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ORIGINAL PAPER

Test of electrodialytic upgrading of MSWI APC residue in pilot scale: focus on reduced metal and salt leaching

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Abstract In this study a pilot plant for electrodialytic treatment of municipal solid waste incineration (MSWI) air pollution control (APC) residue was tested and proposed as a treatment method which can lead to reuse of this otherwise hazardous waste. The pilot plant was developed based on a design that is adapted from conventional electrodialysis, e.g. used in desalination of solutions. The APC residue was treated in a suspension (8 kg APC residue and 80 L tap water) and circulated through an electrodialytic (ED) stack consisting of 50 cell pairs separated by ion exchange membranes. A direct current was applied to the ED stack for removal of heavy metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn) and salts (Cl, Na, SO_4) from the APC residue suspension. Different tank designs for mixing the APC residue suspension were tested as well as changing experimental conditions. A part of the raw experimental APC residue was carbonated by reaction with CO_2 under moist conditions prior to electrodialytic treatment. The carbonation alone reduced the leaching of some heavy metals. However, it was not sufficient to reduce the heavy metal or salt leaching to meet the Danish Category 3 guideline levels for waste material reuse and could not stand as a treatment method alone. Leaching of both heavy metals and salts were significantly reduced by the electrodialytic treatment for both the raw and carbonated APC residue. In the electrodialytically treated carbonated APC residue only Cr exceeded the Category 3 levels while in the electrodialytically treated raw APC residue both Pb and Zn leaching exceeded the Category 3. Optimization of the electrodialytic upgrading method is necessary to meet the Category 3 levels for all heavy metals. Removal of Na and SO_4 to below the Category 3 leaching levels were obtained in all the experiments. Cl removal was not sufficient in all experiments even if up to 1 kg of Cl was removed, the optimal conditions for Cl removal was a constant current of 5 A over the ED stack. The results of this study suggest that, with some optimization, electrodialytic upgrading, possibly in combination with carbonation, could be used as a treatment method for MSWI APC residue.

Keywords Waste incineration · Electrodialysis · Heavy metal · Availability

1 Introduction

Air pollution control (APC) residue from municipal solid waste incineration (MSWI) is classified as hazardous waste due to the high content of salts, heavy metals and other contaminants. MSWI APC residue is alkaline and leaching of heavy metals is a major environmental problem with regard to landfilling of the APC residue. Currently, APC residue from Danish MSWI is stabilized and disposed of abroad because legislation prohibits any kind of disposal or reuse in Denmark. Contrarily, APC residue from coal combustion is considered a valuable secondary resource and is reused in production of cement and as pozzolanic supplementary cementitious material in mortar and concrete. Similar to this APC residue, the MSWI APC residue also contains valuable resources that could be useful in the construction and the geotechnical industry [1]. To be able to use the MSWI APC residue it is however necessary to pretreat the APC residue to reduce the heavy metals leaching [2].

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Electrodialytic remediation of MSWI APC residue has been proposed as a pretreatment method for removing heavy metals and several studies have been made in laboratory scale with the aim of removing heavy metals from a MSWI APC residue suspension [3, 4]. The APC residue can be mixed with distilled water or complexing agents. The removal is dependent on acidification by water-splitting at the anion exchange membrane and interdiffusion of H^+ over the cation exchange membrane [5–7] when mixed with distilled water, which can be time consuming due to the high buffering capacity in the alkaline APC residue [8]. Addition of alkaline complexing agents to prevent acidification of the APC residue has shown higher removal than with distilled water [9]. Investigations of the electrodialytically treated APC residue's characteristics are limited. Pedersen and Gardner [10] showed that addition of ammonium citrate as complexing agent increased the availability and leaching potential of several heavy metals compared to the raw APC residue due to mineral dissolution and chelating by residual citrate in the APC residue during electrodialytic remediation. Thus, addition of complexing agents could be problematic if the treated APC residue should be reused. Ottosen et al. [8] showed that the water extractability of Cu increased and Pb decreased in electrodialytic remediation experiments where the APC residue was mixed with distilled water. In the same study, the removal of Cl was very high, which is important if the treated APC residue should be utilized in e.g. concrete [8]. Even though high removals of heavy metals from APC residue are possible to obtain, there is still a high content of heavy metals left in the final APC residue due to dissolution during electrodialytic remediation [3, 4].

The latest development within electrodialytic treatment of APC residue is to regard the APC residue as a material containing resources which can be reused if the toxicity is reduced. To investigate the possibility of reusing the electrodialytically treated APC residue, a new experimental set-up based on conventional electrodialysis (ED) was introduced by Jensen et al. [11]. This set-up can treat APC residue in a continuous process which is a great advantage since APC residue is produced continuously. The principle of electrodialysis is seen in Fig. 1 and is widely used for desalination of solutions in industrial scale. The ED system consists of an ED stack with multiple concentrate compartments (concentrate) and compartments containing the APC residue suspension (diluate) and where both the concentrate and the diluate are pumped through the ED stack. The compartments are separated by ion exchange membranes and the setup is designed to remove anions and cations from the diluate to the concentrate by the applied current. There is a concentrate compartment next to both electrode compartments to limit the occurrence of other ions in the electrode compartments so the only electrode reaction is hydrolysis. The major differences compared to the traditional electrodialytic cell with a contained APC residue compartment described in e.g. Pedersen [9], are (a) that the APC residue suspension is pumped through the ED stack, whereas in the traditional cell, only the electrolyte is circulated, (b) the APC residue suspension is stirred in a contained compartment and (c) larger membrane area and smaller distance between the membranes. This ED method was tested in bench scale laboratory experiments with good results before upscaling to pilot scale [11].

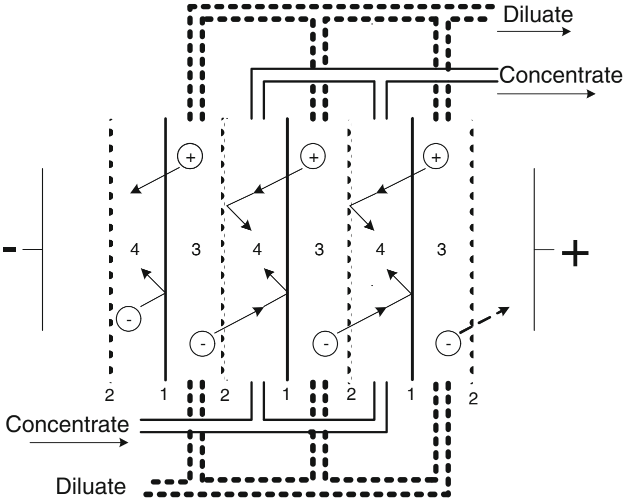


Fig. 1 Principle of electrodialysis of APC residue. 1/2 ion exchange membranes, 3/4 compartments

In this work, the electrodialytic upgrading was upscaled to pilot scale for MSWI APC residue for the first time. The electrodialytic upgrading was made by removing the mobile part of heavy metals and salts. This should significantly decrease the leaching of heavy metals to make the APC residue suitable for reuse. The extracted heavy metals should ideally be reused and replace metal mining and salts should be used in the chemical industry. The aims of this study were to (1) test and develop a pilot plant for electrodialytic upgrading of MSWI APC residue with focus on sufficient mixing of the APC residue and (2) investigate if leaching of heavy metals and salts could be reduced from the MSWI APC residue by electrodialytic upgrading. Furthermore, it was anticipated to produce APC residue that could be tested as a constituent in construction materials in following studies.

2 Experimental

2.1 APC residue

The APC residue used in the experiments was from the MSWI plant REFA I/S in Nykøbing Falster, Denmark. The raw APC residue was collected 13 March 2008 after a dry process in big bags and kept at room temperature until use. A part of the APC residue was subsampled and kept at room temperature under moist conditions. This part of the APC residue reacted with CO_2 in the air to be carbonated, which will result in decreased pH in the APC residue with subsequent possible changed heavy metal leaching and mobility. The carbonated APC residue was used in one experiment and had a higher water content than the raw APC residue, but no leachate was formed during the carbonation.

2.2 Analytical methods

Heavy metal concentrations (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn) in the APC residue were measured by ICP-AES after pretreatment by Danish Standard DS259 [12] where 1 g of APC residue and 20 mL 7.3 M HNO_3 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. The units used in this paper are mg/kg for concentrations in dry matter.

Water content was measured by weight loss at 105 °C for 24 h. Loss on ignition was measured at 550 °C for 1 h. The carbonate content was determined by a volumetric calcimeter method as described in Loeppert and Suarez [13]. The pH was measured in 1 M KCl at a liquid-to-solid ratio (L/S) of 5 and after 1 h of agitation, pH was measured by a Radiometer Analytical pH electrode. The amount of water soluble APC residue was estimated as mass reduction when mixing 1 g APC residue with 20 mL distilled water which was agitated for 24 h.

Leaching experiments were made according to CEN prEN 12457-3 part 1. The liquid to solid (L/S) ratio was L/S 2, mixing 40 g APC residue and 80 mL distilled water. The suspension was shaken for 6 h on an end-over shaker before vacuum filtration through a 45 μm filter and the filtrate was divided into two subsamples. One subsample for analysis of anions (Cl, SO_4) on ionic chromatograph (IC) and the other subsample was acidified by addition of concentrated HNO_3 before analysis of Na on AAS and heavy metals on ICP-OES.

Batch extraction experiments were made with HNO_3 and as reference distilled water was used. The extractions were made by mixing 1.0 g APC residue with 25 mL HNO_3 in concentrations 0.01–1 M in 50 mL acid rinsed plastic bottles. For the carbonated APC residue, NaOH in concentrations of 0.01–0.5 M was also added to increase the pH. All the extractions were made in triplicates and shaken for 72 h on a horizontal shaker operating at 250 rpm. Thereafter the samples settled for 15 min before pH was measured. The extractants were filtrated though 45 μm and acidified if $pH > 2$ by addition of concentrated HNO_3 before measurements of metals by ICP.

2.3 Electrodialytic pilot plant

The pilot plant consisted of two major parts: a rack with tanks and pumps and a compartment with the electrodialysis stack and the electrical devices see Fig. 2 and schematically in Fig. 3.

The concentrate tank (100 L) and the electrode clean solution tank (100 L) were installed with electrical conductivity electrodes. The diluate tank was installed with an

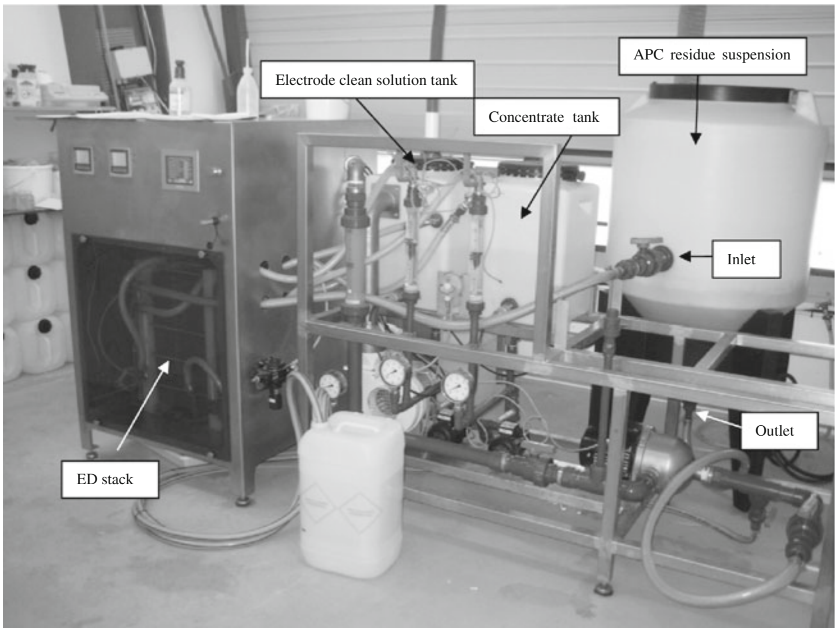


Fig. 2 The pilot plant with the conical tank

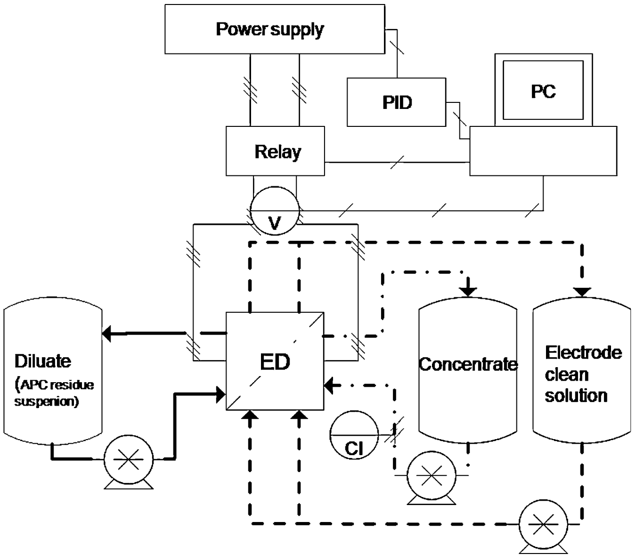
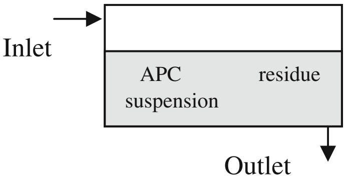
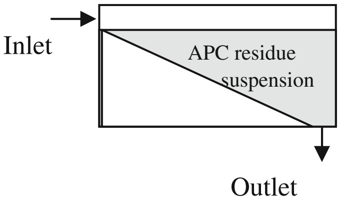
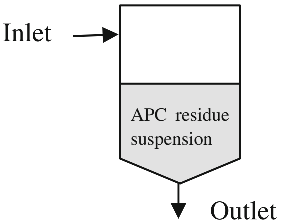


Fig. 3 Simple flow diagram for electrodialytic pilot plant

electrical conductivity and a pH electrode. Data from the electrodes were registered and collected continuously during the experiments. The APC residue suspension tank was developed and optimized during the study and three different tanks were tested to find the optimal design for keeping the APC residue in suspension, see Table 1. Electrodialytic experiments were made with all tank types. The best working tank was a conical PEH plastic 500 L tank and the inlet and outlet of the APC residue suspension to the tank is shown in Fig. 3.

The ED stack consisted of 50 cell pairs (530 cm^2 active surface area per cell) and Neosepta cation and anion exchange membranes were used. The spacers were 0.6 mm and 5 mm thick for the concentrate and diluate respectively. The diluate spacers were thicker than the concentrate spacers to avoid clogging due to the high solids content in the APC residue suspension. In Fig. 4 it is seen how the ion exchange membranes and flow spacers were mounted in the ED stack. There were electrode compartments in each end of the ED stack. The electrodes were titanium plates covered by a layer of metal oxides. The electrode compartments shared electrode clean solution, which was circulating. The maximum flowrates were 500–600 L/h for the diluate, 1000 L/h for the concentrate and 800 L/h for the electrode clean solution. The flowrates were adjusted in each experiment to maintain overpressure in the diluate compared to the concentrate, but the diluate flow rate was always kept at a maximum. The electrode clean solution tank was ventilated for exhaust gases from the electrode reactions, especially toxic chlorine gas. The pilot plant was built by Jurag Separation A/S.

Table 1 Development of APC residue tank for optimal mixing

Tank	Observations	Design
Rectangular	Insufficient mixing, APC residue deposited in the tank	
Diagonal	Improved mixing, APC residue still deposited in the tank	
Conical	Sufficient mixing, no deposition of APC residue in the tank	

2.4 Electrodialysis experiments

Five electrodialytic experiments were made and the experimental conditions are seen in Table 2. The APC residue was sieved through a 1 mm sieve to avoid clogging in the flow spacers during the experiments. In all the experiments a constant L/S 10 was used. In experiment 1; 10 kg APC residue and 100 L tap water was mixed and in experiments 2–5; 8 kg of dry APC residue and 80 L of tap water was mixed. As concentrate, 25 L tap water was used. In the electrode clean solution, 25 L distilled water was used, which was acidified with HNO_3 to reach an electrical conductivity ~100 mS/cm to avoid desalting during the experiment. Current strength, voltage and electrical conductivity in all the tanks and pH in the diluate tank were logged every 30 s during the experiments.

The different experimental conditions were chosen to test the effectiveness of the electrodialysis in the pilot plant under several operational conditions such as diluate tank system and constant current versus constant voltage drop. The current in experiments 1, 4 and 5 was set to be constant at 5 A. However, due to increased resistance in the ED stack, the voltage was increasing during the experiments 1 and 5 to the maximum of the power supply (250 V) with the result of a decreasing current. The effective time with the constant current strength at 5 A is shown is shown in Table 2. Experiments 2 and 3 were run with constant voltage of 25 and 68 V respectively. Between each

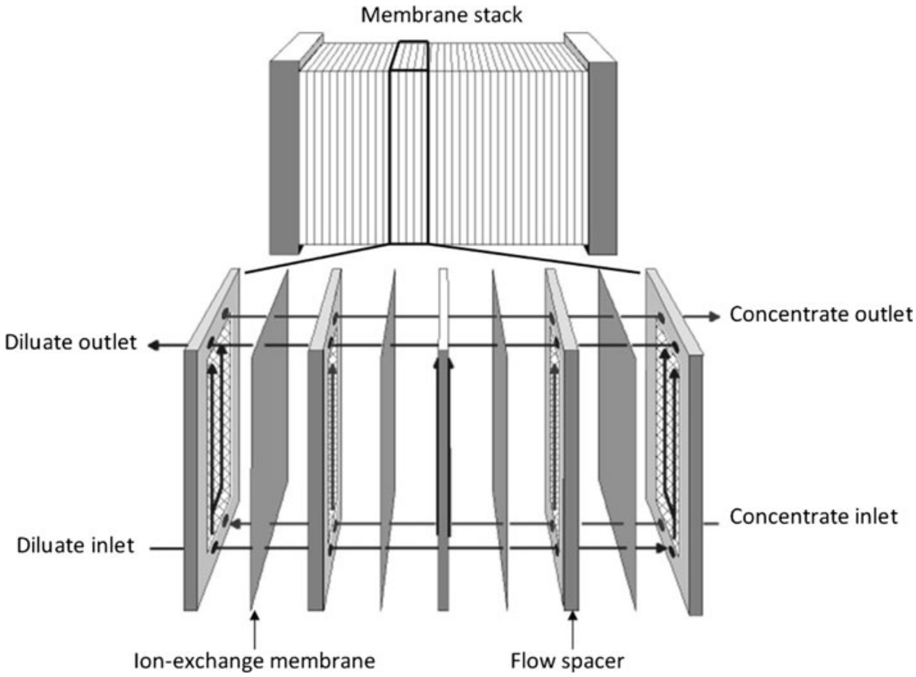


Fig. 4 Sketch of the ED stack showing placement of flow spacers and ion exchange membranes

Table 2 Experimental conditions for the electrodialytic experiments

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
Effective exp. time (h)	4	20:30	21:15	1:15	14:30
Current strength (A)	0.2–5	1.6–8	3.25–5	0–5	4–5
Voltage (V)	20–250	25	68	24–179	16–250
Diluate tank	Rectangular	Diagonal	Diagonal	Diagonal	Conical
Concentrate	Tap water	Tap water	Tap water	Tap water + 20 g $NaNO_3$	Tap water
APC residue	Raw	Raw	Raw	Raw	Carbonated

experiment, the pilot plant was flushed with acid and water to remove all APC residue particles from the previous experiment.

After the experiments, the APC residue was separated from the diluate by filtering the suspension through 45 µm filters. The APC residue was dried at 40 °C prior to digestions for measuring the total heavy metal content, pH and leaching experiments. Samples from the filtered diluate solution, concentrate and electrode clean solution were measured for metals on ICP and anions on IC.

3 Results and discussion

3.1 APC residue characteristics

The raw APC residue characteristics showed a high content of several heavy metals and alkaline pH 12.2, Table 3. The heavy metal content in the APC residue was high and can be divided into three groups according to the heavy metal content: (1) As, Cd, Cr and Ni (low content), (2) Ba, Cu and Mn (medium content) and (3) Pb and Zn (high content). Relatively large variations were seen in the heavy metal concentrations, as APC residue is highly heterogeneous [14]. Before each electrodialytic experiment the heavy metal content was determined in a representative sample of the APC residue used for the experiment. The variations in the heavy metal content in these samples were smaller than the overall variations showed in Table 3. The heavy metal content in the carbonated APC residue was similar to the raw APC residue. The pH was 10 in the carbonated APC residue, so the carbonation was effective. This was also seen in the carbonate and water content of the two samples; 9.4% carbonate and 0.5% water and 19.6% carbonate and 19.7% water in the raw and carbonated samples respectively.

Table 3 Characteristics of the experimental APC residue

Characteristic	Level
pH (raw APC residue)	12.2 ± 0.1
pH (carbonated APC residue)	10.0 ± 0.0
$CaCO_3$ (%) (raw APC residue)	9.4 ± 0.2
$CaCO_3$ (%) (carbonated APC residue)	19.6 ± 1.9
Water content (%) (raw APC residue)	0.5
Water content (%) (carbonated APC residue)	19.7
As (mg/kg DM)	134.3 ± 44.8
Ba (mg/kg DM)	372.9 ± 25.5
Cd (mg/kg DM)	141.0 ± 36.8
Cr (mg/kg DM)	101.2 ± 10.1
Cu (mg/kg DM)	488.4 ± 78.2
Mn (mg/kg DM)	410.1 ± 43.4
Ni (mg/kg DM)	31.2 ± 4.4
Pb (mg/kg DM)	2,527 ± 1.020
Zn (mg/kg DM)	15,264 ± 4,695

DM dry material

Table 4 Heavy metal and salt leaching from the raw and carbonated APC residue

	Raw APC residue	Carbonated APC residue	Category 3
pH	12	9	
As (μg/L)	**110.4**	25.0	50
Ba (μg/L)	**33,900**	**16,800**	4,000
Cd (μg/L)	22.1	**1,860**	40
Cr (μg/L)	64.8	**925**	500
Cu (μg/L)	**2,920**	833	2,000
Mn (μg/L)	22.2	8.9	1,000
Ni (μg/L)	25.0	3.4	70
Pb (μg/L)	**535,300**	**568**	100
Zn (μg/L)	**49,800**	303	1,500
Cl (μg/L)	**88,000,000**	**83,900,000**	3,000,000
SO_4 (μg/L)	1,260,000	725,000	4,000,000
Na (μg/L)	**11,500,000**	**13,900,000**	1,500,000

Numbers in bold represent samples which exceeds the Category 3 guideline level

3.2 Leaching experiments

For reuse of contaminated waste for geotechnical purposes, there are Danish guideline levels for water leachable metals and salts from the waste [15]. In this set of guidelines the Category 3 guidelines represents the most contaminated materials possible used for selected applications (filler in roads, paths, cable ditches, under fundaments and floors), which will be used for comparison in this study.

It is seen in Table 4 that the raw and carbonated APC residue exhibited different leaching of heavy metals. The leaching was generally higher in the raw APC residue, especially for Pb. In the raw APC residue, the Category 3 guideline levels for As, Ba, Cu, Pb and Zn were exceeded and the leached concentrations corresponded to 0.2% As, 17% Ba, 1.2% Cu, 44% Pb and 0.6% Zn of the total heavy metal content. For the carbonated APC residue the Category 3 levels for Ba, Cd, Cr and Pb were exceeded and the leached concentrations corresponded to 9% Ba, 2.4% Cd, 1.8% Cr and 0.04% Pb compared to the total heavy metal content. For the other metals, only a very low percentage of the total heavy metal content was leachable. This indicates that the leaching of heavy metals was pH dependent, which was also seen in other studies [e.g. 9, 16]. In the two APC residues there are some significant differences in the leaching behaviour with regards to heavy metals, especially for the most abundant metals Pb and Zn where the leaching decreased significantly when the APC residue was carbonated, which was also seen by Ecke [16].

Leaching of Cl and Na in both APC residues exceeded the Category 3 guideline level, whereas leaching of SO_4 was below Category 3. The leaching of Cl and Na was similar in the two APC residues and this suggests that the leaching is not pH dependent. Contrarily, Aguiar Del Toro et al. [17] found that carbonation caused higher leaching of Cl due to the lowered pH. This suggests that the leaching pattern is also very dependent on the actual composition of the MSWI APC residue.

The leaching results further showed that carbonation of the MSWI APC residue alone is not efficient enough to minimize the leaching of heavy metals to below the Category 3 guideline levels. Nevertheless, carbonation significantly reduces heavy metal leaching and has been proposed as a method for treating MSWI APC residues [16].

3.3 Batch extraction experiments

The results of the pH dependent desorption of the raw and carbonated APC residue is showed in Fig. 5 as percent leached of total heavy metal content. It was shown that the heavy metals were desorbed more at low pH than at the alkaline pH of the APC residue. For the raw APC residue at pH 12 and at pH 10 for the carbonated APC residue, which represent the water extracted samples for the APC residue significantly higher amounts of Cr were desorbed than in the leaching experiments. In the pH desorption experiments, the L/S was higher and the contact time for extraction was also longer than in the leaching experiments. This indicates that desorption of Cr could be solubility controlled at alkaline pH. In the carbonated sample the leaching pattern was similar as in the raw APC residue. However, the percentage of released heavy metal at low pH

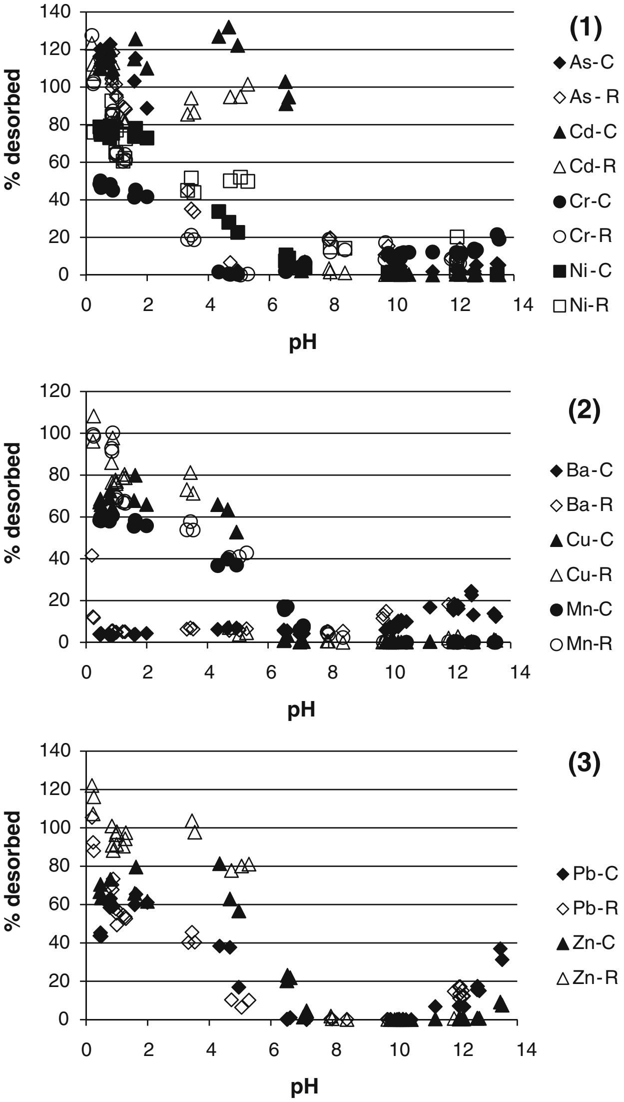


Fig. 5 pH dependent desorption of the raw (R) and carbonated (C) APC residue for (1) As, Cd, Cr and Ni (low content), (2) Ba, Cu and Mn (medium content) and (3) Pb and Zn (high content)

was significantly lower for Cr, Cu, Mn, Pb and Zn than in the raw APC residue. This suggests changed speciation of these metals due to the carbonation.

3.4 Electrodialytic experiments

3.4.1 Operational

In Fig. 6, the current over the ED stack in the different electrodialytic experiments is shown. It was not possible to keep the current in experiments 1 and 4 at a constant level of 5 A during the experiments. In experiment 1, the constant current 5 A was kept for about 4 h while the voltage over the stack was steadily increasing to the maximum of the power supply and thereafter, the current strength decreased. In the experiments with constant voltage (experiments 2 and 3), it was possible to keep the current over the ED stack during the whole experiments. The automatically current and voltage logging stopped after 4 h in experiment 3, but manual readings showed that when the experiment stopped, the current was 3.25 A and the voltage still 68 V. In experiment 5, with the carbonated APC residue, it was possible to keep the current at 5 A much longer than for experiment 1 where the current was set at 5 A for the raw APC residue. The total power consumption was 3.5 kWh (exp. 1), 1 kWh (exp. 2), 1.5 kWh (exp. 3), 0.5 kWh (exp. 4) and 13 kWh (exp. 5).

In Table 5, the pH, electrical conductivity and carbonate content of the APC residue suspensions before and after the experiments are seen. The initial electrical conductivity in the APC residue suspension was high due to dissolution of salts. There was continuously logging of the electrical conductivity during the experiments, but this did not work properly in all the experiment. Only in experiment 1 was the final electrical conductivity in the APC residue suspension close to 0 mS/cm^2 achieved. In experiments 2 and

Fig. 6 Current strength over the ED stack in the electrodialytic experiments

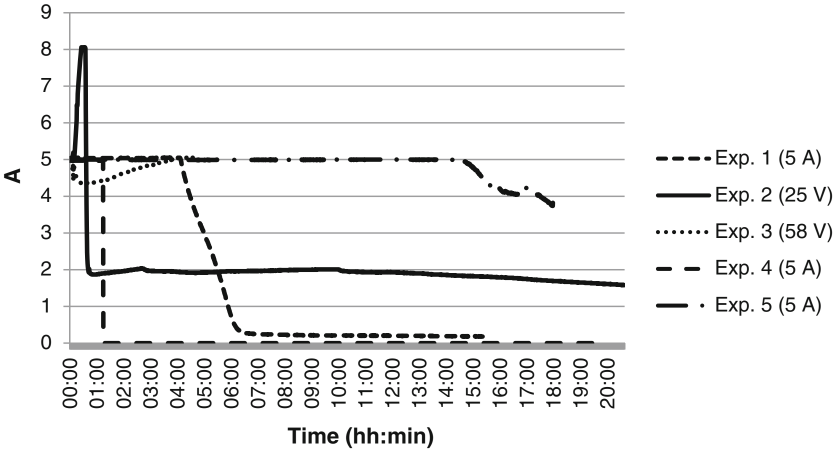


Table 5 Initial and final electrical conductivity (EC) in the APC residue suspension and final pH and carbonate content of the APC residue after the experiments

	Initial EC (mS/cm^2)	Final pH	Final EC (mS/cm^2)	Final $CaCO_3$ (%)
Exp. 1	30	12.2	0.1	35.2
Exp. 2	37.1	11.8	9.22	27.6
Exp. 3	40.0	12.4	n.a.	24.8
Exp. 4	43.4	12.4	n.a.	24.0
Exp. 5	29.2	9.92	6.7	38.9

n.a. not analysed

5 there was still a high electrical conductivity in the APC residue suspension after the treatment, which is also expected to be the case in experiment 3 since the current was kept high during the experiment. No significant changes in pH of the APC residue were seen due to the electrodialytic treatment.

When using the rectangular tank in experiment 1, the mixing was insufficient and APC residue deposited in the tank. Changing the tank to a diagonal one, improved the mixing of the APC residue, however this tank was changed for a more robust conical tank, where the mixing worked properly. This could explain why the initial levels for the electrical conductivity were not at the same level for experiments 1–4.

3.4.2 Heavy metal content

Generally, the total heavy metal concentrations in the APC residue were higher or at the same level as before the electrodialytic treatment, due to dissolution of salts and minerals. The water soluble fraction of the APC residue was 42% and it can be expected that a similar percentage of the APC residue was dissolved during the electrodialytic experiments. This resulted in a concentration of heavy metal in the treated APC residue, even if significant amounts of heavy metals were removed during the electrodialytic treatment.

3.4.3 Leaching after electrodialytic experiments

In Table 6, leaching of heavy metals and salts from the APC residue after the electrodialytic experiments compared to the guideline levels in Category 3 are shown. It is seen that the leaching of all heavy metals but Cr decreased significantly compared to the initial leaching (Table 4) due to the electrodialytic treatment.

In the experiments with the raw APC residue, leaching of Pb and Zn decreased from 535 to <3 mg/L and 50 to <2 mg/L, respectively. Of the varying experimental conditions, there was not a clear tendency to which settings were the most optimal on reducing the heavy metal leaching for all metals. For Pb and Zn the leaching was lowest after experiment 1, even if the mixing of the APC residue suspension in this experiment was not optimal. However, the final carbonate content in the APC residue was higher than in experiments 2–4, which could include stable metalcarbonates such as e.g. $PbCO_3$ [18]. In experiment 4, which as experiment 1 had a constant current, it was seen that the experimental time was too short for optimal removal of the mobile part of the heavy metals. The significant decrease in the leaching in this experiment suggests however a fast removal of the mobile parts of the heavy metals, since only leaching of As, Pb and Zn exceeded the guideline levels of Category 3. Since the total heavy metal concentrations in the APC residues were at the same level or even higher after the experiments only a very small part of the heavy metals were leached after the experiments. After the experiments less than 2% of the total concentration of all the heavy metals was leached.

Table 6 Leaching of heavy metals and salts (μg/L) in the APC residue after electrodialytic treatment

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Category 3
As	<25	20.2	<25	**131**	<25	50
Ba	n.a.	n.a.	449	1,720	109	4,000
Cd	<25	11.9	0.1	1.9	0.7	40
Cr	191	207	242	209	**1,630**	500
Cu	129	87.3	15.3	136	8.8	2,000
Mn	<25	1.0	<25	<25	6.0	1,000
Ni	<25	<25	<25	<25	<25	70
Pb	**1,590**	**2,630**	**3,780**	**16,700**	27.0	100
Zn	989	**2,560**	**1,660**	**4,870**	160	1,500
Cl	953,000	**4,498,000**	2,008,000	**11,978,000**	1,345,000	3,000,000
SO_4	1,160,000	918,000	1,063,000	950,000	1,800,000	4,000,000
Na	417,000	520,500	281,000	1,295,000	645,500	1,500,000

Numbers in bold represent samples which exceeds the Category 3 guideline level

For the carbonated APC residue, the leaching decreased for all heavy metals, except Cr, due to the electrodialytic treatment compared to the initial leaching. Even though the Cr leaching increased, Cr was the only metal that exceeded the Category 3 guideline levels after experiment 5. This suggests that the combination of carbonation and electrodialytic treatment might have a higher potential as treatment method of APC residue rather than electrodialytic treatment of raw APC residue alone. The leaching of Cr increased in all the experiments as the only heavy metal. This indicates possible changed speciation of Cr during electrodialytic treatment and should be studied further.

Leaching of Cl and Na also decreased significantly after the electrodialytic treatment and Cl leaching only exceeded the Category 3 guideline levels in experiments 2 and 4. It is important for several reuse options with a low Cl content. The constant voltage of 25 V in experiment 2 and the shorter remediation time in experiment 4 resulted in insufficient charge transfer to remove enough Cl compared to the Category 3 guideline levels from the APC residue suspension. As for the salts, there were no significant differences in the leaching from the carbonated APC residue in experiment 5 compared to the raw APC residue. The SO_4 leaching was slightly reduced in all the experiments with the raw APC residue, contrarily leaching of SO_4 in the carbonated APC residue more than doubled after the electrodialytic treatment. Jianguo et al. [19] identified anhydrite ($CaSO_4$) as a mineral phase in raw APC residue and gypsum ($CaSO_4{\cdot}(H_2O)_2$ as well as anhydrite in carbonated APC residue. If a similar change in the mineral phases happened in the APC residue in this study during carbonation, the electric current could enhance dissolution of gypsum. Still, however, the leaching of SO_4 in all experiments was below the Category 3 guideline level.

3.4.4 Distribution of heavy metals and salts after the electrodialytic experiments

The distribution of heavy metals in the solutions after the experiments is seen in Fig. 7. Removed heavy metals were found in the concentrate and the electrode clean solution. If the experimental conditions were optimal for removal of the mobile heavy metal fraction, small or no amount of metals should be found in the diluate solution. In the experiment 5 with the conical tank, the lowest concentrations of heavy metals and salts were found in the diluate. This was also expected since the mixing was sufficient with this tank. Generally, the amounts of heavy metals found in the electrode clean solution were low, which indicate that the ion exchange membrane set-up in front of the electrodes was working adequately.

As, Cd, Ni and Mn were removed from the APC residue in limited amounts (<35 mg) during the electrodialytic experiments are not included in Fig. 7. The leaching of these metals was also very low (Table 6).

Divalent metal ions can form stable complexes with Cl and the complexes can be positive, negative or uncharged ($MeCl^{+}$, $MeCl_2$(aq), $MeCl^{3-}$ and $MeCl_4{}^{2-}$) [18]. It was not possible to determine the charge of the removed metal species in the ED based on transportation direction since there was not a separate anolyte and catholyte, but only one electrode clean solution. Previous electrodialytic remediation experiments with MSWI APC residue has shown metal removal towards both the anode and the cathode [8, 9]. In the presence of Cl complexes there can be formation of uncharged species which could explain the amount of metals found in the diluate after the experiments.

It is seen that the shorter treatment time in experiment 4 resulted in lower removals than for the other experiments, except for Ba where the removal was at a similar level. This suggests that Ba was the most mobile metal in the APC residue, which is also confirmed by the significant decrease in Ba leaching after the experiments.

In experiment 5 with the carbonated APC residue highest removal of Cr was seen. This could be due to higher availability of Cr in the carbonated APC residue compared to the raw APC residue, as seen in the leaching experiments. For Pb, a similar trend was seen: the low availability in the leaching experiment for the carbonated APC residue resulted in a lower removal. The removal of Zn from the carbonated APC residue was similar to the Zn removal in experiments 2 and 3 with the raw APC residue. The Zn removal from the carbonated APC residue was higher than could be expected from the leaching experiments, where a significantly higher Zn concentration was leached from the raw APC residue compared to the carbonated APC residue. This suggests that the availability of some heavy metals increase during electrodialytic treatment with subsequent higher removal in the APC residue.

Salt distribution after the electrodialytic experiments is seen in Fig. 8. Cl_2 gas was formed and removed by the ventilation system if Cl reached the anode and an accurate distribution of Cl after the experiments was not possible to make. The set-up of ion exchange membranes closest to the anode should prevent Cl_2 gas formation, but it was seen that Cl had reached the electrode clean solution in all the experiments and thus, oxidation of Cl has most likely happened. Still, amounts of Cl up to 1 kg were found in the concentrate of the different experiments. Highest Cl removal occured from the carbonated APC residue. In experiments 2 and 4 up to 0.5 kg Cl was also found in the diluate, which shows that the experimental conditions in these experiments did not efficiently remove all the Cl from the APC residue suspension. After these two experiments,

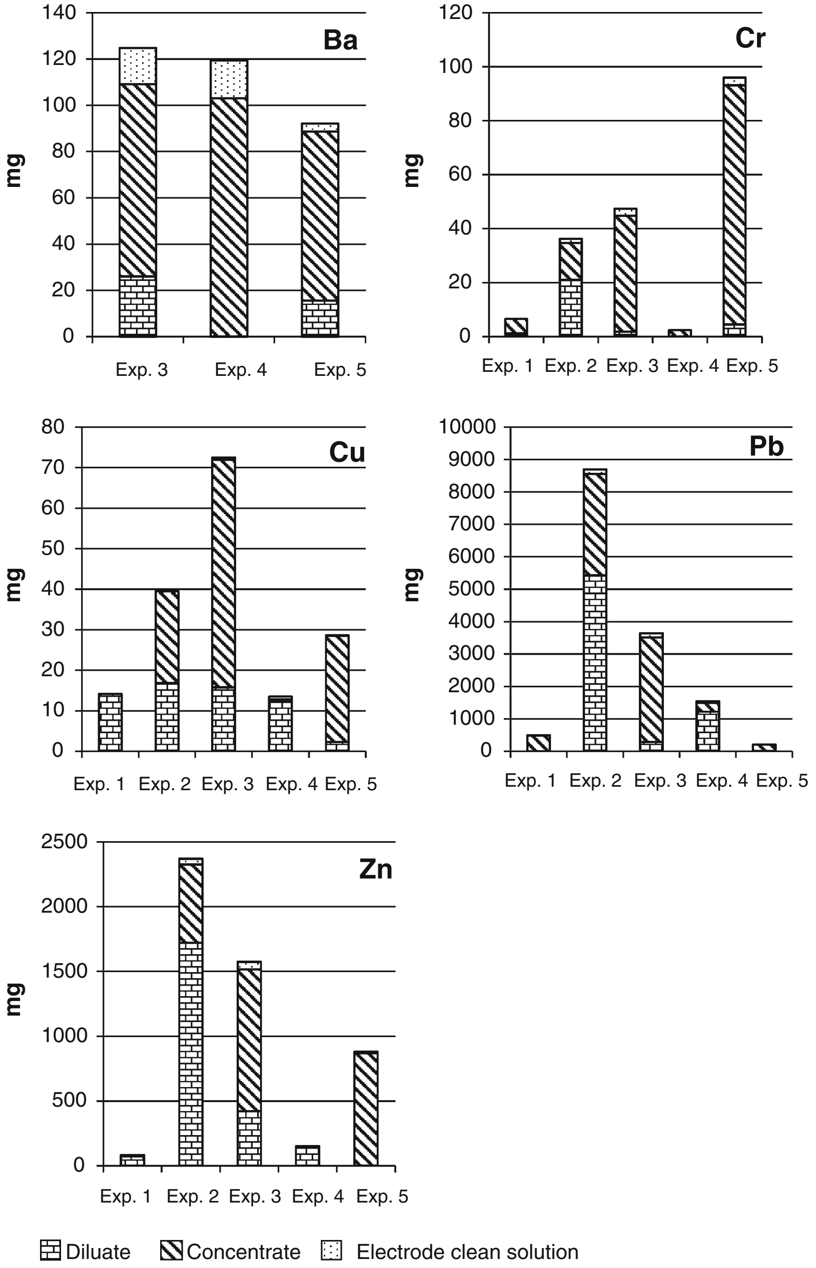


Fig. 7 Distribution of heavy metals in the solutions after the electrodialytic experiments

the Cl leaching also exceeded the Category 3 guideline level. With regards to Cl removal applying a constant current (exp. 1 and 5) was most efficient, since the experiments with constant voltage (exp. 2 and 3) as well as the shorter treatment time (exp. 4) led to considerable amounts of Cl in the diluate. Na showed a similar behaviour in the different experiments.

Removal of sulfate from the APC residue is important if the upgraded APC residue should be used in concrete production. Sulfate in concrete materials could lead to delayed expansion due to ettringite formation [2]. The sulfate removal was highest in experiments 1, 2 and 5. Sulfate did neither exceed the Category 3 guideline levels before or after the electrodialytic upgrading and is thus considered environmentally safe, but considerations should be made with regards to reuse in concrete.

4 Conclusion

In this study an electrodialytic pilot plant for reduction of heavy metal and salt leaching from raw and carbonated MSWI APC residue was tested. The carbonated APC residue showed lower initial leaching of As, Cr, Mn, Ni, Pb

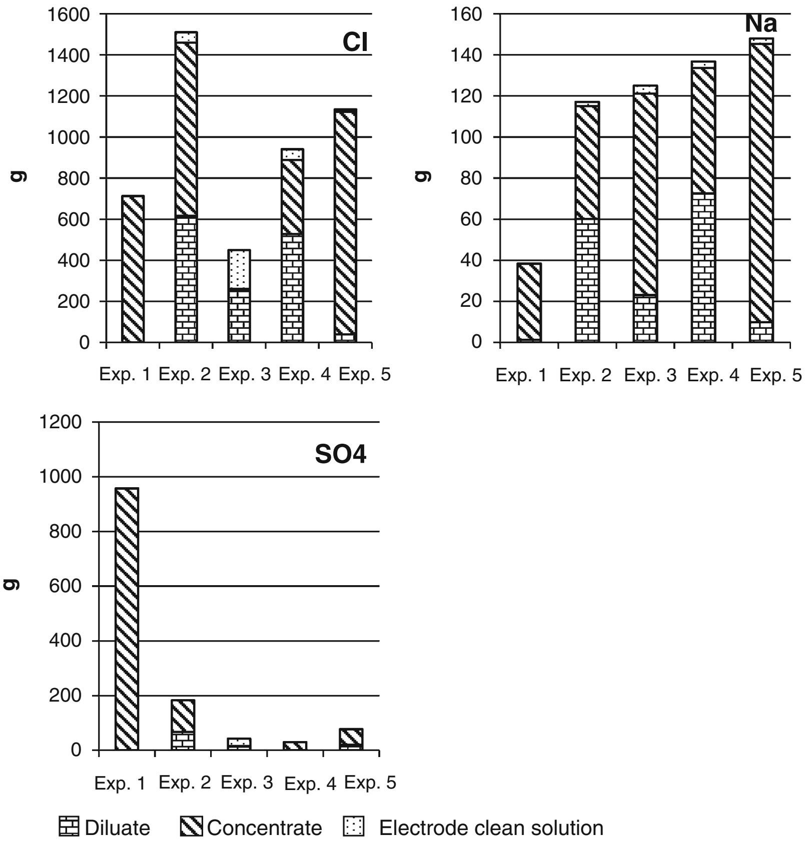


Fig. 8 Distribution of salts in the solutions after the electrodialytic experiments

and Zn than the raw APC residue; while the initial leaching of Cd and Cr was higher in the carbonated APC residue. The heavy metal leaching was clearly pH dependent. Leaching of salts was identical for the two APC residues.

In the electrodialytic upgrading experiments with different experimental conditions, leaching of both heavy metals and salts was significantly reduced within the treatment time of up to 20 h. The pH changes in the treated APC residue were negligible. Experiments with constant current resulted in the lowest leaching of heavy metals and salts from the treated APC residue as well as the lowest amounts of dissolved heavy metals and salts still in the APC residue suspension. In general, the final leaching of target metals was lower from the carbonated APC residue. Only Cr leaching was higher and still exceeded the Danish Category 3 guideline levels for waste material reuse. In the electrodialytically treated raw APC residue, leaching of Pb and Zn exceeded the Category 3 levels. Optimization of the electrodialytic upgrading method is necessary to meet the Category 3 levels for all heavy metals. The combination of carbonation and electrodialytic treatment seems to be a very promising combination for upgrading of APC residues.

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