Electrodialytic upgrading of three different municipal solid waste incineration residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and SO_4

Jensen, Pernille Erland; Kirkelund, Gunvor Marie; Pedersen, Kristine B.; Dias-Ferreira, Celia; Ottosen, Lisbeth M.

Published in:
Electrochimica Acta

Link to article, DOI:
10.1016/j.electacta.2015.06.012

Publication date:
2015

Document Version
Peer reviewed version

Electrodialytic upgrading of three different municipal solid waste incineration residue types with focus on Cr, Pb, Zn, Mn, Mo, Sb, Se, V, Cl and SO_4

Pernille E. Jensen[a,*], Gunvor M. Kirkelund[a], Kristine B. Pedersen[b], Celia Dias-Ferreira[c], Lisbeth M. Ottosen[a]

[a]*Department of Civil Engineering, Brovej building 118, Technical University of Denmark, 2800 Lyngby, Denmark.*
[b] *Department of Chemistry, University of Tromsø, The Arctic University of Norway, Postbox 6050 Langnes, N-9037 Tromsø, Norway.*
[c] *CERNAS, Research Centre for Natural Resources, Environment and Society, Instituto Politecnico de Coimbra, Escola Superior Agrária de Coimbra, Bencanta, 3045-601 Coimbra, Portugal and Materials and Ceramic Engineering Department, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
**Corresponding author: pej@byg.dtu.dk, +45 45252255*

Abstract
Handling of air pollution control (APC) residues from municipal solid waste incineration (MSWI) is a challenge due to its toxicity and high leaching of toxic elements and salts. Electrodialysis (ED) of the material has shown potential for reduction of leaching of toxic elements and salts to produce a material feasible for substitution of cement in mortar. In this work results of 23 pilot-scale experiments (5-8 kg APC residue each) in electrodialysis stack designed to investigate the leaching properties as a function of time and current density for APC residue from semi-dry and wet flue-gas cleaning systems, as well as MSWI fly ash without flue-gas cleaning products are reported. Significant leaching reduction of the critical elements Pb, Zn and Cl was obtained. The final leaching, however, depended mostly on the initial leaching, thus as leaching from fly ash and residue of wet flue-gas cleaning was lower before treatment compared to residues from semidry flue-gas cleaning, both Pb and Zn leaching could be reduced to lower levels in those materials, and they therefore appear more suitable for use in construction materials. The leaching reduction of Zn and to some degree Pb decreased with longer retention times and higher current densities. Cr and SO_4 leaching increased during ED treatment, with lower increase at higher current. Washing or carbonation in combination with ED significantly reduced leaching of Pb and Zn from semidry residue. An indication of a similar effect to carbonation by simultaneous aeration with ED was observed and should be investigated further. While Mn and Mo leaching did not, Se, V and Sb leaching exceeded threshold values in semidry residue. The leaching of V seemed to increase while Se and Sb remained more or less constant during ED treatment.

Key words: Electrokinetics, MSWI, carbonation, fly ash, heavy metal.

1 Introduction
A major challenge of municipal solid waste incineration (MSWI) technology is the residues generated, in particular the fly ash (FA) and air pollution control (APC) residues. In Denmark incineration with energy recovery has long been the chosen strategy for handling of municipal solid waste except for a few fractions like glass, paper, metal and hazardous waste which are sorted out at the source. Around 100,000 t of fly ash and APC residues characterized as hazardous waste are

produced annually [1] and exported to Norway [2] or Germany [3] where they are placed in abandoned mines at controlled conditions. The hazard of the material arises from high amounts of mobile toxic elements - in particular Pb and Zn; and salts - in particular Cl; as well as from trace quantities of toxic organic compounds [4, 5]. Also the high alkalinity (pH 10-12) poses a hazard.

Since the mid 1990'es various methods have been tested for treatment and reuse of MSWI APC residue and some of them patented [4, 6]. The methods can be divided into three categories: (a) separation; (b) solidification and stabilization; and (c) thermal treatment [4]. Advantages and disadvantages of various methods and combinations of methods have been evaluated: the high cost [4], and global warming potential [3] of thermal treatments are documented. In separation processes, aqueous solutions are used to wash/leach out leachable fractions, which in turn results in dilution of the contamination by production of wastewater of at least twice the original material volume [4]. By solidification and stabilization methods the solid mass volume increases significantly, and a lack of efficiency in binding soluble salts has been documented [4]. Utilization of the product in construction material e.g. as substitute of concrete in cement production has been discussed [6], but it is agreed upon that the bulk material requires pretreatment to remove soluble salts prior to eventual reuse in building materials [4, 6, 7]. The current trends on handling of MSWI APC residues are towards recovery of valuable metals from the residues to support a circular resource economy [8, 9], and utilization of the bulk material in construction industry [10-12].

1.1 ED treatment of MSWI APC residues

In line with these trends we developed electrodialysis (ED) for upgrading of MSWI APC residue in a previous work [13] with the aim to extract mobile toxic elements and salts; produce a stable residual bulk material appropriate for use in construction materials [11] and render valuable elements available for recycling. A pilot scale facility was developed, and a first mapping of the effect of different process conditions on the characteristics of treated APC residue from a semi-dry air pollution control system (SD) was made [14]. Primarily salts were extracted, but also the mobile fraction of toxic elements was removed, and the final product showed a significantly reduced leaching of salts and toxic elements [14]. In contrast to washing, the ED method results in a concentrated wastewater-stream of limited volume, which potentially enables recovery of easily separable elements from the stream such as Cl; valuable and/or metallic elements such as Zn, Cu or even rarer and more valuable elements.

The results showed that leaching of As, Ba, Cu, Cl and Na could be reduced from exceeding to meeting Danish legislative values [14]. Cl leaching, however, was not reduced sufficiently and still exceeded the leaching of Cl from certified coal fly ash (CFA) by several orders of magnitude [11]. The high Cl leaching may limit the utilization of the product in concrete, as Cl is harmful for reinforcements as well as it may affect the hydration of the concrete [11]. Likewise leaching of sulfate may be problematic to the properties of cement [11] because, even though legislative limits were met in the SD [14], SO_4 concentration only reduced slightly during ED treatment and was still almost an order of magnitude higher than that of CFA after treatment [15]. Ni and Cd leaching was reduced by ED treatment although not exceeding neither legislative nor CFA values in the original APC residue [14, 15]. Leaching of Cr also met threshold values prior to treatment [14], but during ED treatment leaching of Cr increased; although not enough to exceed neither the legislative nor the CFA values [14]. Nevertheless special attention to the mobilization of Cr should be paid if the material is to be reused in concrete, because Cr(VI) can give eczema, justifying the EU limit for cement of less than 2 mg kg^{-1} soluble Cr(VI) [16]. Leaching of Pb and Zn was reduced several size-orders by ED treatment, however legislative values were not met [14]. Pre-washing of the APC residue with water prior to treatment, was shown to efficiently reduce leaching of Pb and Zn in

bench scale experiments [13], and to prevent clogging during treatment [17]. However this method, apart from introducing an extra treatment step, results in the production of large volumes of wastewater. Leaching of Pb and Zn was reduced even more efficiently in SD pretreated by carbonation prior to ED, and in this case legislative values were met [14]. In contrast, Cr and Cd were mobilized by carbonation, and for Cr enough to finally exceeded regulatory limits [14], thus carbonation prior to ED may be a solution for Pb and Zn, while it seems not to be for Cr. Furthermore an extra treatment step is introduced which makes the treatment more complicated and time consuming. An alternative could be to carbonize the material during ED treatment, which may partly already occur.

Based on the previous findings, the aim of this work was: 1) to investigate whether optimization of the ED method regarding the minimization of leaching of target elements Cr, Pb, Zn, Cl and SO_4 from SD is possible by control of current density and treatment time; 2) to investigate whether by active aeration (simultaneous carbonation) during ED treatment, leaching of Pb and Zn may be reduced as much as by ED treatment preceded by carbonation or washing; 3) to compare the upgrading of SD with FA and APC residue from a plant with Wet Scrubbing System (W); 4) to report results on previously uninvestigated elements (Mn, Mo, Sb, Se and V).

2 Experimental

2.1 Materials

Six batches of SD APC residue (SD1-6) were obtained on different days from the MSWI plant REFA I/S in Nykøbing Falster, Denmark. The residues were a mixture of FA and flue gas cleaning residues from three lines of semidry treatment which were collected in big bags. In lines 1 and 2 the flue gas was treated by simultaneous water sprinkling and lime injection. In line 3 the flue gasses were mixed directly with slaked lime. In all lines activated carbon was also added. Two batches of residue were obtained from the MSWI plant Vestforænding, Glostrup, Denmark. W was a mixture of fly ash and sludge from wet flue-gas cleaning, while FA was obtained after ash silo 5 prior to the mixing with Scrubber liquids. In order to avoid clogging of the ED apparatus, the fraction >1 mm was dry sieved out and only the fraction <1 mm representing 99% of the mass was used in the experiments.

CFA that meets the requirements of EN 450-1: 2012 for reuse in concrete was obtained from Emineral A/S. CFA is a valuable reference material for evaluation of upgraded MSWI residue as it is regularly used as substituent of cement in concrete production. *Accelerated carbonation*, by which reaction with CO_2 and water transforms metal-hydroxides into more stable carbonates, was induced into SD5 by keeping the sample at room temperature under moist conditions for several weeks. Carbonation has previously been observed to reduce leachability of a number of heavy-metals [14, 18, 19] from MSWI APC residue.

2.2 ED experiments

The pilot plant (figure 1) consisted of two major parts: a rack with tanks and pumps and a compartment with the ED stack and the electrical devices as described in [14]. The ED stack consisted of 34 or 50 cell pairs (530 cm^2 active surface area per cell) with Neosepta cation and anion exchange membranes. The spacers were 0.6mm and 5mm thick for the concentrate (30 dm^3 tap water and 0.4 dm^3 7 M HNO_3) and diluate respectively. The diluate spacers were thicker than the concentrate spacers to avoid clogging due to the particles in the APC residue suspension (mixed tap water and APC residue). There were electrode compartments in each end of the ED stack with

electrode clean solution (30dm^3 distilled water and 0.4 dm^3 7 M HNO_3) circulating between them. The electrodes were titanium plates covered by a layer of metal oxides. The flow rates were adjusted in each experiment to maintain overpressure in the diluate compared to the concentrate, with the diluate flow rate always kept at a maximum. The electrode clean solution tank was ventilated for exhaust gases such as chlorine from the electrode reactions.

Sixteen ED experiments were made with SD1-4 (experiments 1-16). One experiment was made with W (17) and two experiments (18-19) were made with FA according to table 1. In addition two experiments were made with carbonized SD5 (experiments 20-21), one experiment was made with SD6 with simultaneous application of pressurized air over the stack (experiment 22), and one experiment was made with pre-washed SD3 according to the following procedure: 8 kg sieved (<1 mm) SD3 was washed with 16 L distilled water, water was decanted, and washing was repeated three times in total. The experiments were designed to test different current densities 0-6 A (i.e. 0-11.3 mA cm^{-2}) and stack residence times up to 3 h, which equaled experimental times of 24 h for the experiments with 34 cell pairs and 16 h for the experiments with 50 cell pairs when running with 80 dm^3 of diluate (residue suspension). The experiments with the highest current density had short (0.8-0.9 h) residence times only, because voltage increased beyond feasible levels. In all the experiments, L/S was kept constant at 10 dm^3/kg with either 8 kg APC residue, and 80 dm^3 tap water when using 50 cell pairs or 5.3 kg APC residue and 53 dm^3 tap water when using 34 cell pairs in the diluate. The only exception was experiment 14 in which 5.3 kg APC residue and 80 dm^3 tap water was used. Current strength, voltage and electrical conductivity in all three tanks and pH in the diluate tank were logged every 30 s during the experiments. 1 dm^3 samples of the diluate were taken for leaching-tests according to table 1. The samples were filtered, and the filtrate dried in an oven at 40°C prior to the leaching experiments. By the end of the ED experiment, the tanks were emptied and samples of all liquids were taken for analysis. Samples of the diluate were immediately filtered through filter paper at normal pressure. The remainder diluate was stored in closed containers until filtrated before element analysis and leaching tests. The filtrate was dried in an oven at 40°C prior to the leaching test. Between each experiment, the pilot plant was flushed with water and acid and rinsed with water to remove APC residue particles from the previous experiment, and the function of the stack was tested with a NaCl solution as diluate to check for any malfunctions prior to next experiment.

2.3 Analytical methods

pH was measured by a Radiometer Analytical pH electrode in 1M KCl at a liquid-to-solid ratio (L/S) of 5 after 1 h of agitation. *Leaching* experiments were made according to DS/EN 12457-1 in batch test at L/S 2 by mixing 10 g of MSWI residue with 20 mL deionized water. The suspension was shaken for 23 h on an end-over-shaker. The suspension pH was measured before vacuum filtration through a 0.45 µm nucleo filter. One subsample was analyzed for Cl and SO_4 on ionic chromatograph (IC) dionex, DX-120 and the other subsample was acidified by addition of concentrated HNO_3 before measurement of cationic elements (As, Ba, Cd, Cr, Cu, Mn, Mo, Na, Ni, Pb, Sb, Se, V, Zn) by inductively coupled plasma atomic emission spectroscopy (ICP-OES) Varian 720-ES, software version: 1.1.0. *Total content* of the elements was also analyzed by ICP-OES after digestion according to Danish Standard DS259 [20] by which 1g of APC residue and 20 mL 7.3 M HNO_3 was heated at 200 kPa (120°C) for 30 minutes. The liquid was thereafter separated by vacuum filtration through a 0.45 µm filter and diluted to 100 mL. *Water soluble content* of Cl and SO_4 was determined by Ion Chromatography (IC) after extracting 10 g of MSWI residue with 50 mL of deionized water overnight.

2.4 Multivariate analysis – PLS modelling

Multivariate analysis has proven to be a useful tool to evaluate results of electrodialytic remediation experiments [21]. In this study SimcaP11 software was used for PLS (projections onto latent structures) modelling in which the X-matrix consisted of the experimental variables and the Y matrix consisted of final concentrations of metals and salts in the treated residue. In order to include the discrete variables in the modelling, they were arbitrarily set to -1 or 1. The quality of the models was evaluated by R2Y, the fraction of the Y-matrix explained by the models, and the predictive power, Q2, an estimate of the reliability of the model calculated by cross-validation. Variable importance in the projection (VIP) plots was used to assess the variable importance in the calculated models. The plots do however not convey the numerical influences of variables, so in order to establish whether a given variable has a positive/negative influence on the model, coefficient plots were used.

3 Results

3.1 Evaluation criteria and initial characteristics

As use of MSWI FA and APC residue in constructions is prohibited in general, no legislative limits have been defined. Limits, however, exist on use of other types of contaminated material in constructions in Denmark [22]. For such materials three categories exist. Category 1 (free use) is defined by a low total content of contaminants, and the limits are shown in table 2. Category 2 (restricted use) and category 3 (severely restricted use) are based on water leachability of the contaminants, and the limits are given in table 3. In tables 2 and 3 the measured total content and leachability from CFA are also given, as well as the legislative values that must be met for deposition as inert or mineral waste [23], in case the residues remain inappropriate for use in constructions. The limits for category 1 use were met by CFA except for slightly exceeded by Cd and Ni (table 2). In contrast, the leachability (table 3) of all the measured elements from CFA (table 3) exceeded legislative limits of category 2 use except for As and Mn, category 3 limits for Cd, Cr, Mo, Pb and Se, and the limit for deposition as inert waste for Cd, Cr, Mo, Pb, Se, Cl and SO_4, while it met limits for deposition as mineral waste for any constituents.

3.1.1 Total contents

In table 2 the total concentration of elements and salts in the untreated APC residue is shown. The SD, W and FA exceeded the category 1 limits significantly for As, Cd, Pb and Zn. For some batches Cu and Ni also exceeded the category 1 limits. For the elements for which no legislative limits have been set, both the SD, W and FA exceeded the content in CFA significantly for Sb, slightly for Mn and Se; while not for Ba, Mo and V. The FA and W in general contained higher amounts of most (As, Cd, Cr, Cu, Mn, Pb, V and Zn) analyzed elements compared to SD although there was variability in the content of elements between the different batches.

3.1.2 Leaching

In table 3 the leaching of the untreated FA, W and SD and pre-treated (washed and carbonized) SD is shown. All regulatory limits were exceeded for Cl and Pb in all batches including those for deposition as mineral waste. W, however almost met the regulatory limit for mineral waste for both elements. Further, for Zn and Ba category 3 limits were exceeded by all SD batches and for Zn also W and FA. Compared to CFA, leaching of Pb, Cl, Zn and Ba was high from SD. Also leaching of As, Cu, Sb, Se, V and Na exceeded that of CFA, while Cd, Cr, Mn, Mo, and Ni leaching was lower from SD compared to CFA. For all constituents except Cr and Se, the leaching was higher from SD compared to FA and W: Ba, Pb, Zn and Cl leaching was much lower from FA and W than from SD,

and almost meeting the limits for mineral waste and values for CFA. Washing and carbonation clearly reduced leaching of most elements except Cd, Cr.

3.2 ED Stack treatment progress

In many of the experiments problems with unstable hydraulics was observed. This meant that liquid was transferred over the membranes from the concentrate to the diluate (the APC residue suspension) in large quantities, and new water had to be added to the concentrate. This again meant that concentration of the elements and salts in the concentrate solution was partly hampered. Salt precipitations in the pump, tubes and stack on the concentrate side occurred as the experiments proceeded and hampered liquid circulation if pH was not kept below 2, which was therefore done by addition of HNO_3. At 6 A (11.3 mA cm^{-2}) the resistance over the stack increased and the output potential difference increased to the limit of the power supply, why these experiments had to be terminated after a shorter retention time than initially planned (the actual retention times are given in table 1). The output potential difference also increased beyond feasible values for treatments at 4A (7.5 mA cm^{-2}). An example of this behavior is shown in figure 2 a). The pH decreased slightly during treatments with a maximum decrease around 1 unit. Examples of the pH development are shown in figure 2 b).

3.3 Total contents after ED

The total content of the elements after ED treatment of SD is shown in figure 3a and b, FA in figure 3c and d; and W in figure 3e and f. The values given for untreated APC residue are average and standard deviation for all used batches, and the values given for ED treated material are average and standard deviation for all ED treated materials regardless of batch, treatment time and current density; only control experiments with no applied current and experiments with washed, carbonized material or applied pressurized air have been omitted. In general the content of the analyzed elements increased by ED treatment of SD and W while it decreased by ED treatment of FA. Only exceptions are Cd and Sb in the FA, which increased, and Ba and V in W which decreased. This effect may be attributed to the higher content of soluble salts in the SD and W, giving a higher overall solubility, and leaving the less soluble elements at higher concentrations in the treated material. In particular Zn, Cu and Mn appeared less soluble than the average material in the SD and W. For some elements the standard deviation increased after ED treatment while for others it decreased, showing that the ED treatment leaves a material with approximately the same heterogeneity as the original one.

In figure 4 the influence on total contents of pre-carbonation, pre-washing and aeration combined with ED of the SD is illustrated. For all elements the carbonation reduced total content of the investigated elements due to the uptake of CO_2 from the air, and thus mass increase of the material. After ED treatment, however, the total contents increases again, and in most cases to above initial values. As for the non-carbonized SD, in particular Zn, Cu and Mn increased by ED. The total content of the batch (SD6) which was used for the aeration experiment was in general high compared to the other batches, and the total content of in particular Cu and Zn increased even more during the aerated experiment (22). Washing affected the total contents of most elements only little, but by the following ED treatment content increased similar to when carbonized and ED treated.

3.4 Metal leaching after ED treatment of SD APC residue

The leaching after each ED treatment of SD can be seen in table 4. In all experiments leaching of As was reduced to below 20 µg dm^{-3}, i.e. within the category 3 limit for use in constructions and the limit for deposition as inert waste. Likewise leaching of Ba was reduced in all experiments except from experiment 16 to below 3.5 mg dm^{-3} which means below the category 3 limit for use in

constructions and the limit for deposition as inert waste. The high leaching of Ba after experiment 16 was probably due to the extremely high initial leaching of Ba from the batch used for this experiment. Cd leaching remained below 20 µg dm^{-3} after all treatments, i.e. well below threshold limits and also below that of leaching from CFA. Cr leaching in general increased slightly by ED treatment, but remained below threshold limits and well below the leaching of Cr from CFA in all cases except experiment 6, in which the leaching exceeded the category 3 limit for reuse in constructions slightly, but not that of leaching from CFA. Cu leaching was reduced to below 150 µg dm^{-3} after all ED treatments thus well below threshold limits and only slightly above the leaching of Cu from CFA. Ni leaching remained or was reduced to below 20 µg dm^{-3} in most experiments, however in one experiment (15) Ni leaching increased to values above the limit for reuse in constructions and that of leaching from CFA. Leaching of Pb, Zn, Cl and Na was reduced significantly in all experiments. In some cases Zn (experiments 14 and 15) and Na (experiments 1-7) leaching was reduced to below threshold values and even below the leaching from CFA for Zn in experiment 15. In most experiments, however, leaching remained above threshold values for the two elements, which was also the case for Pb and Cl in all experiments. SO_4 leaching remained below threshold limits and close to the leaching from CFA.

3.4.1 Leaching of previously unreported elements (Mn, Mo, Sb, Se and V)

Mn leaching from SD remained below 20 µg dm^{-3} after all treatments, i.e. well below threshold limits and also below that of leaching from CFA. Mo leaching was only reduced slightly but remained well below the leaching from CFA, while still exceeding the limit for deposition as inert waste. Sb leaching remained unchanged, and well above the leaching from CFA and the limit for deposition as inert waste. Se leaching exceeded the category 3 limit for reuse in constructions and level in CFA after most treatments. V leaching also exceeded that from CFA.

3.4.2 Leaching of Cr, Pb, Zn, Cl and SO_4 from SD APC residue as function of current density and treatment time

Leaching of Pb, Zn, Cr, Cl and SO_4 is illustrated in figure 5 as a function of time for experiments 8-12. Lead leaching was reduced from 334 mg dm^{-3} to 5-10 mg dm^{-3} during the first 0.4 h independently of current density (figure 5a). This effect must primarily be an effect of the removal of immediately soluble lead compounds, and may take place at an even shorter time-scale as no sampling was made before this point of time. Even beyond the first 0.4 h, Pb leaching remained rather constant around 5-10 mg dm^{-3} for all experiments. Leaching increased again during post experimental storage of the diluate, particularly for the 0 A, 1A and 2 A experiments to14-18 mg dm^{-3} (results not shown in figure), while the reduced leaching seemed to be more permanent in the 4 A and 6 A experiments, which remained at approximately 6-11mg dm^{-1}. Thus the short treatment at 6 A resulted in lower permanent leaching than longer treatment at lower current densities. Leaching, however still exceeded the legislative limit by at least 10 times.

Zn leaching also reduced significantly during the first 0.4 h of the experiments from 25 mg dm^{-3} to around 1-4 mg dm^{-3} (figure 5b). The development for Zn seemed to be more dependent on current density, with the lowest reduction obtained in the 0 A and 1 A experiments. Further, no significant change in leaching during post experimental storage was observed for Zn. Although somewhat unstable during time, the highest reduction occurred in the 2 A experiment, which, at several points was below the legislative limit of 1.5 mg dm^{-3}, and which also had the lowest permanent reduction to 2.6 mg dm^{-3} which is very close to the legislative limit, and might well be acceptable.

In contrast to Pb and Zn, Cr leaching (figure 5c) increased significantly during the first half hour of treatment from 63 µg dm^{-3} to 600-1,000 µg dm^{-3}. Following, the leaching remained at that level,

with a tendency towards higher leachability after experiments with lower current density. During post experimental storage of the diluate, the leachability however decreased again to the original level (100-400 µg dm^{-3} in all five experiments).

Cl leaching reduced during the first 0.8 h of the residence time in all experiments (figure 5d). Like Zn, also Cl reduction appeared to depend on current density as the highest reduction was obtained in the 4 A experiment, followed by the 6 A experiment. The only experiment which reached a leaching below the regulatory limit was the 4 A experiment after 0.3 and 0.8 h, however leaching increased again during further treatment to values resembling those of the remainder experiments. During post experimental storage of the diluate the Cl leaching increased to around 20 g dm^{-3} for the experiments with 0-2 A while it remained at 8 g dm^{-3} in the 4 A experiment. The lowest permanent leaching was obtained in the 6 A experiment: 5 g dm^{-3}, well below the initial value and just above the legislative value of 3 g dm^{-3}, however still several size orders higher than leaching from CFA.

Like Cr leaching, SO_4 leachability increased during the first half hour of the experiments, although only slightly, and then remained rather constant during all experiments at 1000-1400 mg dm^{-3}.

Leaching before and after ED treatment is illustrated in figure 6. Average leaching from SD increased for Cr and slightly for SO_4. While Pb and Cl on average had slightly higher leaching reduction with no current applied and Zn leaching on average was the same with and without current applied, the standard deviation after ED treatment was much higher after ED, suggesting that experimental conditions has an effect on those three elements, and illustration how low leaching could be obtained in some experiments. Similar trends were observed for FA and W, with the exception that Cr leaching increased even more, while SO_4 leaching reduced significantly.

Figure 6 also illustrates how carbonation significantly reduced Pb and Zn leaching and further reduction was obtained by subsequent ED treatment to obtain values below threshold limits. Carbonation also induced enhanced mobilization of Cr while it did not affect the mobility of the remainder elements significantly. Simultaneous aeration with ED treatment also induced an enhanced reduction of Pb and Zn leaching to levels below those obtained by ED treatment alone despite the fact the batch used had the highest initial leaching. Again the leaching of the remainder elements was not affected. This suggests that simultaneous aeration induces carbonation as aimed for. An advantage of this treatment was that Cr leaching did not increase significantly. Pre-washing also reduced mobility of Pb and Zn significantly in particular after subsequent ED treatment. For Zn final leaching was as low as after carbonation. Leaching of Cl was, however, not affected by the prewashing, and the final leaching remained at the same level after any treatment, which is surprising and is most likely due to the fact that the stack system was very difficult to clean between experiments and that salt precipitates were been left in the system between experiments.

In table 5 it is illustrated how SD reached leaching behavior similar to or lower than CFA by combine carbonation and ED except from Cl, while FA and W reached levels almost as low as CFA by ED alone.

Multivariate analysis of the results (figure 7) revealed fairly good models for Pb, Zn and SO4 (R2Y: 0.43-0.78; Q2: 0.32-0.75) while the PLS models for Na and Cl were poor (R2Y<0.3 and Q2 around 0). The models for Na and Cl are hence not viewed as good enough to evaluate effects of variables on the leaching of these two components. Again this is most likely due to the salt precipitation in the stack. The PLS models for Pb, Zn and SO4 were however adequate for assessing the influence of variables on the treatment.

The first calculated PLS model was based on the data of experiments without any prior treatment and thus was used to evaluate the influence of the initial batch concentrations, current density, retention time and pH. As is illustrated in the VIP plot (figure 7a), the initial concentrations of the salts and heavy metals by far have the highest influence on the final leaching concentration with higher initial leaching resulting in higher final leaching. The type of batch hence was more important for the efficiency of the treatment than current density and retention time of which current density had the highest effect.

A second PLS was calculated to evaluate the influence of pre-washing (not enough samples were available to include the experiments with carbonation and aeration in the statistical analysis), including the non-treated batches as reference. The VIP values (figure 7b) showed that pre-washing had the highest influence on the final concentrations of the three components. Further evaluation of the PLS model, by applying coefficient plots, revealed that pre-washing significantly decreased the final concentration.

Interestingly, the VIP plots illustrated that the influence of current density and retention time vary depending on the element, generally the trend appears to be similar for Pb and Zn. Further evaluation of the models in Simca revealed that the final leaching concentrations decrease with longer retention times and higher current densities.

4 Discussion

4.1 Leaching from SD MSWI APC residue

The reduced leaching of As, Ba and Cu by ED treatment from exceeding the legislative limit (category 3) to meeting it was consistent with previous observations [14], although in a single incident this was not the case for Ba for batch (SD4) with significantly higher initial concentration than the remainder batches. In contrast to the earlier findings [14], Cl was not reduced sufficiently to meet legislative values in any of the present experiments. This was observed despite the fact that the initial Cl leaching was similar to or below that found in the batch used in the earlier work. Likewise Na was reduced sufficiently to meet legislative values only in experiments 1-7, and not in experiments 8-16. The higher leaching of Cl and Na may indicate that the observed precipitation of salts in the stack system, pumps and pipes is not completely avoided by pH control, and that salts are not rinsed out completely between experiments in the extensive rinsing procedure between experiments. It indicates that the stack treatment system may not be a practically feasible solution for treatment of a solution as high in particulate matter and salts. As also previously observed [14], SO_4 remained below the category 3 limit and within the level of CFA leaching in all batches and experiments. It was however documented in the present work that the ED treatment has no influence on SO_4 leaching and that the treatment cannot be optimized towards lower SO_4 leaching, in addition, however, higher levels of leaching from CFA was documented in this work than in the previous [15], and the SD SO_4 leaching seems to be within the level of CFA, and must thus be acceptable from the point of view of use in concrete. In line with previous findings [15], Ni and Cd leaching did not exceed threshold values neither before, nor after ED except for one experiment. Cr also did not exceed the legislative limit and previous results [15] were verified in that the leaching increases by ED treatment. In this work however, it was also observed that the leaching reduced again during post treatment storage, possibly due to oxidation and reduction reactions between Cr(III) and more mobile oxyanions of Cr(VI). It was also shown that the increased leaching is less significant when higher current densities are applied as opposed when no current is applied, and that Cr leaching remains below that from CFA on a general basis, which indicates that Cr leaching will

not be an obstacle for use of SD in constructions. Pb and Zn leaching was reduced significantly in this work as in previous work [15]. In addition in this work, the reduction was shown to be partly dependent on current density in particular for Zn with higher reduction at higher current densities. In a few cases Zn leaching was reduced to below threshold values in SD by ED alone, which shows that optimization of treatment conditions may possibly result in Zn leaching levels acceptable for use of the material in constructions. This is however not the case for Pb which remained at a level 10-100 times the threshold in ED treated SD, which seems to be the biggest hindrance for use of the material. The present results further confirm that carbonation and pre-washing significantly reduces Pb and Zn leaching, while it increases Cd and Cr leaching. Cr leaching was, however, increased to a smaller degree than earlier observed, and partly reduced again by ED treatment, which is in opposition to the earlier findings, although subject to uncertainty shown by the high standard deviation (figure 7a). In addition the present work indicates that aeration simultaneous with ED treatment infers reactions similar to pre-carbonation and suggests that carbonation and ED can be made in a single step process. This should be investigated further. The weak dependency of ED results on current density and treatment time is contrary to previous results on ED treatment of contaminated soil [24-26] and sediments [27] , which emphasized the necessity of optimization of those parameters, which is thus in fact surprising. Also, compared to previous results [13, 28], leaching observed from raw, water pre-washed, acid-pre-washed and acid-treated ED treated SD was significantly lower for especially Pb but also Zn than what was found in the present work. Those previous experiments, however, were made in different setups, and all had a much longer retention-time, showed larger pH-decrease during treatment (below pH 8), and had much lower initial leaching, thus direct comparison is inappropriate.

4.2 Content and leaching of Mn, Mo, Sb, Se and V

The fate of the elements Mn, Mo, Sb, Se and V during ED treatment had not been investigated in the earlier works. No legislative value exists on the total content of these elements. Sb content was high in the MSWI residues compared to CFA (several hundred times higher), while the leaching was one size order higher, and not reduced after ED treatment. The Mn content was on average double/three times the content in CFA in SD and FA, respectively, but the leaching was lower than that from CFA and remained low after ED treatment. The Se content and leaching was approximately the same as in CFA, and the leaching seemed to remain constant during ED treatment. Both the Mo and V content and leaching were in general lower in the MSWI residues than in CFA, but V leaching seemed to increase during ED. Thus there were no signs that Sb and Mo formed mobile oxyanions during treatment such as they might be expected to [29], but V may just as Cr is suspected to do.

4.3 Leaching from FA and W

Wet, dry and semi-dry systems are widely used throughout Europe [30]. A compilation of 352 MSWI in Europe (based on the results presented by [31, 32] showed that approximately 55% of European incinerators have APC residues from dry or semi-dry systems. In some countries however, more than 50% of incinerators use the wet flue gas cleaning system, and such is the case with Austria, Czech Republic, Germany, the Netherlands, Denmark, Norway, Sweden and Switzerland. In the United States wet scrubbers are not as common as in Europe [32].

Significant changes have occurred in the incineration sector over the last 20 years. In some countries, such as Sweden, the requirements set by the authorities are more stringent than the EU emission requirements [33] Wet flue-gas cleaning systems generally offer an advantage with respect to the emission levels of air pollutants [30] and currently there is an emerging trend in the incineration sector to upgrade from dry and semi-dry to wet, in countries such as Denmark, most

probably driven by legislation. Our results suggest that upgrading and use of FA and APC residues from wet systems is more feasible than upgrading of residues from SD systems from an environmental point of view, because SD systems produce residues with higher salt content and higher mobility of toxic elements.

5 Conclusion

The residues before treatment presented excessive leaching of some components, exceeding regulatory limits (threshold levels). More specifically, leaching of As, Ba, Cl, Na, Pb, Sb and Zn exceeded threshold levels in most batches. Cu and Se leaching exceeded maximum threshold values for some batches, while Cd, Cr, Mn, Ni and V did not. For all elements leaching was significantly lower from FA and W than from SD. By ED treatment leaching of As and Ba was reduced to below threshold values. Cd and Mn leaching remained below threshold values, and while Cr and Ni leaching increased, they also remained below threshold values. Leaching of Se , Sb and V remained rather constant above the level in CFA. Pb, Zn, Cl and Na leaching reduced significantly by ED, however in most (for Zn and Na) or all (for Pb and Cl) cases not sufficiently, to stay within regulatory limits. Final leaching depended primarily on initial leaching, thus leaching from W and FA could be reduced to lower levels by ED than leaching from SD, and use of W and FA residues in construction materials appear more feasible than use of SD residues. Zn , Cr and to some extent Pb leaching also partly depended on current density, and for all three elements lower leaching was observed for higher current densities. Cl and Na leaching reduction was hampered by buildup of salt precipitates in the stack. The most significant leaching reduction for Pb and Zn from SD was obtained after both carbonation and ED. Pre-washing also resulted in improved leaching reduction and simultaneous aeration and ED treatment indicated effects similar to pre-carbonations, which should be investigated further.

Acknowledgements

The Danish EPA is recognized for funding of the work thorough the Eco-innovation program.

Reference List

[1] Miljøstyrelsen. Affaldsstatistik 2012. 2014. Report No.: MST-7761-00562.

[2] G.Okkenhaug, G.D.Breedveld, T.Kirkeng, M.Lægreid, T.Mæhlum, J.Mulder. Treatment of air pollution control residues with iron rich waste sulfuric acid: Does it work for antimony (Sb)? Journal of Hazardous Materials 2013;248-249:159-66.

[3] T.Fruergaard, J.Hyks, T.Astrup. Life-cycle assessment of selected management options for air pollution control residues from waste incineration. Science Of The Total Environment 2010;408:4672-80.

[4] M.J.Quina, J.C.Bordado, U.Qvarfort, R.M.Quinta-Ferreira. Treatment and use of air pollution control residues from MSW incineration: An overview. Waste Management 2008;28:2097-121.

[5] C.Ferreira, A.Ribeiro, L.Ottosen. Heavy metals in MSW incineration fly ashes. Journal de Physique Iv 2003;107:463-6.

[6] C.Ferreira, A.Ribeiro, L.Ottosen. Possible applications for municipal solid waste fly ash. Journal of Hazardous Materials 2003;96(2-3):201-16.

[7] M.J.Quina, J.C.M.Bordado, Qu., R.M.Quinta-Ferreira. Environmental impact of APC residues from municipal solid waste incineration: Reuse assessment based on soil and surface water protection criteria. Waste Management 2011;31:1984-91.

[8] M.E.Boesch, C.Vadenbo, D.Saner, C.Huter, S.Hellweg. An LCA model for waste incineration enhanced with new technologies for metal recovery and application to the case of Switzerland. Waste Management 2014;34:378-89.

[9] H.Lassesson, K.K.Fedje, B.M.Steenari. Leaching for recovery of copper from municipal solid waste incineration fly ash: Influence of ash properties and metal speciation. Waste Management & Research 2014;32(8):755-62.

[10] M.Keppert, K.Polozhiy. Residual strength of thermally loaded mortars with Municipal Solid Waste Inceineration fly ash used as Supplementary Cementitious Material. Advanced Materials Research 2014;982:114-8.

[11] G.M.Kirkelund, M.R.Geiker, P.E.Jensen. Electrodialytically Treated MSWI Residue as Substitute for Cement in Mortar. Nordic Concrete Research 2014;49:1-16.

[12] M.J.Quina, J.M.Bordado, R.M.Quinta-Ferreira. Recycling of air pollution control residues from miunicipal solid waste incineration into lightweight aggregates. Waste Management 2014;34:430-8.

[13] P.E.Jensen, C.M.D.Ferreira, H.K.Hansen, J.U.Rype, L.M.Ottosen, A.Villumsen. Electroremediation of air pollution control residues in a continous reactor. Journal of Applied Electrochemistry 2010;40:1173-81.

[14] G.M.Kirkelund, P.E.Jensen, A.Villumsen, L.M.Ottosen. Test of electrodialytic upgrading of MSWI APC residue in pilot scale: focus on reduced metal and salt leaching. Journal of Applied Electrochemistry 2010;40:1049-60.

[15] P.E.Jensen, G.M.Kirkelund, L.M.Ottosen, I.V.Christensen, A.J.Pedersen. Opgradering af farligt røggasaffald. Dansk Kemi 2010;91(4):16-9.

[16] EU council. Council directive 2003/53/EC of 18 June 2003 relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement). 17/7/2003. L178/24. 2003.

[17] C.Ferreira, P.E.Jensen, L.M.Ottosen, A.B.Ribeiro. Preliminary treatment of MSW fly ash as a way of improving electrodialytic remediation. Journal of Environmental Science and Health Part A 2008;43(8):837-43.

[18] S.Arickx, T.Van Gerven, C.Vandercasteele. Accelerated carbonation for treatment of MSWI bottom ash. Journal of Hazardous Materials 2006;137(1):235-43.

[19] P.Colombi, A.Bosio, A.Zacco, L.Borgese, N.Rodella, L.Benassi, L.Depero, E.Bontempi. A sustainable technology for Pb and Zn stabilization based on the use of only waste materials: A green chemistry approach to avoid chemicals and promote CO2 sequestration. Chemical Engineering Journal 2014;253:377-84.

[20] Dansk Standardiseringsraad. DS259:2003. Determination of metals in water, sludge and sediments - General guidelines for determination by atomic absorption spectrophotometry in flame/DS259:2003. 2003.

[21] K.B.Pedersen, L.M.Ottosen, P.E.Jensen, T.Lejon. Comparison of 2-compartment, 3-compartment and stack designs for electrodialytic removal of heavy metals from harbour sediments. Electrochimica Acta 2015;doi:10.1016/j.electacta.2014.12.003.

[22] Miljøministeriet. Bekendtgørelse om genanvendelse af restprodukter og jord til bygge- og anlægsarbejder. Bekendtgørelse nr. 1662 af 21. december 2010. 2010.

[23] Miljøstyrelsen. Bekendtgørelse om deponeringsanlæg. BEK nr 719 af 24/06/2011. 2011.

[24] P.E.Jensen, L.M.Ottosen, C.Ferreira. Electrodialytic Remediation of Pb-Polluted Soil Fines (< 63my) in Suspension. Electrochimica Acta 2007;52:3412-9.

[25] P.E.Jensen, L.M.Ottosen, C.Ferreira. Kinetics of Electrodialytic Extraction of Pb and Soil Cations from Contaminated Soil Fines in Suspension. Journal of Hazardous Materials 2006;B138:493-9.

[26] T.R.Sun, L.M.Ottosen, P.E.Jensen, G.M.Kirkelund. Electrodialytic remediation of suspended soil - Comparison of two different soil fractions. Journal of Hazardous Materials 2012;203-204:229-35.

[27] G.M.Nystroem, L.M.Ottosen, A.Villumsen. Acidification of harbour sediment and removal of heavy metals induced by water splitting in electrodialytic remediation. Separation Science and Technology 2005;40(11):2245-64.

[28] G.M.Kirkelund, C.Magro, P.Guedes, P.E.Jensen, A.B.Ribeiro, L.M.Ottosen. Electrodialytic removal of heavy metals and chloride from MSWI fly ash and APC residue in suspension - test of a new two compartment experimental cell. Electrochimica Acta 2015;Doi: 10.1016/j.electacta.2015.03.192.

[29] J.Hyks, T.Astrup, T.H.Christensen. Long-term leaching from MSWI air-pollution-control residues: Leaching characterization and modeling. Journal of Hazardous Materials 2009;162:80-91.

[30] European Comission. Integrated Pollution Prevention and Control Reference Document on Best Available Technologies for Waste Incineration (BREF). 2006.

[31] Haukohl J. ISWA Waste-to-Energy State-of-the-Art-Report - Statistics. 2012.

[32] G.McKay. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. Chemical Engineering Journal 2014;86(3):343-68.

[33] Herrlander B. Novel Gas Cleaning With Integrated Energy Recovery. 2011; 2014 p. 205-8.

*Table 1: List of pilot scale ED experiments. SD = Semi-dry residue, W = Wet residue, FA = Fly ash, Car= Pre-carbonized, Air= aerated during ED treatment, Wash = pre-washed. *S/E = Samples taken by experimental Start and End, 1h/2h/3h= Samples taken by experimental start and end + every, or every 2nd/3rd h.*

Exp.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Batch	SD 1	SD 1	SD 1	SD 1	SD 1	SD 2	SD 2	SD 3	SD 3	SD 3	SD 3	SD 3	SD 3	SD 3	SD 3	SD 4	W	FA	FA	SD 5	SD 5	SD 6	SD 3
Treatment	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Car	Car	Air	Wa sh
Cell pairs	50	50	50	50	50	50	50	34	34	34	34	50	50	34	34	34	50	34	34	50	50	34	50
Time (h)	10	10	10	10	5	10	5	24	6	24	24	16	14. 5	16	10	10	5	8	5	10	10	5	21
Residence time (h)	1.8	1.8	1.8	1.8	0.9	1.8	0.9	3	0.8	3	3	3	2.4	1.8	1.7	1.7	0.9	1.4	0.9	1.8	1.8	0.9	3.5
Current (A)	3	3	3	0	6	3	6	2	6	0	1	4	3	3	3	3	6	3	4-6	3	3	3	3
Sampling of ash*	S/E	S/E	S/E	S/E	S/E	S/E	S/E	3h	3h	3h	3h	2h	S/E + afte r 2h	2h	2h	2h	S/E	2h	1h	S/E	S/E	S/E	2h

*Table 2: Solid content threshold limit according to [18], analyzed concentrations in CFA ([1]Average of triplicates from one batch; [2]Average of triplicates from two different batches), and initial total contents and pH of the used SD, W and FA batches (*Average of two different subsamples of the batch; **Average of three different subsamples of the batch) [mg kg^{-1}] ± Std. dev except Pb and Zn which are in [g kg^{-1}]. Bold values exceed threshold limits.*

	Category 1 [18]	CFA	SD1	SD2	SD3	SD3 Wash	SD4	SD 5	SD 5 Carb.	SD 6	SD average	W	FA
pH	-	12.4	12.2	10.7	11.7		11.9	12.2	10.0	11.7	11.6	10.9	11.8
As	20	14±14[2]	**102**	**104**	**108±72***	**109**	**110**	**134**	**92**	**197**	**134±38**	**193**	**170±118****
Ba	-	1,082±30[2]	392	360	387±18*	458	358	373	330	228	352±63	329	514±252**
Cd	0.5	**1.5**±0.5[2]	**92**	**129**	**146±16***	**132**	**95±9***	**141**	**107**	**181**	**134±33**	**136**	**140±76****
Cr	500	48±3[2]	52	97	104±1*	119	76±3*	101	92	61	82±22	120	150±89**
Cu	500	32±0.2[2]	482	445	**520±1***	**531**	**555±5**	**488**	386	**1,233**	**621±302**	**860**	**863±230****
Mn	-	210±16[2]	**398**	**427**	**382±42***	**472**	**470**	**410**	**392**	**355**	**412±38**	**538**	**666±24****
Mo	-	21±0.2[1]	-	-	26±13*	12	16	-	-	12	15±3	-	31±34**
Ni	30	**36**±7[2]	29	**35**	**32±7***	**32**	**33**	**31**	29	20	**31±6**	<2	**81±47****
Pb	0.04	0.03±0.02[2]	**2.9**	**2.2**	**2.5±0.2***	**2.6**	**3.4±0.4***	**2.5**	**1.6**	**3.4**	**2.8±0.5**	**2.9**	**3.5±1.2****
Sb	-	0.9±1.6[1]	-	-	**651**	**370**	**382**	**-**	**-**	**777**	**603±202**	**-**	**194±46****
Se	-	4.5±5.0[1]	-	-	4.1	4.7	1.6	-	-	**10**	**5±4**	-	<2
V	-	148±2[1]	42	34	44±13	18	42	-	30	15	37±14	52	60±20**
Zn	0.5	0.14±0.07[2]	**13**	**15**	**16±1 ***	**17**	**19±0.3***	**15**	**13**	**19**	**16±3**	**21**	**25±7****

*Table 3: Threshold leaching limits according to [18], analyzed leaching from CFA ([1]Average of triplicates from one batch; [2]Average of triplicates of two different batches; [3]Average of triplicates from three different batches); and initial leaching from SD, W and FA batches (Average of triplicate analysis of one subsample except: *Average triplicates of two different subsamples of the batch). As, Cd, Cr, Cu, Mn, Mo, Ni, Sb, Se, V: [μg dm^{-3}]; Ba, Pb, Zn: [mg dm^{-3}]; Cl, Na and SO_4: [g dm^{-3}]. Bold: threshold values exceeded.*

	Category 2 [18]	**Category 3 [18]**	**Inert waste IA1 [19]**	**Mineral waste MA1 [19]**	**CFA**	**SD1**	**SD2**	**SD3**	**SD4**	**SD 5**	**SD6**	**SD average**	**SD3 wash**	**SD 5 Carb**	**W**	**FA**
pH	-	-	-	-	12.9	11.8	9.8	11.9	12.1	12.0	11.8	-	-	9.0	10,7	12.6
As	8	50	50	200	2.9±1.7[2]	<20*	**59**	**<91***	**94**	**110**	**321**	**146 ±119***	**51**	25	38	<20*
Ba	0.3	4	3.5	15	0.6±0.5[3]	**8 ±2***	**10**	**17 ±5***	**6**	**34**	**60**	**21 ±21***	2	**17**	0.7	0.4 ±0.03*
Cd	2	40	15	300	**62±21**[2]	<20*	<20	<20*	<20	22	<20	<22	<20	**1,860**	<20	<20*
Cr	10	500	100	2,000	**1,136±210**[3]	117 ±128*	128	61 ±2*	25 ±7*	65	44	83 ±58*	345	**925**	432	20 ±0*
Cu	45	2,000	450	12,500	75±21[2]	313 ±84*	592	889 ±397*	339 ±97*	**2,920**	**4,469**	1,551 ±1,734*	23	833	35	23 ±11*
Mn	150	1,000	-	-	123±139[2]	<20*	<20	<100*	<20	22	<20	<22	<20	<20	<20	<20*
Mo	-	-	150	2,500	**1,655±62**[1]	577	-	770	380	-	948	635 ±288*	370	-	-	**2024 ±48***
Ni	10	70	100	2,500	23±26[2]	<20*	<20	<20	28	25	55	<55	<20	<20	<20	<20*
Pb	0.01	0.1	0.1	2.5	**0.9±1.3**[3]	**304 ±24***	**343**	**453 ±168***	**441 ±12***	**535**	**1,107**	**509 ±107***	**22**	**0.6**	**2.6**	40 ±2*
Sb	-	-	10	100	<2[1]	**35**	-	-	**39**	-	**79**	**51 ±24**	**21**	-	-	<20*
Se	10	30	30	150	**47±61**[2]	**265**	-	-	< 20	-	**114**	**<114**	**62**	-	-	**49 ±40***
V	-	-	-	-	75±102[2]	**680**	18	<20	20	-	66	**109 ±107***	<20	-	<20	43 ±55*
Zn	0.1	1.5	1	12.5	0.4±0.4[3]	**7 ±1***	**18**	**32 ±10***	**9.3 ±4.7***	**50**	**55**	**27±21**	**2.3**	0.3	**2.2**	**3.3 ±1.1***
Cl	0.150	3	0.275	5	0.31±0.4[2]	**49 ±0***	**87**	**87 ±3***	**43 ±25***	**88**	**100**	**79 ±20**	**15**	**84**	**6**	**31 ±1***
Na	0.1	1.5	-	-	0.35±0.02[3]	**6 ±2***	**9**	**13 ±2***	**4**	**12**	**12**	**9.1 ±3.3***	**1.9**	**14**	**12**	**14 ±2***
SO_4	0.25	4	0.28	5	0.7±0.7[2]	1 ±0*	1	0.9 ±0*	1.0 ±0.2*	1.3	0.7	0.9 ±0.5*	1.2	0.7	**5.3**	9 ±0.5*

*Table 4: Leaching from SD MSWI APC residue after ED treatment As, Cd, Cr, Cu, Mn, Mo, Ni, Sb, Se, V: [μg dm^{-3}]; Ba, Pb, Zn: [mg dm^{-3}]; Cl, Na and SO_4: [g dm^{-3}].. Different grey shade for different batches. Italic: No current applied. Bold: threshold values exceeded. (Average of triplicate analysis of one subsample except: *Average triplicates of two different subsamples of the batch)*

Experiment	1	2	3	*4*	5	6	7	8	9	*10*	11	12	13	14	15	16
pH	11	11	12.1	*12.2*	12.1	11.2	12.0	11.3 ±0.7*	12.2	*12.1 ±0.1**	12.0 ±0,2	12.0 ±0.1*	12.2 ±0.2*	11.1 ±0.8*	10.2 ±0.2*	11.9 ±0.3*
As	< 20	<20	<20	*<20*	<20	<20	<20	<20*	<20	*<20**	<20*	<20*	<20*	<20*	<20	<20*
Ba	0.7	0.8	0.5	*0.5*	0.7	1.0	0.4	2.6 ±0.2*	650	*1.6 ±0.8**	2.2 ±0.1*	1.7 ±0.1*	1.7 ±0.9*	1.6 ±1.0*	3.0 ±0.5*	**8.5 ±1.1***
Cd	< 20	<20	<20	*<20*	<20	<20	<20	<20*	<20	*<20**	<20*	<20*	<20*	<20*	<20*	<20*
Cr	89	69	125	*39*	48	**554**	443	**386 ±404***	430	*216 ±192**	114 ±76*	129 ±54*	212 ±45*	273 ±42*	**1015 ±339***	151 ±41*
Cu	23	49	<20	*39*	50	<20	<20	34 ±21*	40	*63 ±81**	67 ±47*	65 ±64*	141 ±3*	83 ±79*	32	44
Mn	<20	<20	<20	*<20*	<20	<20	<20	<20*	<20	*<20**	<20*	<20*	<20*	<20*	<20*	<20
Mo	-	-	-	-	-	-	-	658	-	*239*	421	219	211 ±74*	317 ±225*	708 ±81*	249 ±166*
Ni	**307**	<20	<20	*<20*	<20	<20	<20	<20*	<20	*<20**	<20*	<20	<20	<20	72	<20
Pb	**13**	**12**	**14**	***23***	**24**	**12**	**62**	**18**	**6**	***11 ±2****	**14 ±5 ***	**11 ±3***	**21 ±4 ***	**1.5**	**1.0**	**149 ±23***
Sb	-	-	-	-	-	-	-	**40**	-	***35***	**32**	**33**	**61**	**42**	**58 ±32***	**51**
Se	-	-	-	-	-	-	-	**251**	-	***102***	**183**	**117**	25	**104 ±18***	**379 ±441***	317
V	-	-	-	-	-	-	-	**562**	-	***311***	**490**	**397**	**402**	**540**	**662**	**820**
Zn	**1.9**	**4.9**	**2.0**	***4.4***	**4.6**	**3.3**	**1.6**	**2.6**	**3.4**	***3.6 ±1.3****	**3.0 ±1.3***	**3.1 ±1.6***	**3.7 ±0.0***	0.8	0.1	**4.0 ±1.0***
Cl	**3.4**	**3.2**	1.9	***6.8***	**7.0**	**6.5**	**5.1**	**35 ±12***	**5.1**	***14 ±7***	**20 ±0***	**11 ±4 ***	**12 ±1***	**12 ±0***	**16 ±0***	**16**
Na	0.5	0.4	0.4	*0.2*	1.5	1.3	1.0	**7.8 ±2.4***	**1.6**	***2.8 ±1.4****	**5.1 ±1.2***	**3.7 ±0.1***	**2,5 ±0.4***	**2.9 ±0.0***	**3.6 ±0.2***	**11.8 ±1.5***
SO_4	1.3	1.3	-	*1.3*	1.2	1.3	1.4	1.0 ±0.0*	1.2	*1.2*	1.1 ±0.0*	0.9 ±0.4*	1.2 ±0.0*	1.0 ±0.1*	0.9 ±0.0*	1.0 ±0.0*

*Table 5: Leaching after ED treatment of APC from wet flue-gas cleaning (W): 17; Fly ash without flue-gas cleaning products (FA): 18, 19; and ED treated semidry residue (SD) combined with other treatment: Pre-carbonized (20, 21), Aerated (22) and Washed (23). As, Cd, Cr, Cu, Mn, Mo, Ni, Sb, Se, V: [μg dm^{-3}]; Ba, Pb, Zn: [mg dm^{-3}]; Cl, Na and SO_4: [g dm^{-3}]. Bold: threshold values exceeded. (Average of triplicate analysis of one subsample except: *Average triplicates of two different subsamples of the batch)*

Experiment	17	18*	19*	20	21	22	23*
pH	-	10.1±0.1	11.9±0.4	10.6	-	10.5	10.8±0.2
As	37	<20	<29	<20	<20	**58**	<20
Ba	0.5	0.8±0.9	2.6±0.1	0.9	0.6	1.3	1.8±0.6
Cd	20	<20	<20	<20	31	<20	<20
Cr	**1838**	**991±234**	341±146	410	**974**	105	482±183
Cu	<20	37±14	28±25	26	<20	28	57±23
Mn	16	<20	<20	<20	<20	<20	<20
Mo	-	704±76	497±16	-	-	400	691±22
Ni	<20	**<193**	<47	<20	<20	<20	<37
Pb	0.1	**1.8±2.2**	**18±11**	<0.020	0.038	**1.3**	**0.40±0.35**
Sb	**118**	**337±136**	94±58	-	-	**225**	<40
Se	**344**	**<56**	<20	-	-	<20	**<204**
V	-	**135±177**	**264±339**	-	**418**	21	**<527**
Zn	0.4	0.2±0.0	**3.5±2.8**	0.1	0.08	0.8	0.12±0.07
Cl	**5.8**	**14±11**	**20±7**	**14**	**7.1**	**9.5**	**12±0**
Na	**2.8**	**3.6±1.1**	**3.1±0.6**	1.3	-	1.4	**1.8±0.1**
SO_4	1.6	1.9±0.4	1.0±	1.0	0.9	1.0	0.9±0.0

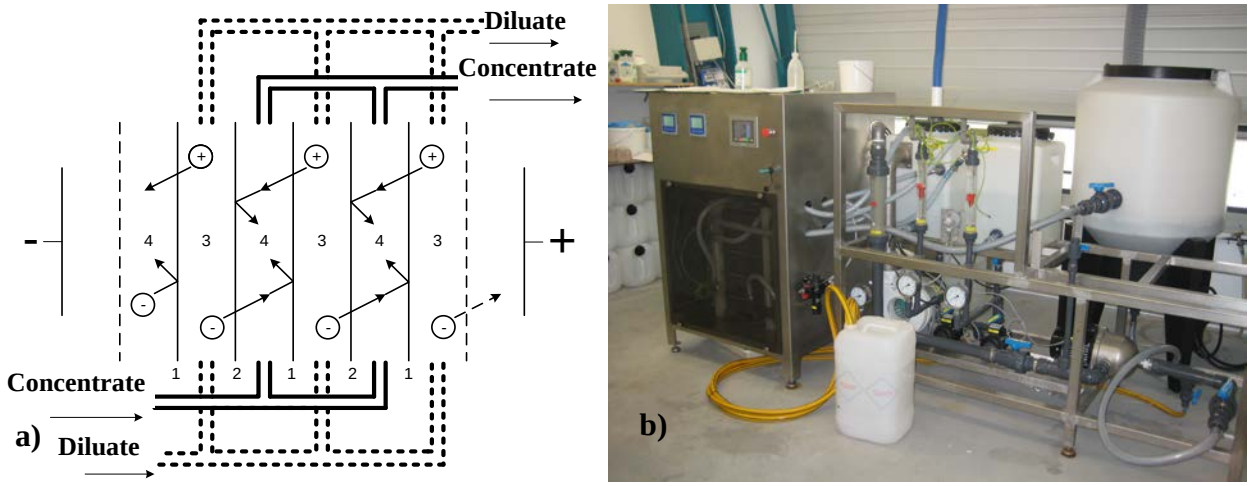

Figure 1: Experimental setup: a) Principle of ED stack, b) the pilot plant in full.

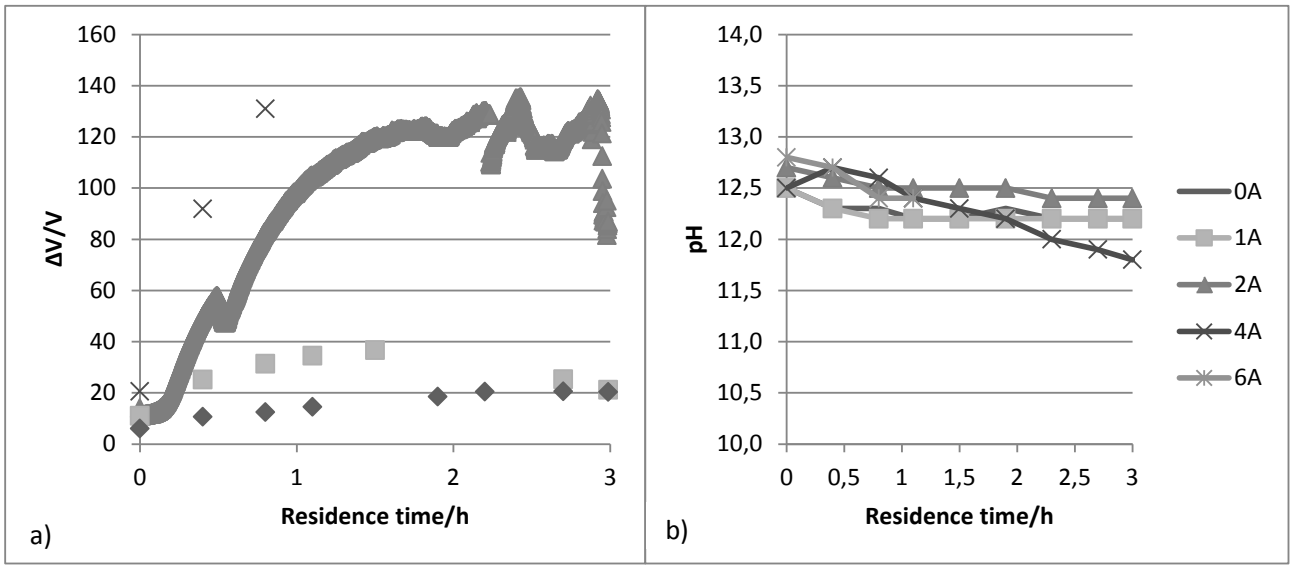

Figure 2: a) Output potential difference for experiments 8, 9, 11, and 12 [V], and b) pH development of diluate (APC suspension) in experiments 8-12.

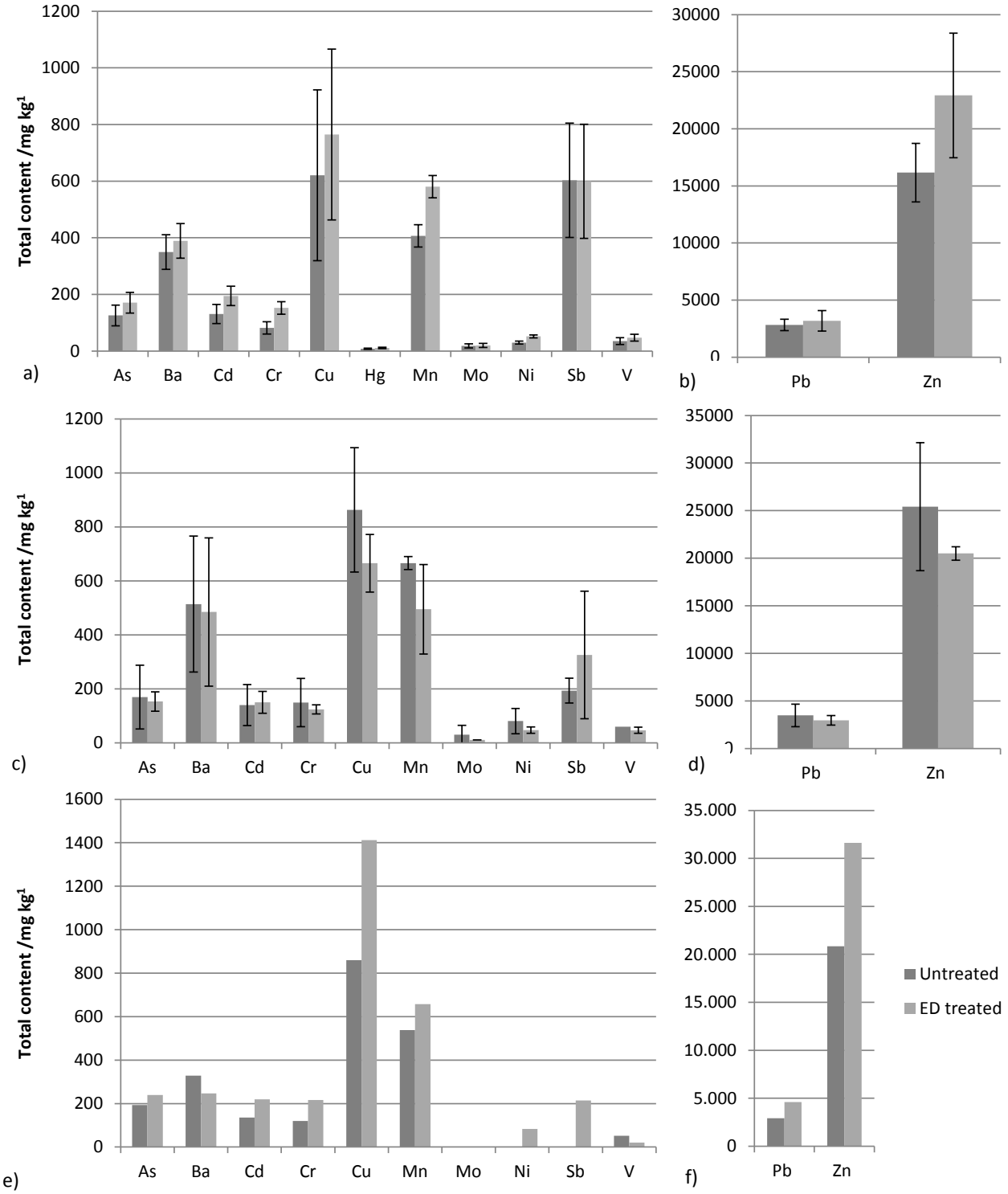

Figure 3 a)-b) total contents with standard deviations of elements in the SD APC before (average of batches SD1-6) and after (average after ED experiments 1-3,4-9,11-16, except Mo, Sb and V which were measured only after experiments 12-16; c) and d) total contents in the FA before and after

ED treatment (average after ED experiments 18-19); e)and f) total contents in the W before and after ED treatment (experiment 17).

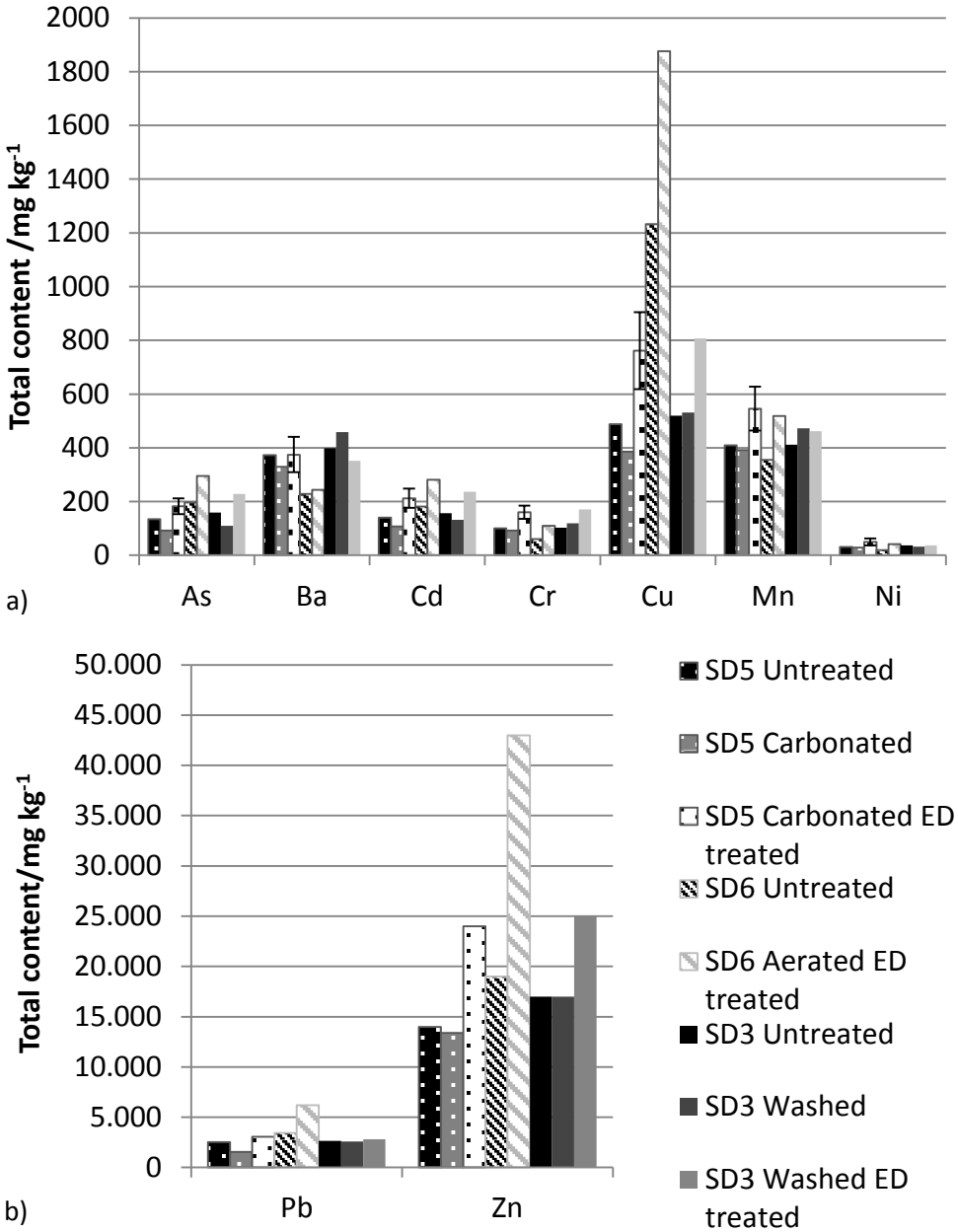

Figure 4 a) and b) Influence of pre-treatments and simultaneous aeration: total contents of elements in the carbonated (average and standard deviation of experiments 20 and 21), aerated (experiment 22) and washed (experiment 23) material prior to treatment and after.

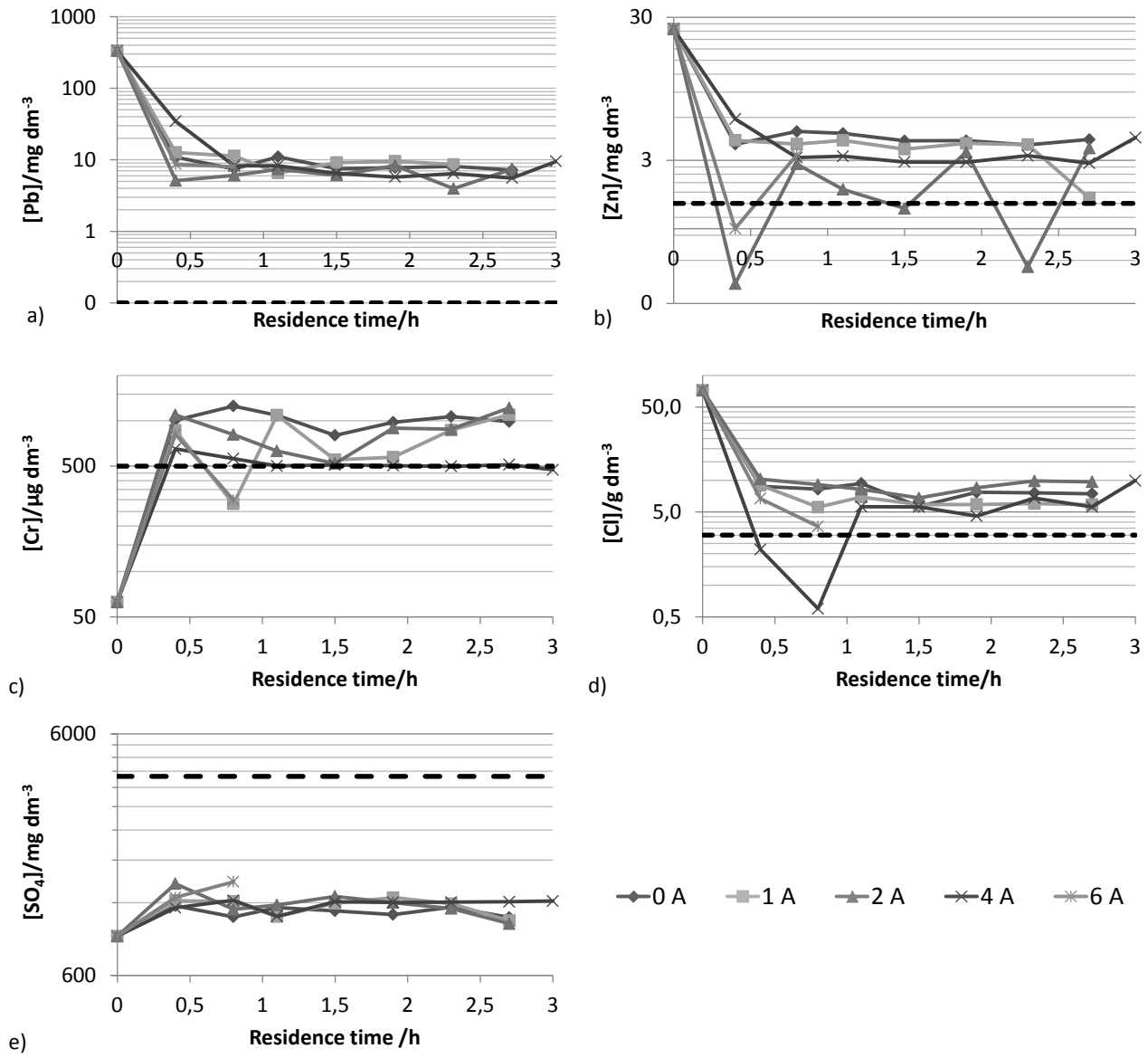

Figure 5: Leaching of Pb, Zn, Cr, Cl and SO_4 as a function of time and current density (experiments 8-12).

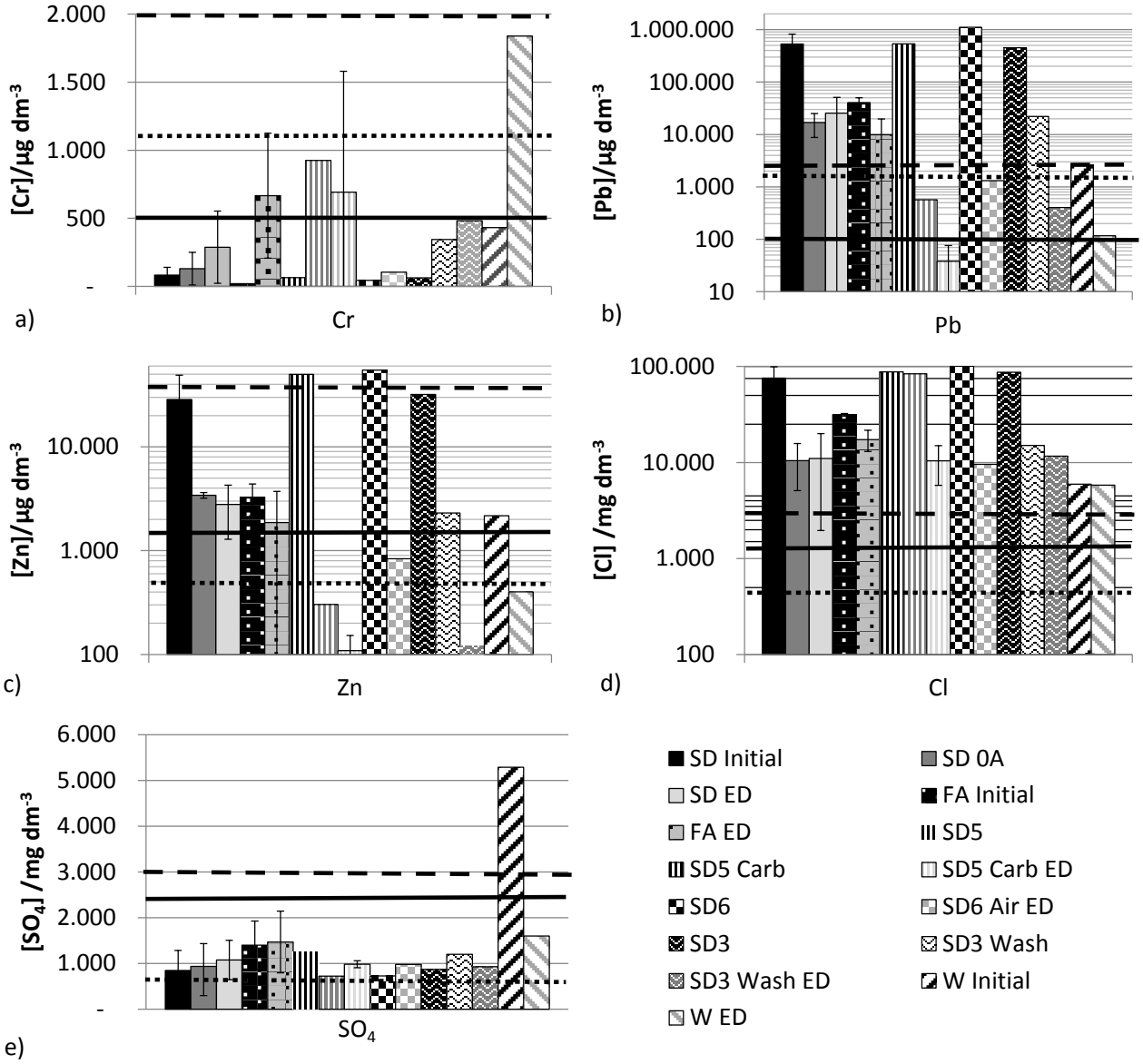

Figure 6: Average leaching and standard deviation before and after ED treatment. SD initial: initial leaching from SD batches 1-6. SD 0A: Leaching after experiments without current applied. SD ED: Leaching from SD after ED treatment (average of experiments 1-3, 5-9, 11-16). FA initial: Initial leaching from FA. FA ED: Leaching from FA after ED treatment (experiments 18-19). Carb initial: leaching from SD5 after carbonation. Carb ED: Leaching from carbonized and ED treated SD. Air initial: leaching from SD 6. Air ED: leaching after ED of SD6 with simultaneous aeration. Solid line =limit category 3 use, dashed line: limit Mineral Waste, dotted line: CFA level.

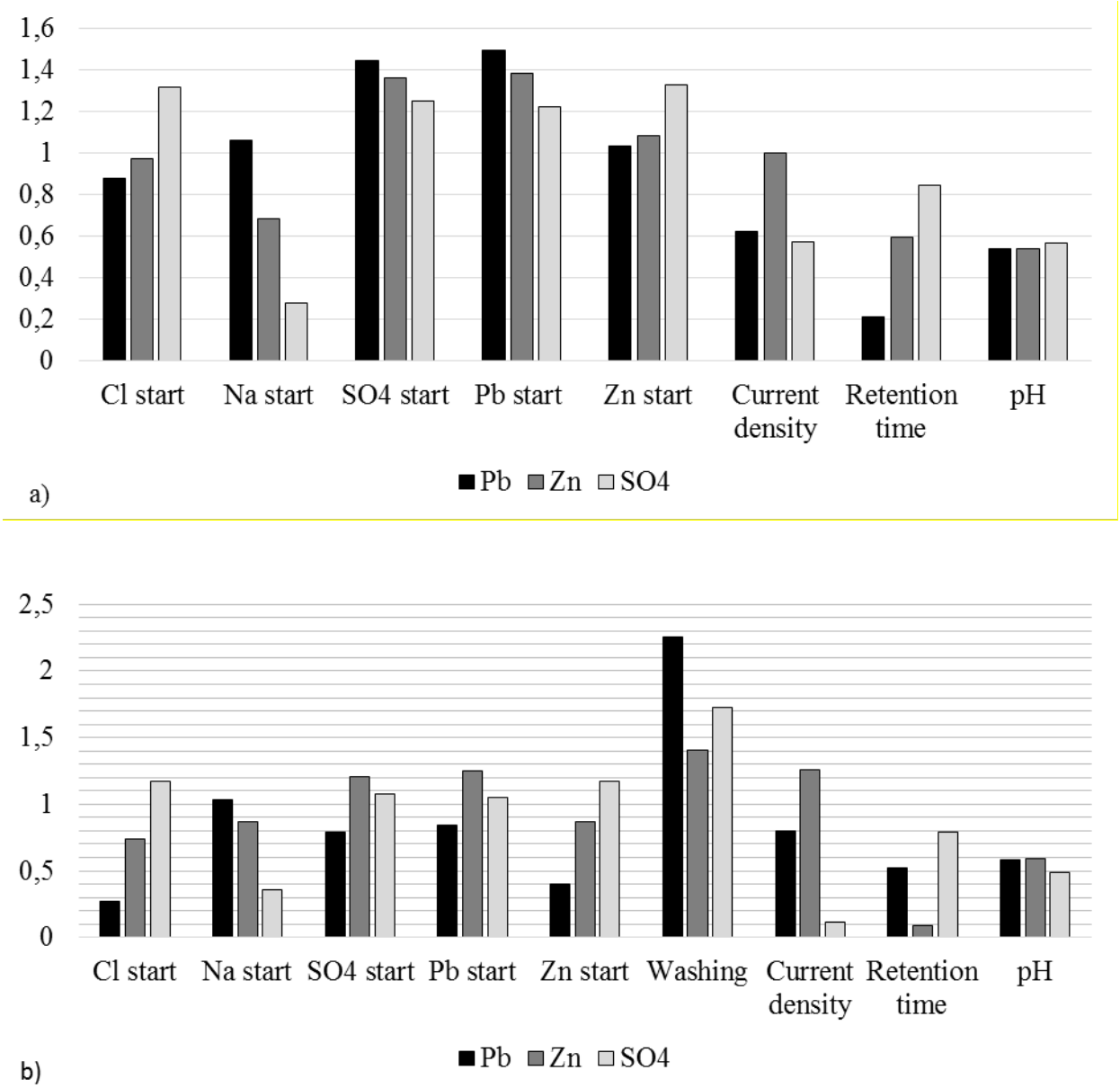

Figure 7: VIP values of a) experiments without any prior treatment, and b) experiments with and without pre-washing. Variables with high VIP values have the highest influence on the final concentrations of Pb, Zn and SO4.