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Electrodialytic extraction of Cr from water-washed MSWI fly ash by changing pH and redox conditions

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Abstract

Electrodialytic process offers a range of possibilities to waste management by electrodialytic separation (EDS) of heavy metals, depending on how the process is designed. Using three EDS cell setups (two two-compartment and one three-compartment) and their combinations, the extraction of Cr from municipal solid waste incineration fly ash by changing pH and redox conditions was investigated in the present work. The experiments were designed into single, two and three steps, based on the number of setups (by changing EDS cells) or effective setups (by shifting working electrode pairs) used. Prior to EDS the ash studied went through pretreatments such as water-washing and dry-sieving with a 50 μm sieve. The results showed that Cr was strongly bound in the ash, and the major fraction remained bound after the different treatments. Two/three-step treatment, which obtained the maximum Cr extraction rate of 27.5%, is an improvement on the single-step that extracted maximum 3.1%. The highest extraction was obtained due to the combined extraction of Cr(III) under low pH/oxidizing conditions and Cr(VI) under high pH/reducing conditions subsequently. The Cr leaching from the treated ashes with acidic pH was lower than from those with alkaline pH; after the three-step treatment, Cr leaching was much lower from the coarse fraction ($> 50 \mu\text{m}$), as compared to the fine ($\leq 50 \mu\text{m}$) or the unsieved ash. As for the coarse fraction, two/three-

step treatment reduced the leaching of Cr compared to the single-step in the same pH range (either acidic or alkaline).

1. Introduction

Recycling of valuable metals from municipal solid waste incineration (MSWI) fly ash (e.g. full-scale Zn recovery in Switzerland (Purgar et al., 2016)) and/or recycling of the ash itself as secondary material resources (e.g. for cement production (Pan et al., 2008)) have become the focus of research in the management of this kind of residual waste. However, as one type of ash residues from solid waste management process, MSWI fly ash is commonly considered as hazardous, which means it can cause environmental concerns if recycled or utilized. Leaching of toxic substances (e.g. As, Cr, Cu, Sb and Zn) is one of the possible aspects concerning environmental issues; for instance, the leaching of Cr, Cr(VI) in particular, contributes to carcinogenic human impact (Allegrini et al., 2015). The high health risk is seemingly linked to the fine particles in the ash due to the enrichment of unstable heavy metals (Zhou et al., 2015). Size-based separation e.g. by sieving could be applied to separate out the fine particles for metal recovery, and meanwhile the coarse fraction could be recycled or used (De Boom and Degrez, 2015).

With respect to metal extraction and MSWI fly ash treatment, electrodialytic separation (EDS) is one option (Chen et al., 2017). Metals are extracted from ash when suspended in e.g. water, attributed mainly to the electromigration of mobile free ions in the suspension through ion exchange membranes in current field: cations towards the cathode end and anions to the anode. Fig. 1 illustrates three EDS cell setups. Setup-a (Fig. 1a), a two-compartment (2C) cell, has an anode and a cathode compartment separated by a cation exchange membrane. The distilled water-ash suspension to be treated is placed in the anode compartment (as anolyte) (Chen et al., 2015). The two compartments in a 2C cell can also be separated by an anion exchange membrane for anion removal, i.e. setup-b

(Fig. 1b). However, setup-b is not commonly seen in MSWI fly ash treatment, and with good reason: most heavy metals are mobilized to the highest extent at low pH values in mainly cationic form. In setup-c (Fig. 1c), a three-compartment (3C) cell, there are anode and cathode compartment for electrolyte solutions, plus a center compartment for ash suspension. These three compartments are separated by a pair of cation and anion exchange membranes.

When electricity is supplied to an electrodialytic cell, water is electrolyzed to hydrogen ions and oxygen at the anode, and to hydroxyl ions and hydrogen at the cathode. In ash suspension, current is carried by ions that are either in the suspension originally or released along the treatment process because of ash dissolution caused by the changing properties of the suspension such as pH and redox potential.

The development of pH and redox potential differs between the EDS setups. Setup-a (Fig. 1a) and setup-c (Fig. 1c) acidify ash suspension due to water electrolysis and water splitting, respectively; whereas, setup-b alkalizes ash suspension due to the production of hydroxyl ions. The redox potential of ash suspension is affected by the generation of oxygen and hydrogen from electrode reactions if they enter into the suspension. Thus, setup-a creates an oxidizing environment, whereas setup-b reducing.

The pH plays an important role in the mobilization of heavy metals and has great impact on the species of charged mobile ions, therefore influencing the electrodialytic extraction rate. Most metals form soluble cations at acidic pH (e.g. Zn^{2+}), and amphoteric metals (e.g. Pb and Zn) also exist as soluble hydroxides at alkaline pH (e.g. $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$). Some metals, especially oxyanion forming elements such as Cr, develop different mobile species not only depending on pH but also on redox potential (Cornelis et al., 2008). This suggests that using different EDS setups might lead to different extraction rates of Cr from MSWI fly ash. However, relevant information has not been reported yet. In addition, a deep understanding of the migration patterns of Cr found in MSWI fly ash

during EDS treatment under different conditions might be of importance considering that, in most cases without using assisting agents such as ammonium citrate (Pedersen, 2002), the extraction of Cr was low compared to that of other heavy metals such as Cd, Cu and Zn. For instance, compared to 3.3-15% of Cu, 1.1-61% of Cd and 1.5-53% of Zn, the extraction of 1.1-4.5% of Cr was obtained by Kirkelund et al. (2015) through treating a MSWI fly ash using either 2C EDS cell (Fig. 1a) or 3C (Fig. 1c) under the conditions: water-to-ash ratio (L:S) of the suspension of 3.5; current density of 0.1/1 mA/cm²; and 14 days treatment. Chen et al. (2017) treated the same washed ash which was used in the present study through single-step 2C (Fig. 1a) and two-step 2C+3C (Figs. 1a+1c) EDS. A slight increase in Cr extraction from the washed ash was observed by introducing the second treatment step (effective 3C), but the extraction rate was still less than 1.5% under the conditions: L:S of 3.5; current density of 1 mA/cm²; and 3/7/12 days treatment.

In view of the above-mentioned facts, the present study investigated the possibility for chromium extraction from water prewashed MSWI fly ash under different pH and redox potential conditions, which were created by using different combinations of the 2C and 3C electrodialytic setups, without using any assisting agents. Setup-b (Fig. 1b) was especially used to investigate the feasibility of extracting Cr under high alkaline and reducing conditions. The Cr extraction was compared between the different EDS combinations: one-step treatment with either acidification or alkalization of ash suspension; two-step using the two 2C setups to combine acidification and alkalization; and three-step involving all the three setups illustrated in Fig. 1. As for ash pretreatment prior to EDS, by prewashing the consumption of current on moving soluble salt ions can be reduced, and the generation of toxic chlorine gases during EDS treatment can be suppressed; and by one-size sieving of the washed ash the differences in Cr extraction between the coarse and the fine fractions were studied. Moreover, the Cr leaching from the variously treated ashes was discussed.

2. Materials and methods

2.1. MSWI fly ash and pretreatment

The MSWI fly ash studied was collected after electrostatic precipitator but before the neutralization of acidic components by a wet scrubber process, from the Vestforbrænding MSW incineration plant located in Glostrup, Denmark. The incinerator has a capacity of 600 000 t/year and generates about 15 000 tons of air pollution control (APC) residue annually, including fly ash. The as-received sample was sieved in the laboratory to remove the few particles exceeding 1 mm.

The ash passing through the sieve was washed with distilled water at a L:S ratio of 5 for 5 minutes. The suspension was filtered (12-15 μm filter) and the ash retained on the filter paper was dried at 105 °C for 24 h. One part of the washed ash was directly used in the EDS experiment, and another part was fractionated by dry-sieving using a 50 μm sieve prior to EDS treatment.

2.2. EDS treatment

The three setups illustrated in Fig. 1 were used in the present lab-scale study. The ash suspension was placed in the compartments (with a length of 10cm) highlighted in grey – setup-a: compartment I; setup-b/c: compartment II. The overall experimental design is outlined in Table 1. Each experiment was named based on the ash sample treated (C=coarse fraction; F=fine fraction; W=the whole washed ash unsieved) together with the setup(s) arranged in order of appearance (e.g. b – single-step treatment using setup-b; a-b/b-a – two-step treatment in the order of setup-a and setup-b or in reverse order; and so forth). The experiments were made in three phases:

Phase I (C-a, C-b and F-a): Single-step treatments comparing setups -a and -b, as well as comparing the treatment of the two ash fractions using setup-a.

Phase II (C-a-b and C-b-a): Two-step treatments examining the Cr extraction by combining the two types of setups used in Phase I. Instead of changing the cells directly, the setup shift was achieved by shifting electrodes in a three-compartment cell (Fig. 1c) to form effective setups. There were four electrodes in the 3C cell, two in the ash suspension and one in each of the electrolytes (Fig. 2). By

connecting the electrode in the cathode compartment (separated from the suspension by a cation exchange membrane) and the electrode in the opposite side of the ash suspension with power supply, an effective 2C cell as illustrated in Fig. 1a was formed. Connecting the other two electrodes resulted in an effective setup-b cell.

Phase III (C-a-c-b, F-a-c-b and W-a-c-b): Extending the two-step treatment of a-b to three-step by including an intermediate step using setup-c (Fig. 1c), i.e. a-c-b. This setup combination was used to treat unsieved ash (W) and the ashes after sieving (C and F). In the experiments F-a-c-b and W-a-c-b the cells used for treatment changed according as which setup was planned for each step, meaning the suspension was transferred from one cell to another between the steps. Whereas, the experiment W-a-c-b followed the practice of Phase II by shifting electrodes in a 3C cell to achieve the transfer from one step to another. The termination of the first two steps (e.g. -a-c- : 2C+3C) was pH-controlled at the ash suspension pH of ~4 and ~2, respectively.

Being suspended in 350 ml of distilled water by stirring, 50.0 g of ash was treated in each experiment. Platinum coated titanium bar electrodes with a diameter of ~2 mm were used. Electrolyte solutions (0.01 M NaNO₃; 500 ml per electrolyte compartment per step) were kept circulating in the electrolyte compartment(s) (with a length of 5cm) during treatment. The experiments were conducted at a constant current of 50 mA when using setup-a, and 25 mA when using setups -b and -c. The pH and the electric conductivity of the ash suspension were measured at least once a day. The pH of the electrolytes was adjusted to between 1 and 2 for setups -a and -c, and adjusted to between 10 and 11 for the steps involving setup-b by 1:1 HNO₃ or 6 M NaOH, respectively. The electrolytes were renewed between each shift in cell.

2.3. Ash characterization

The concentration of Cr in the ash was determined according to Danish Standard DS 259 (2003) by HNO₃ digestion. One gram of dry ash was allowed to react with 20 ml of 1:1 HNO₃, and this

mixture was autoclaved at 200 kPa at 120 °C for 30 min. Afterwards, the digested sample was vacuum-filtered through a 0.45 µm filter. The Cr concentration was measured in the filtrate by ICP-OES (Varian 720-ES, Software version: 1.1.0). Series of three replicates were made. All concentrations are given on a dry mass basis. This digestion procedure only allows partial dissolution of the mineral phases in the ash, since silicate minerals remain undissolved.

The pH of the ash was measured with a Radiometer Analytical pH electrode in 1 M KCl solution at a L:S ratio of 2.5 after 1 hour of agitation.

The buffer capacity of the two ash fractions (C and F) was analyzed in accordance to Reddy et al. (1999) by adding concentrated HCl into the water-ash solution (20 g ash and 300 ml distilled water) every 30 minutes. The pH of the agitated solution was measured after each acid addition, until the pH was between 1 and 2.

Leaching of Cr (triplicate for C-a-b and C-b-a; duplicate for C-a, F-a, C-b and W-a-c-b; one sample for C-a-c-b and F-a-c-b) from the treated ash samples was determined at a L:S ratio of 2 l/kg according to DS/EN 12457-1 (2002). The mixture of 20 ml distilled water and 10 g ash was agitated for 24 hours and then vacuum-filtered (0.45 µm filter). The pH and the oxidation-reduction potential (ORP) of the leachate were measured with a Radiometer Analytical pH electrode and a MC3051Pt-9 combined redox electrode, respectively. The ORP values are expressed as Eh ($Eh = ORP + 210$ mV, where 210 mV is the reference potential of an Ag/AgCl reference electrode with 3M electrolyte solution at 20-30 °C). The concentration of Cr in the leachate was analyzed by ICP-OES.

3. Results

3.1. Characterization of ash

The as-received ash had a HNO₃-digestable Cr concentration of 113±6 mg/kg (Table 2), and a pH of 12.2. After washing in water, the concentration decreased to 112±3 mg/kg, and the pH decreased to 10.2. The washed ash had mass distributions of 42% fine (≤50 µm; Cr concentration:

155-158 mg/kg; pH: 10.3) and 58% coarse ($>50\text{ }\mu\text{m}$; Cr concentration: 114-120 mg/kg; pH: 10.5).

The fine fraction had a higher buffering capacity than the coarse, as is seen from Fig. 3.

As an oxyanion forming element, the leachability of Cr depends on the chemical (e.g. mineralogy, pH and redox potential) and physical (e.g. particle size, porosity and hydraulic conductivity) interactions between the sample and the leaching medium (Sabbas et al., 2003). As is shown in Table 2, the leaching of Cr from the untreated (neither washed nor EDS-treated) ash was 0.47 mg/kg (equals to 0.24 mg/l in the leachate), which was lower than the limiting value of 0.5 mg/l for waste to be used in geotechnical construction work (Category 3) (BEK nr 1414, 2015). This value, however, increased to 1.44 mg/kg after washing. Besides the pH difference, the change in redox potential of the ash leaching system from reducing for the as-received ash (negative ORP -24 mV, equivalent to Eh 186 mV) to oxidizing for the washed was probably responsible for the increase in Cr leaching caused by washing.

3.2. Changes in pH and conductivity in ash suspension during EDS

Fig. 4a shows the pH development in ash suspension during EDS treatment. Setup-a (Fig. 1a) led to the fastest pH decrease. Compared to setup-a, setup-c, which was only used in the three-step treatment after setup-a, caused a relatively slow acidification process.

In relation to the pH-controlled treatment, the time taken to reach the set pH value was not only affected by the setup of the electrodialytic cell used, but also by the buffering capacity of the ash treated (Fig 3). For example, the coarse washed fraction, which had a lower buffering capacity than the fine, was faster (21.5 days; Table 1) to be acidified to pH 2 compared to both the unsieved washed ash and the fine washed fraction (both 23 days). Contrarily, using setup-b, a strong increase in pH was seen in the ash suspension due to the production of OH^- from electrolysis at the cathode in the suspension.

The development of electric conductivity in ash suspension is shown in Fig. 4b. The change in conductivity indicates the change in the concentration of free ions and ionic species. A remarkable increase in conductivity took place during the acidification of ash suspension, which accelerated the ash dissolution and the formation of free ions; that's when setup-a and setup-c were involved in the treatment. However, at the very beginning of the treatment (e.g. within the first day) using setup-a or setup-c, the conductivity of ash suspension had a quick decrease, which was associated with the electrodialytic extraction of the immediately mobilized free ions in the ash after contacting with water (e.g. C-a and F-a), or the further extraction of the free ions already released at the previous treatment step (e.g. W-a-c-b and C-b-a).

When the initial ash suspension was treated with setup-b, the conductivity increased during this treatment step, i.e. -b in C-b or C-b-a, and here it is a result of the strong alkalinity of the suspension. However, when setup-b was used to treat already acidified ash suspension after setup-a or setup-c, the conductivity decreased. This was because, with the generation of OH^- from cathode reaction in the suspension, the acid was neutralized and the dissolved ions at acidic pH possibly precipitated as pH increased to alkaline. The conductivity seemingly stabilized or even increased when the pH of the ash suspension was higher than 10.5, as observed in e.g. experiment C-a-b.

3.3. *Cr extraction*

Table 2 summarizes the mass balance, mass loss of the ashes during treatment, Cr extraction efficiency, Cr leaching from the ash after treatment, and the Cr concentrations in the ashes before and after treatment. The mass balance describes the difference between the total Cr output from the whole EDS system at the end of treatment and the Cr input from the ash initially, with values ranging from 90% to 109%, which is acceptable, taking into account the heterogeneous nature of the MSWI fly ash.

The total Cr extraction varied from 0.4% to 27.5%. Only the Cr found in the separate electrode compartments was included in the calculation of extraction rate, therefore grouped into two i.e. anolyte (including anolyte solution, anode in anolyte and anion exchange membrane) and catholyte (including catholyte solution, cathode in catholyte and cation exchange membranes). However, the Cr found in the filtrate of suspension and attached on the electrode(s) and stirring bar placed in suspension was not regarded as extracted in this work, but all classified as the Cr dissolved (and retained) in the liquid phase of the suspension. The order of extraction percentage was W-a-c-b > C-a-b > C-a-c-b > F-a-c-b > C-b-a > C-a > C-b > F-a. This order reveals that: (1) Combining the setups (Phase II and III) gave higher extractions than single cell treatment (Phase I); (2) The extraction of Cr from the coarse fraction was relatively easier than from the fine, seen from the two experiments which were directly comparable (C-a-c-b > F-a-c-b and C-a > F-a); (3) Combining setup-a and setup-b resulted in a significantly higher extraction when using setup-a first (C-a-b >> C-b-a); and (4) Setup-c did not enhance the Cr extraction from the coarse fraction when used as an intermediate step between setup-a and -b as C-a-b > C-a-c-b; but still the combination of setups a-c-b gave the highest extraction of all, and this was obtained when treating the washed ash (W-a-c-b).

Even though Cr was extracted during the experiments, its concentration in the treated ashes generally increased (Table 2), except in the case of experiments C-b and C-a-c-b. The increase was because the Cr containing particles were dissolved to a lower extent than the ash in total. The ash mass loss, calculated as $\left(1 - \frac{\text{mass of the dry ash after EDR}}{\text{mass of the dry ash before EDR}}\right) \times 100\%$, was between 3% and 53% (Table 2). The highest mass losses were obtained in the experiments of Phase III, and the far lowest (3%) in experiment C-b where the ash was alkaline all through the treatment. There is a tendency for higher mass loss in the experiments with the fine ash fraction compared to the corresponding experiments with the coarse fraction: F-a > C-a and F-a-c-b > C-a-c-b.

3.4. Cr leaching after treatment

The leaching of Cr from the ashes after the EDS experiments, as well as the pH and Eh of the leachates are seen in Table 2. The two experiments in Phase II showed the leaching C-a-b > C-b-a, which is most likely related to the final pH of the leachates (9.9 and 5.3, respectively). Chen et al. (2017) reported the pH-dependent desorption of Cr in the same ash which was used in the present study, and showed that, the desorption was almost non-measurable around the pH 5.3, but about 3% at pH around 10.4. The leaching from the ashes treated in the two experiments in Phase I, C-a and F-a, further confirmed a lower Cr leaching at acidic pH around 5.2/5.8. For the three-step treatments in Phase III, the order of leaching was F-a-c-b > W-a-c-b (average) > C-a-c-b and the pH of the leachates were 7.5, 9.1, and 8.7, respectively. In the pH range from 7.5 to 9.1 a slight increase in Cr desorption with increasing pH was previously observed (Chen et al., 2017), and thus the leaching order was not likely to be determined by pH in this range but rather by the fact that the leaching was the lowest from the coarse fraction in general. Overall, the Cr leaching was in the order of F-a-c-b > W-a-c-b > C-b > C-a-b > untreated > C-a-c-b > F-a > C-a > C-b-a. The redox potential (Eh) of the leachates for the experiments using setup-b as the last step (i.e. F-a-c-b, W-a-c-b, C-b, C-a-b and C-a-c-b) ranged from 400 mV to 450 mV. According to the Eh-pH diagram of Cr (Cornelis et al., 2008), the dominating soluble Cr species in water at 25 °C at Eh 400-450 mV and in the pH range of 7.5-10.7 is Cr(VI) in the form of CrO_4^{2-} . Whereas, the dominating soluble Cr species is Cr(III) in the form of $CrOH^{2+}$ at Eh 520-680 mV and in the pH range of 5.2-5.8 for the experiments using setup-a as the last step.

4. Discussion

4.1. Effect of electrodialytic setups on chromium extraction

Fig. 5a shows the distribution of Cr in the EDS system at the end of treatment. In comparison to the Cr remaining in the ash, the proportion removed was low (the highest total extraction was 27.5%, Table 2). Fig. 5b gives the amount of Cr removed at each treatment step in the three-step EDS

experiments in Phase III. C-a-c-b is not included in Fig. 5b, because the removal in the three steps could not be separated as the shift in treatment step was achieved by shifting working electrodes in the same cell. Cr extraction largely took place at the second and the third step, and between these two steps, the third step had the highest extraction.

The pH and redox conditions in the steps of the experiments in Phase III, and the most likely ionic species of Cr in the ash suspension are shown in Table 3. These species are found by combining the geochemistry of Cr in terms of Eh-pH diagrams for the Cr-O-H system and the Cr-O₂-water system (Jacobs and Testa, 2005) with the conditions of each treatment step. The Cr extraction by each setup is discussed separately as follows.

4.1.1. Two compartment cell, setup-a

Setup-a in the three-step treatment was for cations removal as well as fast acidification of ash suspension from alkaline (up to 10.7) to pH 4. According to Table 3, Cr(III) is the main source of cationic Cr species in this pH interval (e.g. Cr(OH)_2^+ and CrOH^{2+}). Cr(III) is believed to be the main oxidation state in MSWI residues in general, ascribed partially to the resistance of Cr(III) to oxidation and partially to the reduction of Cr(VI) to Cr(III) in the flue gas in the presence of reducing agents such as SO₂ (Cornelis et al., 2008). However, the amount of Cr extracted to the catholyte using setup-a as the first step was the lowest among the three according to Fig. 5b, which is probably linked to a general low solubility of Cr at pH above 4 (Chen et al., 2017). Even by extending the treatment time using setup-a to 7 days, a low extraction rate was seen in e.g. experiment F-a.

Besides Cr(III), Cr(VI) is another prevalent, stable state of Cr in MSWI residues (Cornelis et al., 2008; Jiao et al., 2016). Though the solubility of Cr(VI) is higher than of Cr(III) (Cornelis et al., 2008), Cr(VI) normally forms anionic species in solution (e.g. CrO_4^{2-} and HCrO_4^-), and once it dissolved, it primarily remained in the ash suspension due to the lack of anion separation using setup-a (Chen et al., 2017).

Setup-a creates an oxidizing environment in ash suspension. Sabbas et al. (2003) indicated that in an alkaline environment Cr(III) may be rapidly oxidized by atmospheric oxygen to Cr(VI), and part of the treatment using setup-a was at alkaline pH; however, high values of redox potential are required. The oxidation of Cr(III) to Cr(VI) in spent chromium solution, when treated in an anode compartment, could occur due to anodic oxidation (Phillips and Swink, 1989). However, anodic oxidation of Cr(III) has associations with electrode material (Frenzel, 2005). To have high electrode potentials, the anode material must have a high over potential for the oxygen evolution reaction (Simonsson, 1997). Lead-based anode (e.g. PbO₂ coated titanium or lead-based alloy) has been used in anodic oxidation such as in Soboroff et al. (1982). The efficiency of anodic oxidation of Cr(III) to Cr(VI) though seems unstable, depending on the process or method how you deploy anodic oxidation (Soboroff et al., 1982). The invention of Soboroff et al. (1982) accomplished the oxidation of Cr(III) to Cr(VI) in anode compartment, and they found that anodic oxidation was relatively independent of current density; however, the current density of 0.1 A/dm² used in the present study was significantly lower than in Soboroff et al. (1982), who used 2.15 A/dm². The possibility and the extend of oxidation of Cr(III) to Cr(VI) also depend on the reactive mineralogy of the material, the pH and the form and solubility of Cr(III) related to oxidation (James et al., 1997). In summary, it must be said that, the oxidation of Cr(III) to Cr(VI) in the MSWI suspension is possible, but to which extent it happens, is difficult to foresee based on current knowledge.

Besides electrodialytic extraction to the catholyte, Cr was also detected on the anode that was placed in the ash suspension, corresponding to 2% - 86% of the total amount of the Cr dissolved in the liquid phase of the suspension. Especially in experiment F-a, the amount of Cr precipitated on the anode was larger than that removed to the catholyte. Electrode deposition in a DC electric field can be due to electrophoretic deposition (moving species: solid particles) and electrolytic deposition

(moving species: ions) (Besra & Liu, 2007). In the present work, Cr might be adsorbed onto the anode and/or co-precipitated with e.g. Pb and Fe that were also detected on the anode.

4.1.2. Three compartment cell, setup-c

Setup-c, which was only used in the three-step treatment, allows simultaneous extraction of anions and cations. Fig. 5b shows that at this step most of the Cr was extracted to the catholyte. In fact, the Cr extracted to the catholyte at this step accounted for most of the Cr extracted to the catholyte by all the three steps. This may be because a significant length of time, e.g. 16.2-17.6 days, was spent on reducing the pH of the ash suspension from 4 to 2 using setup-c, during which more Cr(III) could be dissolved in the suspension, probably in the dominating form of Cr^{3+} according to the Eh-pH diagram (Cornelis et al., 2008). Anionic Cr(VI) (e.g. HCrO_4^- and CrO_4^{2-}) is expected to have low mobility under acidic conditions, which is reflected in the limited transport to the anolyte (Fig. 5b). The ratio of HCrO_4^- to CrO_4^{2-} is a function of pH (Hawley et al., 2004), and at pH between 2 and 4, HCrO_4^- might be the prevailing form of Cr(VI).

Kirkelund et al. (2010) conducted electrodialytic remediation experiments on raw and carbonated MSWI air pollution control residues using an electrodialysis (ED) stack (no electrodes in ash suspension) for 4-21.15 hours. They found a slight increase in Cr leaching from the treated residues, which might be due to the shift from Cr(III) to Cr(VI) during ED treatment (Kirkelund et al., 2014). However, the high kinetic stability of Cr(III) could make it hard for Cr(III) to be oxidized using a three-compartment cell, considering the case for soil washing residue treatment in Jensen et al. (2012). In addition to the oxidation of Cr(III) to easily soluble Cr(VI), another explanation for the increase in Cr leaching in the case of Kirkelund et al. (2010) might be the slow extraction rate of Cr during EDS (Pedersen et al., 2005). As aforementioned, Cr in MSWI fly ash is believed to be mainly in the oxidation state of Cr(III), but Cr(VI) is the major concern regarding leaching because of its high solubility at alkaline pH, high toxicity and carcinogenicity. Thus, the leftover Cr(VI) mobilized over

the treatment period after incomplete extraction and the Cr(VI) retaining in the ash might also account for the increased leaching of Cr under alkaline conditions (related to the final pH of the residue after EDS treatment) that favored Cr(VI) desorption.

Nieto Castillo et al. (2008) treated a Cr(VI) contaminated soil (not suspension but static state) using a three-compartment electrodialytic cell under constant-voltage conditions for 7-14 days, and the results showed that over 90% of the Cr removed was found in the anolyte and less than 10% in the catholyte. The migration of Cr towards the catholyte was suggested to be associated with the reduction of Cr(VI) in the soil by reducing agents (e.g. clay minerals and iron oxides) at low pH. Accordingly, the Cr(VI) in the ash suspension, either due to Cr(VI) desorption or as a result of oxidation at the first step in setup-a, might be reduced to Cr(III) in setup-c by reducing agents in the MSWI fly ash such as organic matter, $\text{Fe}^0/\text{Fe(II)}$ and Al^0 at pH 2-4, therefore contributing to the electromigration to the catholyte.

4.1.3. Two compartment cell, setup-b

Setup-b was for anions removal as well as alkalization of ash suspension. The extraction of Cr was very low when setup-b was used alone (C-b). However, the combination of setup-a and setup-b in experiment C-a-b resulted in a more efficient chromium extraction than in C-b-a. This was related to the ash dissolution at low acidic pH in setup-a, which favored the exposure of Cr in the ash sample to the liquid phase. As the pH of the ash suspension increased fast in setup-b, the adsorbed Cr(VI) would be able to desorb and electromigrate to the anolyte. In experiment C-a-b, although the two steps had the same treatment time, Cr primarily electromigrated to the anolyte, which might indicate a lower desorption rate of Cr(III) in setup-a than the desorption rate of Cr(VI) in the pH increasing phase using setup-b. The Cr extraction rate in C-a-b was higher than in C-a-c-b, probably associated with a longer treatment time using setup-b in C-a-b which caused an increase in conductivity at

alkaline pH (Fig. 4b). In addition, the cathode reaction generated OH^- in the ash suspension, and the precipitation of Cr(III) as $\text{Cr}(\text{OH})_3$ could occur.

The presence of cathode reaction in ash suspension creates a reducing environment, which might be sufficient for the reduction of Cr(VI) to Cr(III). However, reduction reaction was not mentioned for example in the case of chromic acid recovery from spent chromium waste solution in Frenzel (2005). Chromate ions can be reduced in acidic solutions, providing excess acid to complete the reaction with reducing agents such as sulfur dioxide, sodium disulfide and ferrous sulfate (Vaughan, 1994). However, the conditions created by setup-b did not seemingly favor the above-mentioned Cr(VI) reduction, such as the alkaline pH. If this reduction occurred, it could only be at the anion exchange membrane where H^+ can be generated by water splitting or at the anion exchange membrane-ash interface; and the reduction efficiency of Cr(VI) in the ash suspension might be affected by both the Cr(VI) reduction rate and its electromigration rate. Furthermore, treating a MSWI fly ash is believed to be more complicated than treating an aqueous waste solution, due to the complicated element matrix in ash.

Larger deposits were seen on the cathode than on the anode when they were placed in the ash suspension. Electrophoretic deposition (EPD) or reduction of metal ions were probably responsible for the cathodic deposition. EPD was likely, as the cathode was wrapped by particles, which could only partially dissolve in strong nitric acid. The particles, which did not dissolve, had a “jelly like” consistency and this consistency of the particles remained after acid digestion and left in the 1:1 nitric acid solution. According to Besra and Liu (2007), the principal driving force for electrophoretic deposition is the charge on the particles and the electrophoretic mobility of the particles in the solvent in electric field. Convection caused by stirring might also contribute to the electrophoresis of colloidal particles. Electrolysis deposition accounted for the disposition of ionic species on the cathode. The Cr found on the cathode corresponded to 11%-77% of the total amount of Cr dissolved in the liquid

phase of suspension in the experiments. Experiment C-b exhibited a higher amount of Cr deposited on the cathode than removed to the anolyte.

4.2. Overall assessment on waste management

Chromium leaching, especially hexavalent chromium, poses carcinogenic human risks. Hawley et al. (2004) reviewed the treatment technologies for hexavalent chromium, and classified them into three groups: (I) reduction of toxicity, (II) destruction and removal, and (III) containment. Electrodialytic treatment provides a way to extract and remove chromium from water-washed MSWI fly ash. Electromigration and other processes such as electrolysis, diffusion (e.g. in C-a-b, C-b-a and C-a-c-b), convection, adsorption/desorption and precipitation/dissolution are involved in the treatment process. In addition, the desorption of both Cr(III) and Cr(VI) can take place and contribute to the overall chromium extraction, depending on the pH and redox potential conditions during a EDS treatment process, which may involve different electrodialytic cells (i.e. setups) arranged into steps. The oxidation-reduction reactions between Cr(III) and Cr(VI) are complicated, and may occur during EDS treatment, but the kinetics in general is believed to be slow (Hawley et al., 2004).

The combination of acidification and alkalization in EDS treatment improved the extraction rate of Cr: mostly likely the extraction of Cr(III) in the acidification phase especially when pH was below 4 and the extraction of anionic chromium mainly in the state of Cr(VI) in the alkalization phase. However, the extraction rate was not higher than 27.5%, and Cr was still largely remained in the ash. First, this is probably related to the low solubility and mobility of Cr(III). In MSWI ash residues Cr(III) can exist in soluble forms such as CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$, as well as insoluble forms such as Cr_2O_3 and FeCr_2O_4 (Hu et al., 2013; Kirk et al., 2002); however, Lima et al. (2008) suggested that Cr was mainly present as oxides in MSWI fly ash and might have low affinity to chloride. Second, this might also be related to the low content of Cr(VI) in MSWI fly ash. Hu et al. (2013) analyzed the total Cr concentration and the Cr(VI) concentration in five MSWI fly ashes collected from five

different incinerators in China using HNO_3 -HF- HClO_4 digestion. They found that the concentration of Cr(VI) was low (varying from 0.48 to 17.42 mg/kg) in comparison to that of the total Cr (varying from 127 to 175 mg/kg); and Cr(VI) as a percentage of the total Cr ranged from 0.4 wt.% to 11.5 wt.%.

Even though EDS treatment (one, two or three-step) influenced the redox potential (Eh) and pH of the leachate, the five treated coarse ash samples had Cr leaching within the limiting value for mineral waste landfill. However, the three-step treated ash W (containing the fine particles) and F (alkaline pH) met the limit for landfill as hazardous material in accordance with Danish regulation BEK nr 252 (2009). The difference in Cr leaching between the coarse and fine fractions indicates that fractionation might be a possible technique to handle or pre-handle MSWI fly ash, and it might be helpful in increasing the possibility of recycling MSWI ash (or the ash treated by other techniques), especially the fraction(s) with low leaching.

5. Conclusion

Three electro dialytic cell setups were investigated, being used individually and/or in series, in order to increase the knowledge about the Cr speciation under different conditions and the possibility for Cr extraction from MSWI fly ash by electro dialytic separation, one technique for MSWI ash residue waste management. Each setup and each setup combination created different pH and redox conditions. The Cr extraction rate was improved by combining the setups to achieve first acidification (especially to pH below 4) and then alkalization. This improvement is related to the different properties of the oxidation states of Cr, mainly trivalent and hexavalent. Acidification enhanced the desorption of Cr(III) and led to the primary extraction of cationic Cr species, and it also enhanced the ash dissolution and the breakdown of the Cr-containing complexes or particles. A fast re-alkalization of the acidified ash increased the desorption rate of anionic chromium species, probably Cr(VI)-dominated, and thus increased the extraction. As the leaching from the coarse and the fine fraction of

the washed fly ash differed, with the lowest leaching from the coarse, size separation might ease handling of this fraction of the ash. In conclusion it must be stated that, Cr is strongly bound in the MSWI fly ash, and the major fraction is not influenced by the prevailing pH and redox conditions in the suspension (in the time span of few days).

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Figure 1: cylindrical electrochemical cell setups with an inner diameter of 8cm (AN - anion exchange membrane; CAT - cation exchange membrane; number of compartment - I, II and III).

Figure 2: the configuration of a three-compartment cell used to form effective setups by shifting working electrodes. Ion exchange membranes: anion (AN) and cation (CAT). E: electrolyte. C: container. P: pump.

Figure 3: The buffer capacity of the washed fly ash: fine fraction $\leq 50 \mu\text{m}$; coarse fraction $> 50 \mu\text{m}$.

Figure 4: Development of pH and electric conductivity in ash suspension.

Figure 5: Chromium extraction and transport during EDS treatment. (a) Distribution of Cr, in %, in the EDS cell at the end of experiment: where Cr dissolved and retained in liquid solution includes electrodes in ash suspension (assumption: ionic Cr species moved and deposited on electrodes), stirring, solvent (water); and (b) Contribution of each treatment step to the total mass extracted.

Table 1: The experimental design (coarse fraction C >50 μm ; fine fraction F $\leq$ 50 μm ; and W unsieved ash)

	Experiment (fraction – setup)	Setup-a (time/day)	Setup-c (time/day)	Setup-b (time/day)
Phase I	C-b	-	-	7
	C-a	7	-	-
	F-a	7	-	-
Phase II	C-a-b	7	-	7
	C-b-a	7	-	7
Phase III	C-a-c-b	3.9 (till pH 4)	17.6 (till pH 2.04)	4
	F-a-c-b	7 (till pH 4.4)	16.2 (till pH 2.01)	4
	W-a-c-b	6 (till pH 3.9)	17 (till pH 2.08)	4

Table 2: The mass balance, mass loss and extraction efficiency of Cr from the experiments, the Cr concentration before and after treatment, and the leaching of Cr from the ash after treatment. Limiting leaching values for comparison: mineral waste class 0 (MA0) 0.36 mg/kg TS; mineral waste class 1 (MA1) 4.0 mg/kg TS; hazardous waste class 2 (FA2) 12 mg/kg TS. (n.d. = not determined; blank space = irrelevant parameter)

	Exp.	Mass balance %	Extraction %	Mass loss %	pH ash	pH leachate	Eh leachate mV	Leaching mg/kg TS	Concentration	
									mg/kg TS before treatment	mg/kg TS after treatment
Untreated					12.2	11.5	186	0.47	113±6	
Washed					10.2	10.8	213	1.44	112±3	
EDS-treated										
Phase I	C-b	96	0.91	3	10.8	10.7	399	1.66±0.27	114±2	111±2
	C-a	90	3.1	24	4.3	5.2	682	0.12±0.01	115±1	125±5
	F-a	109	0.4	26	5.3	5.8	658	0.15±0.03	155±2	219±0.8
Phase II	C-a-b	100	21.9	30	10.4	9.9	424	1.01±0.47	114±2	121±0.8
	C-b-a	98	6.6	32	4.1	5.3	521	0.04±0.04	114±2	143±2
Phase III	C-a-c-b	90	16.0	34	n.d.	8.7	409	0.30	120±5	118±5
	F-a-c-b	98	15.5	53	n.d.	7.5	453	8.67	158±9	245±6
	W-a-c-b	105	27.5	50	n.d.	9.1	430	7.57±5.47	112±3	162±8

Table 3: Experimental conditions and possible ionic Cr species for each setup in the three-step treatment. The underlined ionic mononuclear species could migrate to electrolyte(s) for the corresponding setup. The species in brackets is pH dependent such as the interaction between CrO_4^{2-} and HCrO_4^- .

	pH	Eh change	Ionic Cr (Jacobs and Testa, 2005; Cornelis et al., 2008)		Interface	
			cation	anion	ash and membrane	ash and electrode
Setup-a	acidification $4 < \text{pH} < 10.7/10.4$	increasing	<u>Cr(OH)_2^+</u> <u>CrOH^{2+}</u>	CrO_4^{2-} HCrO_4^- Cr(OH)_4^-	CAT	anodic
Setup-c	$2 < \text{pH} < 4$	possibly slightly increasing (Chen et al., 2017)	<u>Cr^{3+}</u> <u>(CrOH^{2+})</u>	<u>HCrO_4^-</u> <u>(CrO_4^{2-})</u>	AN CAT	no
Setup-b	alkalization $2 < \text{pH} < 9/10.7$	reducing	Cr^{3+} CrOH^{2+} Cr(OH)_2^+	<u>CrO_4^{2-}</u> <u>(HCrO_4^-)</u> <u>Cr(OH)_4^-</u>	AN	cathodic