KP, Kirkelund GM, Ottosen LM. Utilisation of Electrodialytically Treated Sewage Sludge Ash in Mortar. Waste and Biomass Valorization. 2018;
4. Ottosen LM, Bertelsen IMG, Jensen PE, Kirkelund GM. Sewage sludge ash as resource for phosphorous and material for clay brick manufacturing. Constr Build Mater . 2020;249:118684. Available from: https://doi.org/10.1016/j.conbuildmat.2020.118684
5. Kirkelund GM, Skevi L, Ottosen LM. Electrodialytically treated MSWI fly ash use in clay bricks. Constr Build Mater. 2020;254:119286. Available from: https://doi.org/10.1016/j.conbuildmat.2020.119286
6. Zhan X, Kirkelund GM. Electrodialytic remediation of municipal solid waste incineration fly ash as pre-treatment before geopolymerisation with coal fly ash. J Hazard Mater. 2021;412 :125220. Available from: https://doi.org/10.1016/j.jhazmat.2021.125220
7. Jensen PE, Kirkelund GM, Pedersen KB, Dias-Ferreira C, Ottosen LM. Electrodialytic upgrading of three different municipal solid waste incineration

residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and SO4. Electrochim Acta. 2015;181:167–78. Available from: http://dx.doi.org/10.1016/j.electacta.2015.06.012

8. Kirkelund GM, Magro C, Guedes P, Jensen PE, Ribeiro AB, Ottosen LM. Electrodialytic removal of heavy metals and chloride from municipal solid waste incineration fly ash and air pollution control residue in suspension - Test of a new two compartment experimental cell. Electrochim Acta. 2015;181.
9. Allegrini E, Maresca A, Olsson ME, Holtze MS, Boldrin A, Astrup TF. Quantification of the resource recovery potential of municipal solid waste incineration bottom ashes. Waste Manag. 2014;34(9):1627–36. Available from: http://dx.doi.org/10.1016/j.wasman.2014.05.003
10. Xu C, Zhang Y, Liu T, Huang J. Characterization and pre-concentration of low-grade vanadium-titanium magnetite ore. Minerals. 2017;7(8):1–11.
11. Kang J, Moon G, Kim MS, Okabe TH. Production of High-Grade Titanium Dioxide Directly from Titanium Ore Using Titanium Scrap and Iron Chloride Waste. Met Mater Int. 2019;25(1):257–67. Available from: https://doi.org/10.1007/s12540-018-0175-7
12. Yang Z, Tian S, Ji R, Liu L, Wang X, Zhang Z. Effect of water-washing on the co-removal of chlorine and heavy metals in air pollution control residue from MSW incineration. Waste Manag. 2017;68:221–31.

Acknowledgements

This project was funded by Amager Ressourcecenter and they also provided the two fly ash samples. Laboratory technician Ebba Schnell is thanked for carrying out the experimental and analytical work.