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Electrodialytic upgrading of MSWI APC residue from hazardous waste to secondary resource

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Foreword

This project, "Electrodialytic upgrading of MSWI APC residue from hazardous waste to secondary resource" aimed at development of the electrodialytic technology by optimization of treatment conditions such as treatment time and current density for production of a material suitable for use in the construction sector from MSWI APC residues.

The project budget was 1.875.097DKK, of which "*Miljøstyrelsens tilskudsordning til miljøeffektiv teknologi 2010*" financed 928.433DKK and Department of Civil Engineering, DTU the remainder.

Preliminary encouraging results on the technology had already been reported in a number of scientific papers, and in this project a further development of the technology towards larger scale implementation was sought for.

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The project was accomplished in the period June 2010-March 2015

Conclusion and Summary

The aim of this project was to contribute to the development of electrodialytic treatment (ED) technology of air pollution control residues (APC) from municipal solid waste incineration (MSWI) to obtain maximal leaching reduction by optimization of treatment time and current density for different types of MSWI APC residues (i.e. wet (W), dry (FA), and semidry (SD)). The concept idea was to reduce the mobility of toxic elements and salts by ED enough for the residual product to constitute an environmentally safe resource for substitution of virgin resources in construction material e.g. for substitution of cement or fillers in concrete. We wanted to investigate the robustness of the method understood as the robustness of the stack-setup, and the homogeneity of the upgraded product after ED treatment. Also reporting of leaching of yet uninvestigated elements of concern: Hg, Mo, Sb, Se, V, F; as well as dioxins and oxide content were intended.

We made 23 pilot scale experiments: 16 of them with 4 different batches of SD, one with W, two with FA and four with SD combined with different co-treatments (two with carbonation, one with washed SD and one with aeration). In addition, we made 8 laboratory scale experiments to investigate the influence of four different membrane brands for SD and FA. This investigation became relevant because the pilot scale experiments did not give the results anticipated from previous laboratory scale investigations, which could be due to the fact that different membrane brands were used. Another 24 laboratory scale experiments were made to investigate the influence of different treatment units, as it became apparent that the differences observed between laboratory scale and pilot scale results could not be explained by different performance of the various membrane brands, and might therefor be attributed to the different treatment unit designs.

Since no legislative criteria are set for the use of MSWI APC residues for any purposes, we evaluated the treatment against the criteria of the Danish legislation on use of waste materials for construction purposes *Restproduktbekendtgørelsen* (BEK nr. 1662 af 21/12/2010) [1] and against measured values for certified coal fly ash (CFA) which is used on a regular basis as substituent of cement in concrete in Denmark. For additional perspective we also evaluated against one of several criteria for landfilling of waste in Denmark *Deponeringsbekendtgørelsen* (BEK nr. 719 af 24/06/2011) [2]. Also we have discussed our results concerning the use of the product in concrete against the criteria set by *Bygningsreglementet* [3-5].

According to *Restproduktbekendtgørelsen* [1], our results show that prior to treatment all three residuals exceeded the category 1 [1] total content limits significantly for As, Cd, Hg, Pb and Zn. For most batches Cu and Ni also exceeded the category 1 limits slightly. For the elements, for which no legislative limits are set, both the SD and FA exceeded the content in CFA significantly for Sb, slightly for Mn; while not for Ba, Mo, Se and V. The FA in general contained higher amounts of most (As, Cd, Cr, Cu, Mn, Pb, V and Zn) analyzed elements compared to SD. There was some variability in the content of elements between the different batches, while the variation among different subsamples from a single batch was smaller than between different batches.

After ED treatment the content of the elements of concern had increased in the SD and W while it had decreased in the FA. Only exceptions were Cd and Sb in the FA, which increased; and V in W which decreased. The dioxin content also increased in both SD and FA. This effect may be attributed to the higher content of soluble salts in the SD APC, giving a higher overall solubility, and leaving the less soluble elements at higher concentrations in the treated material. 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 general, as expected the designed treatment is not suitable to extract toxic elements, - longer and more intensive treatment would be necessary to do that, the focus was to reduce leachability of toxic elements.

XRF analysis showed that the untreated SD and FA mainly consisted of Ca and Cl. Main components were also K, Na and S. ED treatment and washing resulted in similar changes by reducing the K, Na and Cl content significantly. XRD analysis showed that the mineralogy for the untreated SD batches differed, apart from the main phases, and the ED treatment resulted in a slightly more mineralogical homogeneous material consisting of mainly calcite and quartz, because easily soluble minerals and salts (in particular KCl and NaCl) were removed, and the Ca mineralogy changed. None of the materials met the mineralogical criteria set by DS/EN 450-1 for use of CFA in concrete, though the electrodialytically treated FA was closer to meeting the requirements than any of the other materials.

From the untreated residues all target leaching values were exceeded for Cl and Pb by all batches according to *Restproduktbekendtgørelsen* category 3 [1]. Further, for Zn, Cu and Ba regulatory limits were exceeded by most batches. Compared to CFA, leaching of Pb, Cl, Zn and Ba was high from SD. Also leaching of As, Cu, Sb, Se and Na exceeded that of CFA, while Cd, Cr, Mn, Mo, Ni and V leaching was lower from SD compared to CFA. For all constituents except Cr, Se, Na and SO_4, 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 (*Deponeringsbekendtgørelsen) [2]* and values for CFA even prior to treatment. Thus residues from semidry flue-gas cleaning appear more reactive and inappropriate for use than pure FA and residue from wet flue-gas cleaning. Leaching of Hg, Mo, Sb, Se, V, F exceeded target values only slightly in a few instances, and potential leaching of these elements which is reported for the first time, is not anticipated to be the major concern for use of the material in constructions.

In general leaching could not be reduced by optimizing current density and treatment time in the pilot scale stack treatment unit, as hypothesized, even though there was evidence of dependency on current density for e.g. zinc, this was not true for most elements, and it was clear that experimental conditions and pre-treatments affected different target elements differently. Statistical analysis of the results revealed that the final pH was the major parameter determining leachability. For most elements and materials, stack ED treatment did not reduce leaching significantly below what was obtained by mere washing with water. Combinations of ED with the other investigated treatments (carbonation, aeration and washing), however reduced leaching significantly below the level obtained by ED, washing or carbonation alone for almost all of the target values. ED and carbonation combined gave the best results. Further development should be made with combined treatments of FA and W, while it is not recommended to use semidry air pollution control systems if the residue is intended for any kind of use. The observed effect of combined ED and aeration appears particularly interesting and should be further investigated.

Both sets of laboratory scale experiments confirmed that lower leaching could be obtained from FA compared to SD. The study of influence of using different membrane brands showed that the brand affects the final leaching from in particular SD, while not so much FA. A more significant effect observed was, however, that lower leaching could be obtained in laboratory scale experiments compared to the pilot scale stack at similar current density and residence times, suggesting that a different setup with a more efficient suspension mechanism could improve the results. The laboratory scale experiments further showed that a lower leaching and compliance with regulatory limits can be obtained with both the 2 and 3 compartment when pH was reduced to below 10. This is in accordance with the pilot scale results, where the lowest leaching from SD was observed in the experiment with the lowest final pH (10.2).

The robustness of the stack setup proved to be very limited. At several occasions during the project, the diluate spacers clogged, and areas with high resistance and heat development evolved. Membranes burned and had to be changed. 4A (7.5 mA/cm^2) was the highest current density which could be applied, but a lower current density should be preferred to reduce high resistance and thus energy consumption.

Tests with replacement of 5 % of cement in mortar by APC residues showed a higher loss of strength by replacement with raw FA than by replacement with raw SD, which showed no reduction in strength at all. In contrast to this the loss of strength was even higher after replacement by ED treated SD than after replacement by ED treated FA. Use of concrete with 5 % replacement of cement by ED treated SD would thus be restricted based on its compressive strength while by replacement of 5 % cement with ED treated FA the compressive strength requirements for the most critical uses were met. The requirement for Cl content of the mortar were also met despite the fact that the Cl content of the residues was higher than allowed by the CFA standards. The leaching of the critical elements Cl, Pb and Zn did not increase by replacement of 5 % cement with FA compared to the reference without residue, while it increased slightly when the FA was treated by ED and also when replacing with SD and ED treated SD.

Konklusion og sammenfatning

Formålet med dette projekt var at bidrage til udviklingen af elektrodialytisk behandling (ED) af røggasrensningsprodukter (APC) fra forbrænding af husholdningsaffald (MSWI) for at opnå maksimal reduktion af udvaskning af giftige elementer ved optimering af behandlingstid og strømtæthed for forskellige typer af røggasrensningsprodukter (Våd (W), Tør (FA) og Semitør (SD)). Hensigten var at reducere mobiliteten af giftige elementer og salte nok til at restproduktet kan udgør en miljømæssig forsvarlig ressource til substitution af jomfruelige ressourcer i byggematerialer, f.eks. som substitution af cement eller fyldstoffer i beton. Vi ønskede at undersøge robustheden af metoden forstået som robusthed af stakken, og homogeniteten af det opgraderede produkt efter ED behandling; ligesom vi ønskede at undersøge udvaskningen af de endnu ikke undersøgte elementer: Hg, Mo, Sb, Se, V, F; samt dioxiner.

Vi lavede 23 pilotskala-eksperimenter: 16 af dem med 4 forskellige prøver af SD, et med W, to med FA og fire med SD kombineret med forskellige sambehandlinger (to med karbonisering, en med forvasket SD og en med beluftning). Derudover lavede vi 8 laboratorieskala-eksperimenter med SD og FA for at undersøge indflydelsen af fire forskellige membrantyper. Denne undersøgelse blev relevant, fordi pilotskala-forsøgene ikke gav de forventede resultater ud fra tidligere laboratorieskala-undersøgelser, hvilket kunne være fordi forskellige membranmærker blev brugt. Endelig blev der lavet en undersøgelse med 24 laboratorieskalaforsøg for at undersøge indflydelsen af forskellige opsætninger, da det viste sig, at forskellene mellem resultaterne fra laboratorieskala og pilotskala ikke kunne forklares ved de forskellige membrantyper, og måske derfor i stedet kunne tilskrives forskellige opsætninger af elektrodialyseenhederne.

Da der ikke eksisterer nogen lovgivningsmæssige krav til kvaliteten af MSWI APC restprodukter for anvendelse til nogen formål, evaluerede vi vores resultater i forhold til kriterierne i den danske lovgivning vedrørende anvendelse af affaldsmaterialer i konstruktioner, dvs. *Restproduktbekendtgørelsen* (BEK nr. 1662 af 21/12/2010) [1], samt målte værdier for certificeret kulflyveaske (CFA), som anvendes regelmæssigt som erstatning for cement i beton i Danmark. For yderligere perspektivering har vi også evalueret i forhold til et af flere kriterier for deponering af affald i Danmark, dvs. fra "Deponeringsbekendtgørelsen" [2]. Ligesom vi har diskuteret resultaterne vedrørende brug af produktet til produktion af beton mod kriterierne anvist i *Bygningsreglementet* [3-5].

Vores resultater viser, at alle tre restprodukter overstiger kategori 1 grænseværdierne i *Restproduktbekendtgørelsen* (BEK nr. 1662 af 21/12/2010) [1] for totalindhold væsentligt for As, Cd, Hg, Pb og Zn før behandling. For de fleste prøver overstiger Cu og Ni også kategori 1 grænseværdien lidt. For de elementer, for hvilke der ingen lovgivningsmæssige grænser findes, overskrider både SD og FA indholdet i CFA væsentligt for Sb, lidt for Mn; men ikke for Ba, Mo, Se og V. FA indeholder generelt større mængder af de fleste analyserede elementer (As, Cd, Cr, Cu, Mn, Pb, V og Zn) i forhold til SD. Der var nogen variation i indholdet af elementer mellem de forskellige prøver, mens variationen mellem forskellige delprøver fra en enkelt prøve var mindre.

Efter ED behandling var indholdet af elementerne generelt steget i SD og W APC, mens det var faldet i FA. Eneste undtagelser var Cd og Sb, som steg i FA, og V der faldt i W. Denne virkning kan tilskrives det højere indhold af opløselige salte i SD APC, hvilket giver en højere samlet opløselighed, og efterlader de mindre opløselige elementer i højere koncentrationer i det behandlede materiale. For nogle elementer steg standardafvigelsen efter ED behandling, mens den for andre faldt. Det viser, at ED behandling efterlader et materiale med omtrent samme heterogenitet som de originale. Dioxinindholdet steg i både SD og FA. Som forventet er den designede behandling altså ikke egnet til at ekstrahere giftige elementer og nedbringe indholdet af disse. Kraftigere behandling af længere varighed ville være nødvendig for at opnå dette. Her er fokus på at nedbringe udvaskningen af giftige elementer.

XRF-analyse viste, at det ubehandlede SD og FA bestod hovedsagelig af Ca og Cl. Andre hovedkomponenter var K, Na og S. ED behandling og vask resulterede i identiske ændringer af de forskellige materialer ved at reducere K, Na og Cl-indholdet signifikant. XRD-analyser viste, at mineralogien for de ubehandlede SD prøver afveg, bortset fra hovedmineralerne, og at ED-behandling resulterede i et mineralogisk lidt mere homogent materiale bestående hovedsagelig calcit og kvarts, fordi let opløselige mineraler og salte (især KCl og NaCl) blev fjernet, og Ca mineralogien ændret. Ingen af materialerne levede op til kravene vedrørende mineralogisk sammensætning angivet i DS/En 450-1 for brug af CFA i beton. Den elektrodialytisk behandlede FA var tættest på at møde kravene.

Fra de ubehandlede restprodukter overskred udvaskningen samtlige grænseværdier for Cl og Pb i alle prøver. Endvidere blev grænseværdier for Zn, Cu og Ba overskredet i de fleste prøver. Sammenlignet med CFA, var udvaskning af Pb, Cl, Zn og Ba høj fra SD. Også udvaskning af As, Cu, Sb, Se og Na oversteg den fra CFA, mens Cd, Cr, Mn, Mo, Ni og V udvaskningen var lavere fra SD sammenlignet med CFA. For alle elementerne undtagen Cr, Se, Na og SO_4, var udvaskningen højere fra SD i forhold til FA og W: Ba, Pb, Zn og Cl udvaskningen var endog meget lavere fra FA og W end fra SD, og overholdt næsten grænseværdierne for mineralsk affald og værdier for brug af CFA. Røggasaffald indeholdende røggasrensningsprodukter fra semitør røggasrensning virker dermed mere reaktive og mindre anvendelige end ren flyveaske eller flyveaske indeholdende røggasrensningsprodukter fra våd røggasrensning. Udvaskning af Hg, Mo, Sb, Se, V, og F overskred kun grænseværdierne en smule i nogle få tilfælde, dvs. ikke med flere størrelsesordener, og udvaskning af disse elementer vurderes ikke at være en stor bekymring for anvendelse af materialet i konstruktioner.

Generelt kunne udvaskningen ikke reduceres ved at optimere strømtæthed og behandlingstid i pilotskala-stakken, som forudsat i vores hypotese, selv om der var tegn på afhængighed af strømtæthed for fx zink: De eksperimentelle vilkår påvirkede udvaskningen af forskellige elementer forskelligt. Statistisk analyse af resultaterne viste, at pH var den afgørende parameter for udvaskningen. For de fleste elementer og materialer, reducerede ED behandlingen i stak ikke udvaskning betydeligt under hvad, der blev opnået ved simpel vask med vand. Kombinationer af ED med de andre undersøgte behandlinger (karbonisering, beluftning og vask), reducerede til gengæld udvaskningen væsentligt under det niveau, som kunne opnås ved ED, vask eller karbonisering alene. ED og karbonisering kombineret gav de bedste resultater. Yderligere udvikling bør derfor gøres med kombinerede behandlinger af FA og W, mens det ikke anbefales at bruge semitør røggasrensning, hvis der er intentioner om at bruge produktet efterfølgende. Den observerede effekt af kombineret beluftning og ED er særligt interessant og bør underøges yderligere.

Begge laboratorieskala-studier bekræftede at lavere udvaskning kunne opnås med FA i forhold til SD. Undersøgelsen af indflydelsen af forskellige membranmærker viste, at brugen af forskellige membranmærker påvirker udvaskningen efter behandling mere for SD end for FA. En mere signifikant observation var dog at lavere udvaskning kunne opnås ved laboratorieforsøg med samme opholdstid og strømstyrke som pilotforsøgene, hvilket indikerer at bedre resultater ville kunne opnås med forbedret suspension af materialet i et andet pilotskala setup end det her anvendte. Laboratorieskala forsøgene viste desuden, at en lavere udvaskning og overholdelse af grænseværdier kan nås med 2 og 3 kammer opsætning selv for SD, når pH under behandlingen faldt til under 10. Dette er i overensstemmelse med observationerne fra pilotskala-forsøgene hvor den laveste udvaskning fra SD blev opnået efter forsøg 15, hvor pH faldt til 10,2; mens pH var 11 eller derover i all andre forsøg med SD.

Stakkens robusthed viste sig at være begrænset. Ved flere lejligheder i løbet af projektet, blev diluatkredsløbet tilstoppet, og områder med høj modstand og varme udviklede sig. Membranerne brændte og måtte skiftes. 4A (7,5 mA/cm^2) var den højeste strømstyrke, som kunne trækkes over stakken, men en lavere strømstyrke bør anvendes for at undgå høj modstand og dermed højt energiforbrug.

Tests, hvor RGA erstatter 5% cement i mørtel, viste et højere tab af styrke ved erstatning med rå FA end med rå SD, som ikke påvirker styrken overhovedet. I modsætning hertil ses et større tab af styrke ved erstatning med ED behandlet SD end ved erstatning med ED behandlet FA. Brug af beton hvor 5 % af cementen er erstattet af ED behandlet SD ville derfor være mødt med restriktioner baseret på betonens styrke, mens styrken, som opnås ved erstatning af 5% cement med ED behandlet FA er tilstrækkelig til at møde kravene for den mest kritiske brug af betonen. Grænseværdien for kloridindholdet i mørtelen bliver ikke overskredet, på trods af at kloridindholdet i asken var væsentligt højere end standarden for CFA forskriver, og udvaskningen af de kritiske elementer Cr, Pb og Zn fra mørtelen var ikke øget i forhold til referencen, når rå FA erstattede 5 % cement, mens den steg en smule når FA var behandlet med ED, ligesom den steg en smule når SD og ED behandlet SD erstattede cement.

Abbreviations

APC	Air pollution control
CFA	Certified coal combustion fly ash
DC	Direct current
DI	De ionized
ED	Electrodialysis
FA	Fly ash from fluegas excluding fluegas cleaning products
IC	Ion chromatography
ICP	Inductive coupled plasma
LWA	Lightweight aggregates
MSWI	Municipal solid waste incineration
REFA	Renovation Falster
SEM	Scanning electron microscopy
SD	APC residue from semi-dry fluegas cleaning (i.e. FA mixed with APC residue)
W	APC residue from wet fluegas cleaning (i.e. FA + sludge from scrubber)
XRD	X-ray diffraction
XRF	X-ray fluorescence

1. Introduction

1.1 Background

During Municipal Solid Waste Incineration (MSWI), waste by-products are generated, one of them is Air Pollution Control (APC) residue, which results from the treatment of the flue gas coming out of the combustion chamber. MSWI APC residues are considered hazardous waste due to their high alkalinity and content of soluble salts and heavy metals [6].

In Denmark all non-recyclable combustible waste is incinerated for energy production, presently producing around 100,000 tonnes of APC residues every year [7]. APC residues consist of a dominant fraction of amorphous material and a minor crystalline mineral fraction constituted by complex elemental mixture of more or less the full periodic table of elements [8]. Various solutions for the handling of APC residues exist in different regions worldwide; most involve inertization by mixing with reagents or other types of waste. Presently, Danish MSWI APC residues are exported for treatment in Norway or Germany, as the APC residues do not comply with the leaching limit criteria for Danish landfills. The current international trends on handling of MSWI APC residues are towards recovery of valuable metals from the residues to support a circular resource economy [9, 10], and utilization of the bulk material in construction industry [11, 12]: Some elements of commercial value such as Zn and Pb are found in the residues at high concentrations compared to the average earth crusts composition, thus urban mining of the residues for those elements may become interesting as virgin deposits become less abundant and accessible. Several applications of the bulk residue material have been mentioned for recovery of APC residues [13], e.g. filler in mortar for cement production. However such use is restricted by functional, environmental and health concerns arising from the content of soluble salts and heavy metals; thus removal of toxic as well as valuable and damaging constituents is necessary prior to use.

For that purpose, electrodialysis (ED) is investigated in this project. In ED, a Direct Current (DC) resulting from an applied voltage gradient is forcing charged ions out of the waste, while ion-exchange membranes strategically placed in the path of the ions, control the flow of contaminants into specific chambers, from where they can be removed [14, 15]. ED has been investigated for treatment of other types of heavy metal contaminated waste such as soil [16-21], biomass ash [22-24], timber waste [25, 26] and mine tailings [27, 28]. In 2002 the suspended ED system was introduced by Pedersen [29], replacing the earlier static cells and thereby allowing for reduced remediation time and energy consumption. In 2010 this system was further developed to approach a conventional electrodialysis stack treatment as close as possible, however with modifications to allow for circulation of the high solids content APC residue suspension. Also, a paradigm shift was introduced in that focus shifted from reducing the concentration of toxic substances to reduction of the leachability/mobility of toxic substances, acknowledging the fact that reduction of the concentration of many of the elements of concern would require at total disintegration of the products [30]. The first of two works on stack ED treatment were on semidry MSWI APC residue from the incineration facility REFA I/S, and investigated the effect of water washing and acid washing prior to ED in a laboratory scale stack setup [30]. Water washing prior to ED resulted in a slightly reduced final leaching for all investigated elements (Cd, Cu, Pb, Zn) to meet target values for Zn in addition to Cd and Cu, which were reduced sufficiently by ED treatment only; while an increased final leaching was observed when acid washing at pH 10 was introduced prior to ED. Introducing acid washing at pH 2 prior to ED reduced leaching additionally compared to water washing, however rendering the utilization of the final bulk mass in construction materials unlikely. The volume reduction was highest when lowering pH to 2 followed by ED (83%), while higher after only ED treatment (63%) than when ED treatment was preceded by water washing or acid washing (pH 10) (57%). The second work on stack ED treatment [31, 32] was made at the same treatment facility used in the present work, and showed reduced leaching of all investigated elements except Cr (i.e. As, Ba, Cl, Cd, Cu, Mn, Na, Ni, Pb and Zn), as well as of SO_4 by ED treatment only. Although reduced by several orders of magnitude, the leaching of Pb and Zn, however still exceeded target-values after ED. Carbonation was also investigated as a pre-treatment to ED [31, 32], and resulted in a further reduction of leaching of Zn and Pb to meet target values for both elements, while the leaching of Cd and Cr increased upon carbonation followed by ED compared to only ED treatment.

Provided leaching can be reduced sufficiently, the upgraded product may be recognized as appropriate for addition to concrete either as filler or even as substitution for cement, which could induce a positive environmental and economic impact not only due to the prevented export and treatment of the residue, but also due to the avoided CO_2 footprint of cement production. The consumption of chemicals and energy for the electrodialytic upgrading should, of course, be taken into account.

1.2 Project goal

The purpose of this project was to continue the development of ED upgrading of MSWI APC residue, strengthen collaboration and knowledge sharing with actors, and evaluate the potential of the technology relative to other relevant technologies.

Original aims:

- Continue the development of the technology to determine maximal leaching reduction as a function of treatment time and current density.
- Investigate the method for different types of MSWI APC residues (Wet, Dry and Semidry).
- Investigate the robustness of the method understood as the robustness of the stack-setup, as well as the homogeneity of the upgraded product.
- Investigate characteristics of the upgraded MSWI APC residues with respect to a number of additional elements: Hg, Mo, Sb, Se, V, F as well as dioxins and oxide content.
- Provide preliminary data for evaluation of the potential of upgraded MSWI APC residue as constituent in concrete.
- Strengthen collaboration and knowledge sharing between university, company and producer of MSWI APC residues.
- Compare results and environmental potential with other methods in the OECD-counties.

Because the results of the pilot scale stack experiments did not give the anticipated results and tools for optimized up-scaling, the two last items were not found relevant; and instead laboratory investigations were made on the:

- Influence of different membrane brands
- Influence of different experimental setups

1.3 National regulation and target values

MSWI APC residues are defined as hazardous material according to Danish legislation (*Affalds-bekendtgørelsen*) [33], and regulative limits e.g. for acceptable contents and leaching of toxic constituents set for the use of residual products in constructions (*Restproduktbekendtgørelsen*) [1] are not valid for this material.

Due to the fine grained nature of the MSWI APC, the use could be e.g. as substituent for aggregates or cement in concrete production or as substituent of clay in bricks. These are not the uses intended for materials covered by the legislation in *Restproduktbekendtgørelsen,* in which the uses are related to construction works. Nevertheless the values set in [1] are considered to be the most appropriate existing legislative limits to consider to put our results into perspective and discuss the possibility of using upgraded MSWI APC residues in construction materials, since no limits exist for resources used as constituents in building materials (except for Cr (IV), which has a limit in concrete according to EU legislation). In table 1 the total content regulative limit for category 1 use (unrestricted use) according to [1] are given. Also given are the total content of elements in certified coal combustion fly ash (CFA), as we have measured it. CFA is used on a regular basis as substituent of cement in concrete production and can therefore also be used to put our results into perspective. As can be seen the content of Cd and Ni in CFA slightly exceeds the limits for category 1 use, despite this it is used on a regular basis in concrete production. This highlights the fact that *Restproduktbekendtgørelsen* does not formally encompass the use of ashes of any kind as constituents in building materials; rather the limits given should be understood as an indication on an acceptable size-order than strict on the use of the ashes.

TABLE 1
TOTAL CONTENT REGULATIVE LIMITS ACCORDING TO [1] AND MEASURED VALUES OF CERTIFIED COAL FLY ASH: [1]AVERAGE OF TRIPLICATES FROM ONE BATCH; [2]AVERAGE OF TRIPLICATES OF TWO DIFFERENT BATCHES.

mg/kg TS	Category 1 [1]	CFA (measured)
pH	-	12.4
As	20	14±14[2]
Ba	-	1,082±30[2]
Cd	0.5	1.5±0.5[2]
Cr	500	48±3[2]
Cu	500	32±0.2[2]
Hg	1	NA
Mn	-	210±16[2]
Mo	-	21±0.2[1]
Ni	30	36±7[2]
Pb	40	31±17[2]
Sb	-	0.9±1.6[1]
Se	-	4.5±5.0[1]
V	-	148±2[1]
Zn	500	137±70[2]

In table 2 leaching limits for category 2 (restricted) and 3 (severely restricted) uses according to [1] are stated together with leaching observed from CFA. For category 2 and 3 uses no total content limits are set. Alternative relevant limiting values to consider are those given for national Danish landfilling (*Deponeringsbekendtgørelsen*) [2]. Here approval of landfilling is given based on a set of limiting values depending on location of the landfill. Apart from leaching of toxic substances at L/S 2, also criteria for leaching in batch tests at L/S 10 as well as in column test (CEN/TS14405) must be met. In this report the limiting values for leaching at L/S 2 for inert and mineral waste to be landfilled at a medium sensitive disposal site (IA1 and MA1) are used as guiding values, and given in table 2. Apart from the compounds given in table 2, DOC and Phenol index is also regulated by [2]. Those compounds are, however, not anticipated to be of any concern for MSWI APC residue as also observed in [34].

TABLE 2
LEGISLATIVE LEACHING LIMITS ACCORDING TO RESTPRODUKTBEKENDTGØRELSEN **[1]** AND DEPONERINGSBEKENDTGØRELSEN **[2]** (BATCH TEST AT L/S 2 L/kg WITH DE-IONIZED WATER - LIMITING VALUES RECALCULATED FROM mg/Kg TO µg/L FOR DIRECT COMPARISON). FOR MEASURED VALUES OF COAL FLY ASH: [1]AVERAGE OF TRIPLICATES FROM ONE BATCH; [2]AVERAGE OF TRIPLICATES OF TWO DIFFERENT BATCHES; [3]AVERAGE OF TRIPLICATES FROM THREE DIFFERENT BATCHES. NA = NOT ANALYZED.

Limit	**Category 1-2** [1]	**Category 3** [1]	**CFA (measured)**	**Inert waste IA1** [2]	**Mineral waste MA1** [2]
As (µg/l)	8	50	2.9±1.7[2]	50	200
Ba (µg/l)	300	4000	600±500[3]	3500	15000
Cd (µg/l)	2	40	62±21[2]	15	300
Cr (tot) (µg/l)	10	500	1,136±210[3]	100	2000
Cu (µg/l)	45	2000	75±21[2]	450	12500
Hg (µg/l)	0.1	1	NA	1.5	25
Mn (µg/l)	150	1000	123±139[2]	-	-
Mo (µg/l)	-	-	1,655±62[1]	150	2500
Ni (µg/l)	10	70	23±26[2]	100	2500
Pb (µg/l)	10	100	900±1,300[3]	100	2500
Sb (µg/l)	-	-	<2[1]	10	100
Se (µg/l)	10	30	47±61[2]	30	150
V (µg/l)	-	-	75±102[2]	-	-
Zn (µg/l)	100	1500	400±400[3]	1000	12500
Cl (mg/l)	150	3000	310±400[2]	275	5000
SO_4 (mg/l)	250	4000	700±700[2]	280	5000
Na (mg/l)	100	1500	350±20[3]	-	-
F (mg/l)	-	-	3.0±1.4[3]	2	30

Potential construction materials containing upgraded MSWI APC residues also has to meet current regulation on construction materials as defined in [3] (*Bygningsreglementet*), which sets standards on strength, density, durability etc. based on European standards. E.g. limits are set for maximum content of chloride, minimum compressive strength, and maximum content of fly ash (CFA) in EN 206-1/DS 2426 [4], and the requirements for the use of CFA are defined in DS/EN 450-1 [5]. If upgraded MSWI APC residues were to be used as substituent of filler or cement in concrete production, standards would have to be developed for this particular material, thus again, the requirements from DS/EN 450-1 can only be used as guiding principles. According to DS 2426 [4], chloride content in CFA must be maximum 0,1-0,4% depending on environmental class (here environmental class refers to the environment in which the concrete is to be used). And the minimum compressive strength (28 days) must be 12-50MPa depending on the use of the concrete. According to DS/EN 450-1, loss on ignition must be < 5-9%; chloride content (Cl) less than 0.1%, SO_3 < 3%, CaO < 1,5%, SiO_2 > 25%, sum of SiO_2, Al_2O_3 and Fe_2O_3 > 70%, P_2O_5 < 5%, MgO < 4%. Also there are requirements for the content of alkalis, fineness, soundness, particle density, setting time, and water requirement. Regarding content of hazardous substances, the standard tells that the fly ash shall not contain such substances, and that other national laws on such substances regarding the fly ash itself as well leaching from concrete produced by the fly ash must be considered. It is anticipated that content of hazardous substances and chloride is the main obstacle for using MSWI APC residues in concrete thus focus in this report will be on those substances; however comments on some of the other requirements are given in chapter 3.3.

1.4 Other potential methods for treatment of MSWI APC residues

Other potential treatment methods can be divided into three categories. (a) separation; (b) solidification and stabilization; and (c) thermal treatment [35]. Advantages and disadvantages of various methods and combinations of methods have been evaluated: The high cost [35], and global warming potential [36] of thermal treatments are documented. In separation processes, aqueous solutions are used to wash/leach out leachable fractions, which in turn results in production of wastewater of minimum twice the original material volume [35]. By solidification and stabilization methods the solid mass volume increases significantly, and a lack of efficiency in binding soluble salts has been documented [35]. Utilization of the product in construction material e.g. as substitute of concrete in cement production has been discussed [13], but it is agreed upon that the bulk material requires pretreatment to remove soluble salts prior to use in building materials [11, 13, 35, 37]. The current trends on handling of MSWI APC residues are towards recovery of valuable metals from the residues to support a circular resource economy [9, 10], and utilization of the bulk material in construction industry [11, 12]. E.g. leaching procedures for selective extraction of copper and other metals are being developed [10], and in Switzerland recovery of metals such as copper, aluminum, zinc and others from the combustion residues is becoming standard practice [9]. In an investigation of use of MSWI APC residues as substituent of virgin raw materials in light weight aggregates (LWA), it was shown that after a washing pre-treatment and if the percentage of incorporation is low, these residues may be incorporated into LWA. However, the recycling of APC residues from MSW incineration into LWA did not reveal any technical advantage [11]. Similar to the aim of this project Keppert et al. [12] concluded that water extracted MSWI fly ash can be used as 10 % Portland cement substitute without loss of mechanical properties.

2. Methods

2.1 Materials

Six batches of SD APC residue (SD1-6) were obtained on different days in the period 2008-2013 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 SD treatment which were collected in big bags. In lines 1 and 2 the flue gas was treated by simultaneous water sprinkling and dry lime injection. In line 3 the flue gas was mixed directly with slaked lime. In all lines activated carbon was also added. Two batches of residue was obtained from the MSWI plant Vestforbrænding, 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 sludge residue from the flue gas cleaning process. In order to avoid clogging of the ED apparatus, the fraction >1mm was dry sieved out and only the fraction <1mm, representing >99% of the mass, was used in the experiments.

CFA that meets the requirements of EN 450-1: 2012 for use in concrete was obtained from Emineral A/S. CFA is a valuable reference material for evaluation of upgraded MSWI APC residues as it is used as substituent of cement in concrete production on a regular basis.

Carbonation was induced into one of the SD batches (SD5) by keeping the sample under moist conditions at room temperature for several weeks. Washing was done to one portion of the SD batch SD3: 8 kg sieved (<1 mm) SD3 was washed with 16L distilled water, water was decanted - and washing was repeated three times in total.

2.2 Analytical methods

Analyses were made in the laboratories of Department of Civil Engineering, Technical University of Denmark, unless otherwise specified.

2.2.1 Cationic element analysis

The contents of As, Ba, Cd, Cr, Cu, Mn, Mo, Na, Ni, Pb, Sb, Se, V and Zn were measured in liquid samples by inductively coupled plasma atomic emission spectroscopy (ICP-OES) Varian 720-ES, software version: 1.1.0. Hg was analyzed on an atomic absorption spectrometry (AAS) with a hybrid system by ALS Global.

2.2.2 pH

pH was measured by a Radiometer Analytical pH electrode in DI water at a liquid-to-solid ratio (L/S) of 5 after 1h of agitation (triplicate samples).

2.2.3 Leaching

Leaching experiments were made according to DS/EN 12457-1 in batch test at L/S 2 L/kg by mixing 10 g of MSWI residue with 20 L 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, F and SO4 on ionic chromatograph (IC) dionex, DX-120 and the other subsample was acidified by addition of concentrated HNO3 before measurement of cationic elements according to the procedure described in section 2.2.1. (Triplicate samples or more for start and final residue leaching, while the samples taking during the experiments were large enough to make only a single leaching test).

2.2.4 Total contents

Total content of the elements was analyzed after digestion according to Danish Standard DS259 [38]: 1 g of dry (oven dried at 105° overnight) APC residue and 20 mL 7.3 M HNO3 was heated at 200k Pa (120°C) for 30min. The liquid was separated by vacuum filtration through a 0.45 µm filter and diluted to 100 mL (triplicate samples).

2.2.5 Dioxin analysis

Analysis of total content of 17 dioxins and furans were made on dry material by ALS Global and the I-TEQ (International Toxic Equivalent) was calculated for the samples in ng/kg for selected samples before and after ED treatment.

2.2.6 XRD

Residue mineralogy was studied by X-ray powder diffraction (XRD), for identification of major crystalline phases before and after ED treatment. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-100 2Θ within 8 hours. The diffractograms were interpreted using the ICDD PDF-4 database for minerals.

2.2.7 XRF analysis

Major oxide composition was estimated from semi-quantitative analysis by X-ray fluorescence (XRF) on powder samples. The XRF measurements were made by Force Technology.

2.2.8 Water solubility

100 g dried ash was mixed with 500 mL distilled water for 2 min, allowed to settle for 10 min, filtered through VWR qualitative filter paper, 413 5-13 µm. The procedure was repeated three times, after which the remaining sold fraction was oven dried at 105°C overnight and weighed.

2.2.9 Fraction > 1mm

50-100 g ash was dry sieved through a 1 mm sieve and the two fractions weighed.

2.3 Pilot scale upgrading of semidry, wet and dry MSWI APC residue in electrodialytic stack

2.3.1 Experimental setup

The pilot plant (Fig. 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 [32]. 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 0.6 mm and 5 mm thick for the concentrate and diluate respectively. The diluate spacers were thicker than the concentrate spacers to avoid clogging due to the particles in the APC residue suspension. There were electrode compartments in each end of the ED stack with circulating electrode clean solution. 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.

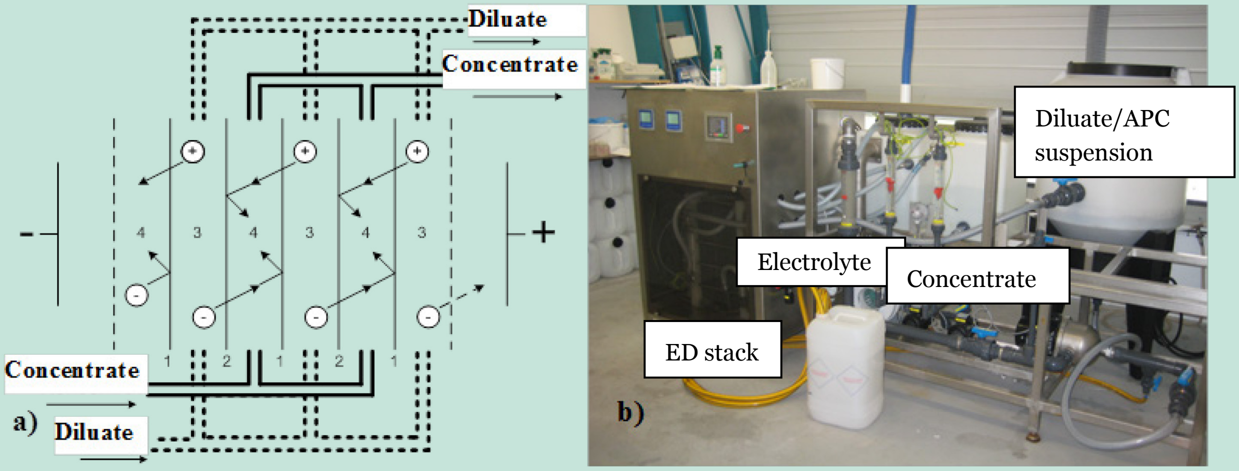

FIGURE 1
EXPERIMENTAL SETUP: A) PRINCIPLE OF ED STACK, B) THE PILOT PLANT IN FULL.

2.3.2 Experimental plan

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 the experimental overview in table 3. 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 (experiment 23) was made with pre-washed SD3 according to the following procedure. The experiments were designed to test residue leaching as a function of current density 0-6A (i.e. 0-11.3 mA/cm^2) and stack residence times up to 3 h, which equaled experimental runs of 24 h for the experiments with 34 cell pairs and 16h for the experiments with 50 cell pairs when running with 80 L of diluate (residue suspension).

2.3.3 Running of experiments and sampling

In all the experiments, L/S was kept constant at 10L/kg with 8 kg APC residue and 80 L tap water when using 50 cell pairs, or 5.3 kg APC residue and 53 L tap water when using 34 cell pairs in the diluate. The only exception was experiment 14 where 5.3 kg APC residue and 80 L tap water were used. The concentrate consisted of 30 L tap water with 400 mL 1:1 HNO3, and the electrode clean solution of 30 L distilled water with 400 mL 1:1 HNO3. Current strength, voltage and electrical conductivity in all three tanks, and pH in the diluate tank were logged every 30 s during most of the experiments. In a few experiments, the logging was unsuccessful and pH and conductivity was noted manually every second or third hour when sampling was done. 1L samples of the diluate were taken for leaching-tests according to table 3. The samples were filtered through filter paper at ambient pressure, and the filtrate was dried in an oven at 40°C prior to the leaching tests. By the end of the ED experiments, the tanks were emptied and samples of all liquids were taken for analysis. The diluate was stored in closed containers for days/weeks until filtrated for investigation of the leachability and total contents of the selected constituents from the final residue. 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 particles from the previous experiment.

The experiments with the highest current density had short (0.8-0.9 h) residence times only, because voltage increased, and reached the maximum of the current supply, which caused current density to decrease to zero.

At two incidents, the stack clogged during experimental running, and some of the diluate compartments ran partly dry, which increased the resistance over that section of the stack, and was reason for heat production to a level at which the membranes got damaged and had to be replaced. To avoid this from repeating, the stack was tested with a NaCl solution as diluate to check for any malfunctions between experiments. This procedure may have left additional NaCl in the stack system possibly affecting the results for Na and Cl of experiments 15, 16, 18, 19, 22 and 23.

2.3.4 Multivariate analysis – PLS modelling

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 were 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.

TABLE 3

LIST OF PILOT SCALE ED EXPERIMENTS: Car= PRE-CARBONIZED, Air= AERATED DURING ED TREATMENT, Wa = PRE-WASHED. *SE = SAMPLES TAKEN BY EXPERIMENTAL START AND END, 1h/2h/3h= SAMPLES TAKEN BY EXPERIMENTAL START AND END + EVERY, OR EVERY 2nd/3rd h.

Exp. No.	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
Treatmt.	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Car	Car	Air	Wa
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	15	16	10	10	5	8	5	10	10	5	21
Res. 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*	SE	SE	SE	SE	SE	SE	SE	3h	3h	3h	3h	2h	2h	2h	2h	2h	SE	2h	1h	SE	SE	2h	2h

2.4 Laboratory scale testing of ED of SD MSWI APC residue with different membranes

2.4.1 Experimental setup

The Electrodialytic (ED) cell used for this part of the investigation consisted of four (I, II, III, IV) compartments (Fig. 2) made of cylindrical Plexiglas® with an internal diameter of 8 cm. Compartment III was 10 cm long; it contained 35 g of residue and 350 ml of DI water for each remediation. An electrolyte solution (0.01M NaNO3, pH < 2 adjusted with HNO_3) was circulated in each of the electrolyte compartments (I, II and IV) using totton Pumps NDP 10/2. The total volumes used were 500 mL for I and IV, and 350mL for II. A plastic strip attached to a glass-stick connected to an overhead stirrer (IKA RW11) was used to stir the ash suspension during remediation. The electrodes were made of platinum coated titanium wire (diameter 3mm) obtained from Permascand®. An Agilent E3612A DC power supply was used to maintain a constant electric DC current.

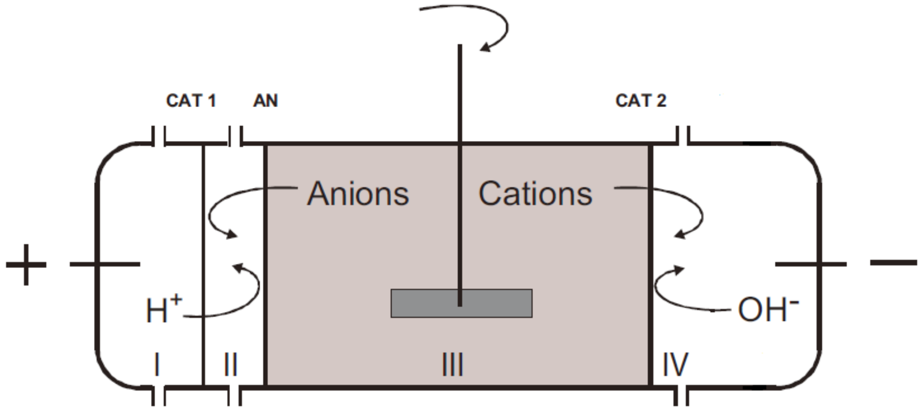

FIGURE 2
SCHEMATIC VIEW OF A CELL USED FOR THE ED TREATMENT. AN: ANION-EXCHANGE MEMBRANE; CAT1 /CAT2: CATION-EXCHANGE MEMBRANES.

Compartment II was included due to the high concentration of Cl^- [4]; to prevent formation of chloride gas at the anode.

2.4.2 Experimental plan

Four different membrane brands were tested (Table 4) according to several criteria: The Ionics membranes have been used in our research on ED at laboratory scale (e.g. [14, 39-41]), and the ASTOM membranes have been use in our research on upgrading of residues in pilot scale stack setup (e.g. [30, 32]). The last two (Mega and Ralex) were selected based on their pH range tolerance and price.

TABLE 4
MEMBRANES USED IN THE ED TREATMENTS.

Company	Membranes	Type	pH tolerance
General Electric	Ionics CR67-HMR AR204-SZRA	Cationic Anionic	NA
ASTOM	CMX AMX	Cationic Anionic	1-13
Mega	Ralex® CM -PP Ralex® AM-PP	Cationic Anionic	0-14
SnowPure	Excellion™ I-100 Excellion™ I-200	Cationic Anionic	0-14

Eight experiments were made with each of the four types of membranes and two of the batches APC residue batches: the semi dry residue (SD3) and the FA.

1) SD3 residue with Ionics membranes
2) SD3 residues with Neosepta membranes
3) SD3 residues with Ralex membranes
4) SD3 residues with Excellion membranes
5) FA with Ionics membranes
6) FA with Neosepta membranes
7) FA with Ralex membranes
8) FA with Excellion membranes

2.4.3 Running of experiments and sampling

The electrodialytic (ED) treatments ran for 70 min at a current of 235 mA equivalent to a current density of 4.7 mA/cm², which is within the range used in the pilot scale stack treatments. Voltage and intensity were monitored during the whole experiment. pH (for all compartments) and electrical conductivity (for compartment III) were measured at the beginning, at the end, and every 20 min during the ED treatment. During the experiments, the pH of the electrolytes was adjusted to <2.5 with 1 M HNO_3. This was especially done in compartment IV (Fig. 2) of the electrodialytic cell, to avoid precipitations in the electrolyte due to the production of OH^- by the electrode reaction at the inert cathode. At the end of the experiments, the suspension in the central compartment was filtered at ambient pressure. The filtrate was dried at 40°C and total contents and leaching of elements were measured according to descriptions in sections 2.2.1, 2.2.3 and 2.2.4. The volumes of the electrolytes were measured; the electrodes were rinsed in 5 mol/L HNO_3, whereas the membranes and the stirrer in 1 mol/L HNO_3, and the concentrations of metals were measured in all of them as described in section 2.2.4. Electrolyte samples were taken in 20 mL vials at the beginning and at the end of all experiment for each compartment. Metal content was measured as described in section 2.2.4. Mass balances were carried out to determine the distribution of the metals in the cell.

2.5 Laboratory scale testing of ED of SD MSWI APC residue and FA with different setups

2.5.1 Experimental setup

Experiments were run in cells of two different setups as illustrated in Fig. 3 to investigate the efficiency of separation of mobile elements and salts from residue in the two setups as opposed to the stack setup. All experiments were made with a suspension consisting of 350 mL of DI water and 100 g MSWI residue, corresponding to an L/S ratio of 3.5. The EDR cells were made of plastic with an internal diameter of 8 cm and the suspension compartment length was 10 cm. Electrode compartments were separated from the suspension compartment by an anion-exchange membrane and/or a cation-exchange membrane from Ionics. The electrodes were platinum coated titanium. A power supply (Hewlett Packard E3612A) was used, maintaining a constant current of 5 mA or 50 mA, corresponding to current densities of 0.1 mA/cm² or 1 mA/cm², respectively. The MSWI residue suspension was stirred in the suspension compartment by a flexible plastic flab, attached to a glass-stick and connected to an overhead stirrer (RW11 basic from IKA) with a rotation velocity rate of up to 2000 rpm.

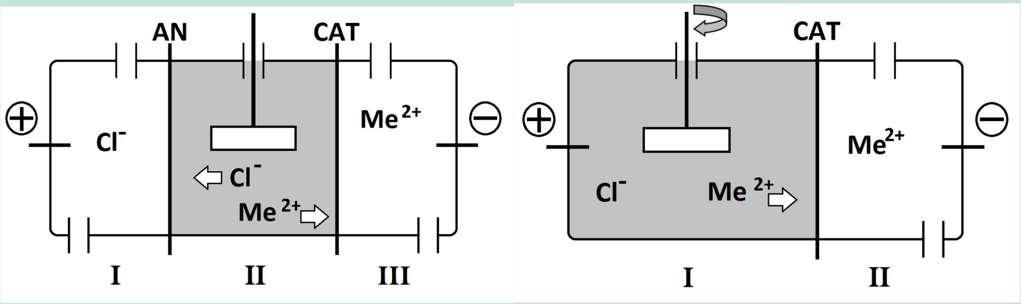

FIGURE 3
THE EXPERIMENTAL SET-UP OF THE 3 AND 2 COMPARTMENT ELECTRODIALYTIC CELLS. AN: ANION EXCHANGE MEMBRANE. CAT: CATION EXCHANGE MEMBRANE.

The electrolytes were 0.01 M NaNO3 with pH adjusted to 2 with HNO3 (1:1). In the experiments with the 3 compartment cell, 500 mL of analyte and 1000 mL of catholyte were used, while in the experiments with the 2 compartment cell, 500 mL of catholyte was used. The recirculation was made using "Pan World" magnetic pumps with a performance rate of 8 L/min.

2.5.2 1.1.1 Experimental plan

Twenty-four EDR experiments were made according to the experimental conditions presented in Table 5. Twelve of them were made in an ED cell with 3 compartments (Fig. 3a) and the other 12 were made in an ED cell with 2 compartments (Fig. 3b).

TABLE 5
EXPERIMENTAL CONDITIONS FOR ELECTRODIALYTIC EXPERIMENTS: (FA/SD-X-Y-ZD, WHERE X = CELL TYPE (2 OR 3 COMPARTMENT CELL), Y = CURRENT DENSITY (mA/cm²) AND ZD = DURATION IN DAYS).

Experiment	MSWI residue	Cell type	Current density (mA/cm²)	Duration (days)
FA-2-0.1-ZD	FA	2	0.1	3, 7, 14
FA-3-0.1-ZD	FA	3	0.1	3, 7, 14
FA-2-1-ZD	FA	2	1.0	3, 7, 14
FA-3-1-ZD	FA	3	1.0	3, 7, 14
SD-2-0.1-ZD	SD3	2	0.1	3, 7, 14
SD-3-0.1-ZD	SD3	3	0.1	3, 7, 14
SD-2-1-ZD	SD3	2	1.0	3, 7, 14
SD-3-1-ZD	SD3	3	1.0	3, 7, 14

2.5.3 Running of experiments and sampling

Voltage, electric current and electrical conductivity in the suspension compartment were measured daily, whereas pH in the electrolytes and the pH of the MSWI residue suspension were measured twice a day. pH in the electrolyte was adjusted with (1:1) HNO_3, if pH > 2. At the end of the experiments the residue suspension was filtered before measurements for heavy metals and chloride. The dried MSWI residue was digested according to DS 259 and measured for heavy metals according to descriptions in sections 2.2.1, 2.2.3 and 2.2.4. The membranes and stirrer were soaked in 1 M HNO3 and the electrodes in 5 M HNO3, to release precipitated metals. The obtained aqueous phase of the membranes, the stirrer, the electrodes and the electrolytes were all analysed for heavy metals (Cd, Cr, Cu, Pb and Zn) as described in section 2.2.4. The pH, heavy metal and chloride leaching were also determined on the dry MSWI resides after the EDR experiments. The chloride concentrations in the liquid from the filtered MSWI residue suspension were measured according to DS 239 [20] by potentiometric titration with AgNO3.

2.6 Investigation of use of MSWI APC residue in mortar

2.6.1 Materials

Mortar bars were cast using raw APC residues SD3 and FA; as well as APC residues SD3 and FA that had been ED treated for 7 days according to the procedure described in chapter 2.5. The selection of the 7 day-remediation was based on the pH of the APC residue, which should preferably be alkaline for a better aggregation with the cement.

2.6.2 Morphology and element distribution

Morphology and element distribution analysis was performed by SEM/EDS (Scanning electron microscope/energy dispersive X-ray spectroscopy). No sample pre-treatment was made. The acceleration voltage of the SEM was 20-25 kV with large field detector, in low vacuum with a magnification of 1000x.

2.6.3 Casting

The mortar samples were mixed according to DS/EN 196-7: 225 mL de-ionized water, 450 g Ordinary Portland cement and 1350 g CEN standard sand (Ø < 2mm), with a water/binder-ratio of 0.5 and a sand/cement ratio of 3. Five percent of the cement was replaced by APC residue except in the reference experiment. Eleven experimental mortars were made, according to Table 6 with the raw residues and residues treated according to specifications given in table 5.

The moulding was carried out according to DS/EN 196-7. The mould consisted of three horizontal compartments such that 3 prismatic specimens of 40 x 40 mm in cross section and 160 mm in length were prepared simultaneously for each mixture. Demoulding was carried out after 24 h and the samples were cured horizontally in a tap water bath for 28 days. The ambient temperature was 20-21°C, as prescribed in DS/EN 196-7 (20 ± 1 °C). After curing in tap water for 28 days, the mortars were set curing for a period of 28 days (20 days at 50 °C and 8 days at ambient air temperature) and the porosity, density and compressive strength were determined.

TABLE 6
EXPERIMENTAL CONDITIONS OF MORTAR BARS-CASTING OF SPECIMENS

Mortar sample	Substitution residue
M_{Ref}	None
M_{FA}	Raw FA
$M_{FA-2-0.1}$	FA-2-0.1-7D
$M_{FA-3-0.1}$	FA-3-0.1-7D
M_{FA-2-1}	FA-2-1-7D
M_{FA-3-1}	FA-3-1-7D
M_{SD}	Raw SD3
$M_{SD-2-0.1}$	SD-2-0.1-7D
M_{SD-2-1}	SD-2-1-7D
$M_{SD-3-0.1}$	SD-3-0.1-7D
M_{SD-2-1}	SD-2-1-7D

2.6.4 Density and porosity

To determinate porosity and density, the mortars were placed in desiccators under vacuum for 3 h (100 N/m^2). The set-up was filled with deionised water (1 h), and then opened to the air (24 h). The mortars bars were weighed under the water with the accuracy of 0.1% to measure the porosity of the mortar.

2.6.5 Compressive strength

Compressive strength measurements were performed in each end of the prismatic mortar specimens (with the end face of the prism overhanging the plate with 1 cm), as prescribed in DS/EN 196-1. The plates were, however, 4 cm long, meaning that the actual pressure area was 40 x 40 mm. A Toni 3000 compression machine was used. From this procedure a double determination of the compressive strength for each mortar recipe was obtained

2.6.6 Heavy metal leachability

Mortar bars were then crushed and tested for heavy metal leachability. The leaching procedure was carried out as described in section 2.2.3.

2.6.7 Chloride content

For chloride determination in the mortars, the procedure was the following: 5 g of crushed mortars were mixed with 50 mL deionised water and 10 mL concentrated HNO_3. After the solution was filtered, approximately 90 mL deionised water was added. The final solution was 150 mL and the chloride determination was performed by Metrohm 727 RI Stand, by titration.

3. Results and discussion

3.1 Pilot scale experiments

In many of the experiments problems with unstable hydraulics were observed most likely due to a high osmotic pressure of the diluate suspension. This meant that liquid was transferred over the membranes from the concentrate to the diluate (the APC suspension) in large quantities, and fresh 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 concentrated HNO_3. At 6A (11.3mA/cm) 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 residence times are given in table 3). The output potential difference also increased beyond feasible levels for treatments at 4A (7.5mA/cm^2). An example of this behavior is shown in figure 4a. The pH decreased slightly during treatments with a maximum decrease around 1 unit. Examples of the pH development are shown in figure 4b.

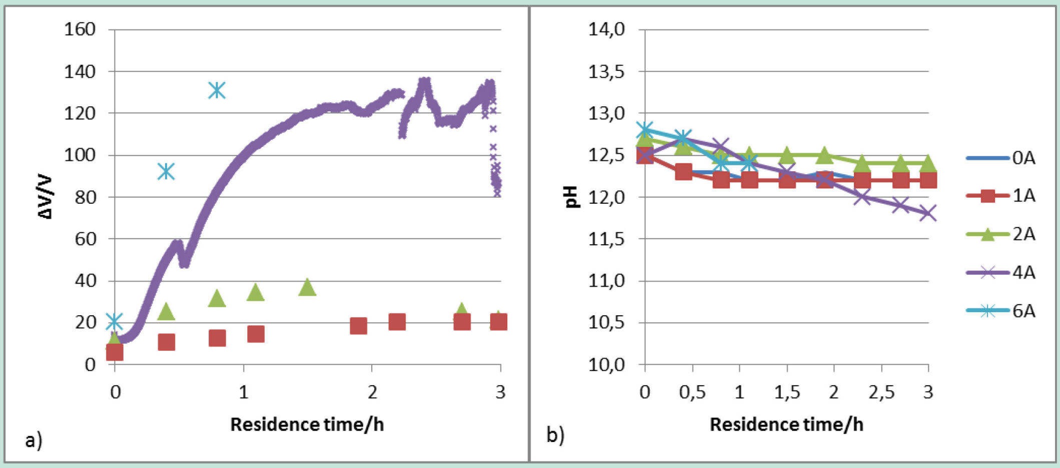

FIGURE 4
A) OUTPUT POTENTIAL DIFFERENCE FOR EXPERIMENTS 8, 9, 11, AND 12, AND B) pH DEVELOPMENT OF DILUATE (APC SUSPENSION) IN EXPERIMENTS 8-12.

3.1.1 Total contents before and after treatments

In table 7 the total concentrations of elements and salts in the untreated APC residues are shown. Both SD, W and FA exceeded the category 1 [1] limits significantly for As, Cd, Hg, Pb and Zn. For most batches Cu and Ni also exceeded the category 1 [1] limits slightly. For the elements, for which no legislative limits are set, both the SD and FA exceeded the content in CFA significantly for Sb, slightly for Mn; while not for Ba, Mo, Se and V.

TABLE 7
INITIAL TOTAL ELEMENT CONTENTS, pH, WATER SOLUBILITY AND FRACTION > 1MM OF THE USED SD, W AND FA BATCHES (AVERAGE OF TRIPLICATE SAMPLES). VALUES EXCEEDING CATEGORY 1 [1] LIMIT FOR UNRESTRICTED USE IN CONSTRUCTIONS IN BOLD. Wash = WASHED, Carb = CARBONIZED, *AVERAGE AND STANDARD DEVIATION OF TWO DIFFERNET SUBSAMPLES, **AVERAGE AND STANDARD DEVIATION OF THREE DIFFERNET SUBSAMPLES.

	SD1	SD2	SD3*	SD3 Wash	SD4*	SD5	SD5 Carb.	SD6	SD average	W	FA**
pH	12.2	10.7	11.7		11.9	12.2	10.0	11.7	11.6	10.9	11.8
Water solubility (%)	7,5	-	45.6	-	10.2	-	-	47.7	-	19.1	12.5
Fraction > 1mm (%)	4.2	-	2.2	-	0.1	-	-	25	-	0.6	0.0
As (mg/kg)	**102**	**104**	**108±72**	**109**	**110**	**134**	**92**	**197**	**126±37**	**193**	**170±118**
Ba (mg/kg)	392	360	387±18	458	358	373	330	228	350±61	329	514±252
Cd (mg/kg)	**92**	**129**	**146±16**	**132**	**95±9**	**141**	**107**	**181**	**131±34**	**136**	**140±76**
Cr (mg/kg)	52	97	104±1	119	76±3	101	92	61	82±22	120	150±89
Cu (mg/kg)	482	445	**520±1**	**531**	**555±5**	**488**	386	**1,233**	**621±302**	**860**	**863±230**
Hg (mg/kg)	**10**	-	**5.0**	-	**9.0**	-	**3.7**	**9.5**	**8.4±2.3**	-	**4.7**
Mn (mg/kg)	398	427	382±42	472	470	410	392	355	407±39	538	666±24
Mo (mg/kg)	-	-	26±13	12	16	-	-	12	18±7	-	31±34
Ni (mg/kg)	29	**35**	**32±7**	**32**	**33**	**31**	29	20	**30±5**	<2	**81±47**
Sb (mg/kg)	-	-	651	370	382	-	-	777	603±202	-	194±46
Se (mg/kg)	-	-	4.1	4.7	1.6	-	-	10	5±4	-	<2
V (mg/kg)	42	34	44±13	18	42	-	30	15	35±12	52	60±20
Zn (g/kg)	**13**	**15**	**16±1**	**17**	**19±0.3**	**15**	**13**	**19**	**16±3**	**21**	**25±7**
Pb (g/kg)	**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**	**3.4±1.1**
Dioxins (ng/kg) I-TEQ	234	-	283	-	263	-	177	-	**260±20**		346

The FA in general contained higher amounts of most (As, Cd, Cr, Cu, Mn, Pb, V and Zn) analyzed elements compared to SD, probably because the SD has been “diluted” by the addition of lime in the flue gas cleaning process . There was some variability in the content of elements between the different batches, while the variation among different subsamples from a single batch (SD3 and SD4) was smaller than between different batches (SD average).

The total content of the elements after ED treatment of SD MSWI APC residue is shown in figure 5. 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 carbonized or washed material or applied pressurized air have been omitted. Se has been omitted from the figure as the content was <20 mg/kg in all SD samples and < 30mg/kg in all FA samples. In general the content of the elements increased by ED treatment of SD and W APC residue while it decreased by ED treatment of FA. Only exceptions are Cd and Sb in the FA, which increased; and V in W, which decreased. This effect may be attributed to the higher content of soluble salts in the SD APC residue, 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 APC residue, just as Cd and Sb did in the FA. 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.

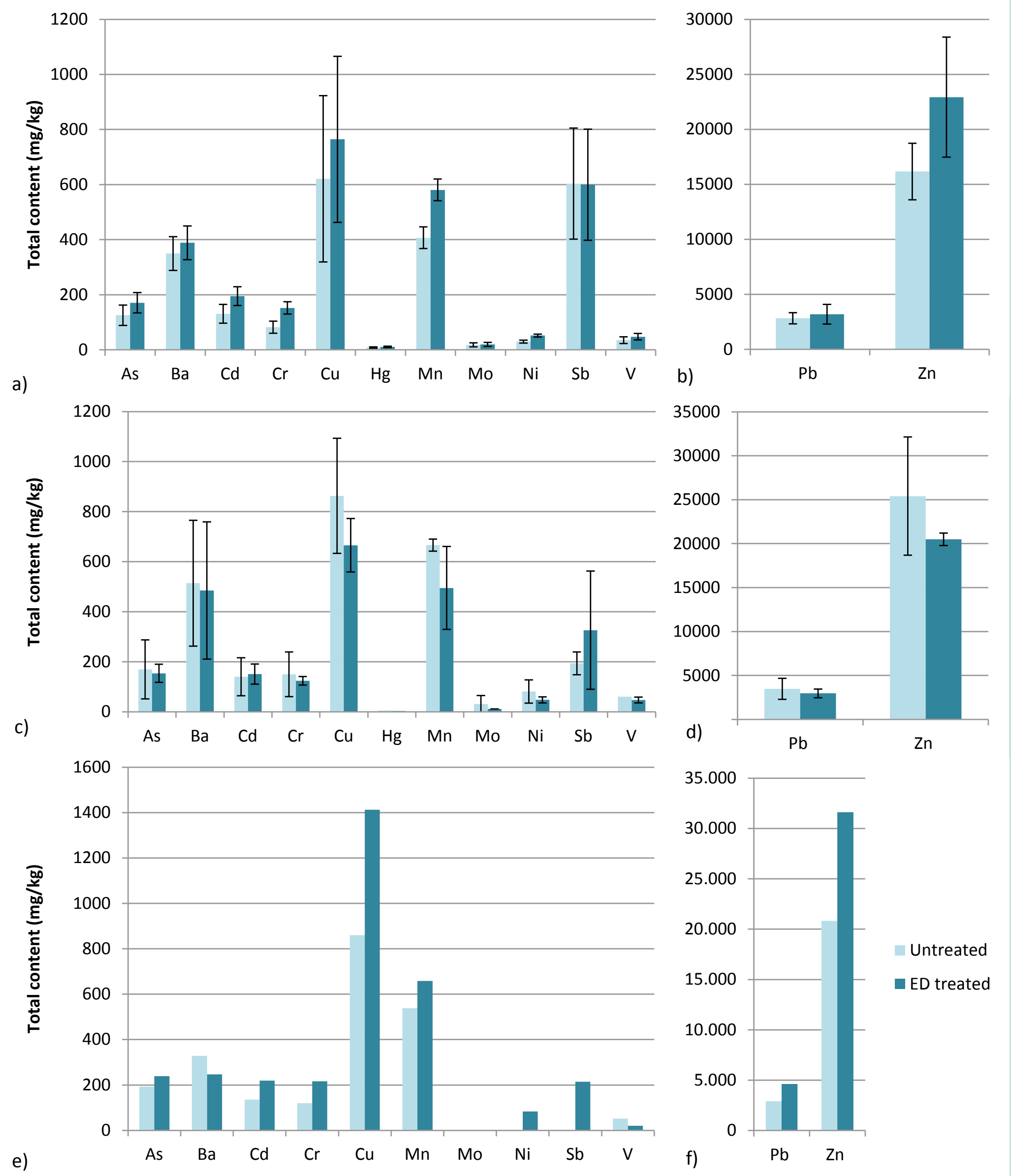

FIGURE 5
a)-b) TOTAL CONTENTS WITH STANDARD DEVIATIONS OF ELEMENTS IN THE SD APC RESIDUE BEFORE (AVERAGE OF BATCHES SD1-6) AND AFTER (AVERAGE AFTER ED EXPERIMENTS 1-3,4-9,11-16, EXCEPT MO, SB AND V WHICH WERE MEASURED ONLY AFTER EXPERIMENTS 12-16; c)-d) TOTAL CONTENTS IN THE FA BEFORE AND AFTER ED TREATMENT (AVERAGE AFTER ED EXPERIMENTS 18-19); e)-f) TOTAL CONTENTS IN THE W BEFORE AND AFTER ED TREATMENT (EXPERIMENT 17).

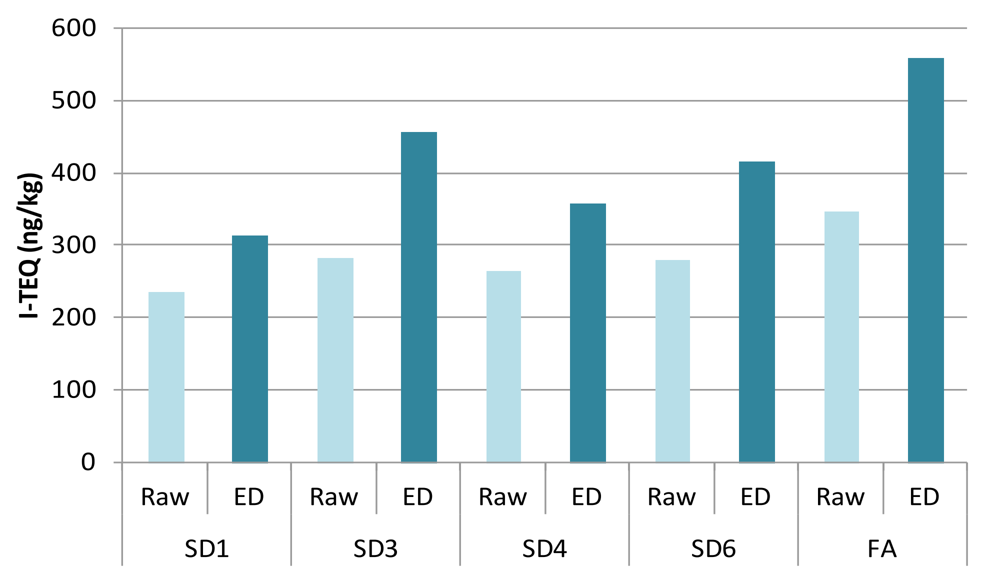

FIGURE 6
DIOXIN CONTENT BEFORE AND AFTER ED TREATEMENT

Figure 6 illustrates the dioxin content before and after treatment. It can be seen that the content consistently increases by 20-30%, because dioxins were less soluble than the average material.

In figure 7 the influence on total contents of the SD APC residue of pre-carbonization and aeration simultaneously with the ED treatment is illustrated. For all elements the carbonization reduced total content of the investigated elements due to the uptake of CO2 from the air, and thus mass increase of the material. After ED treatment, however, the total contents increased again, and in most cases to above initial values. As for the non-carbonized SD APC residue, in particular Zn, Cu and Mn increased. The total content of the batch which was used for the aeration experiment (SD6) was in general high compared to the other batches, and the total content of Cu and Zn increased even more during the aerated experiment (22).

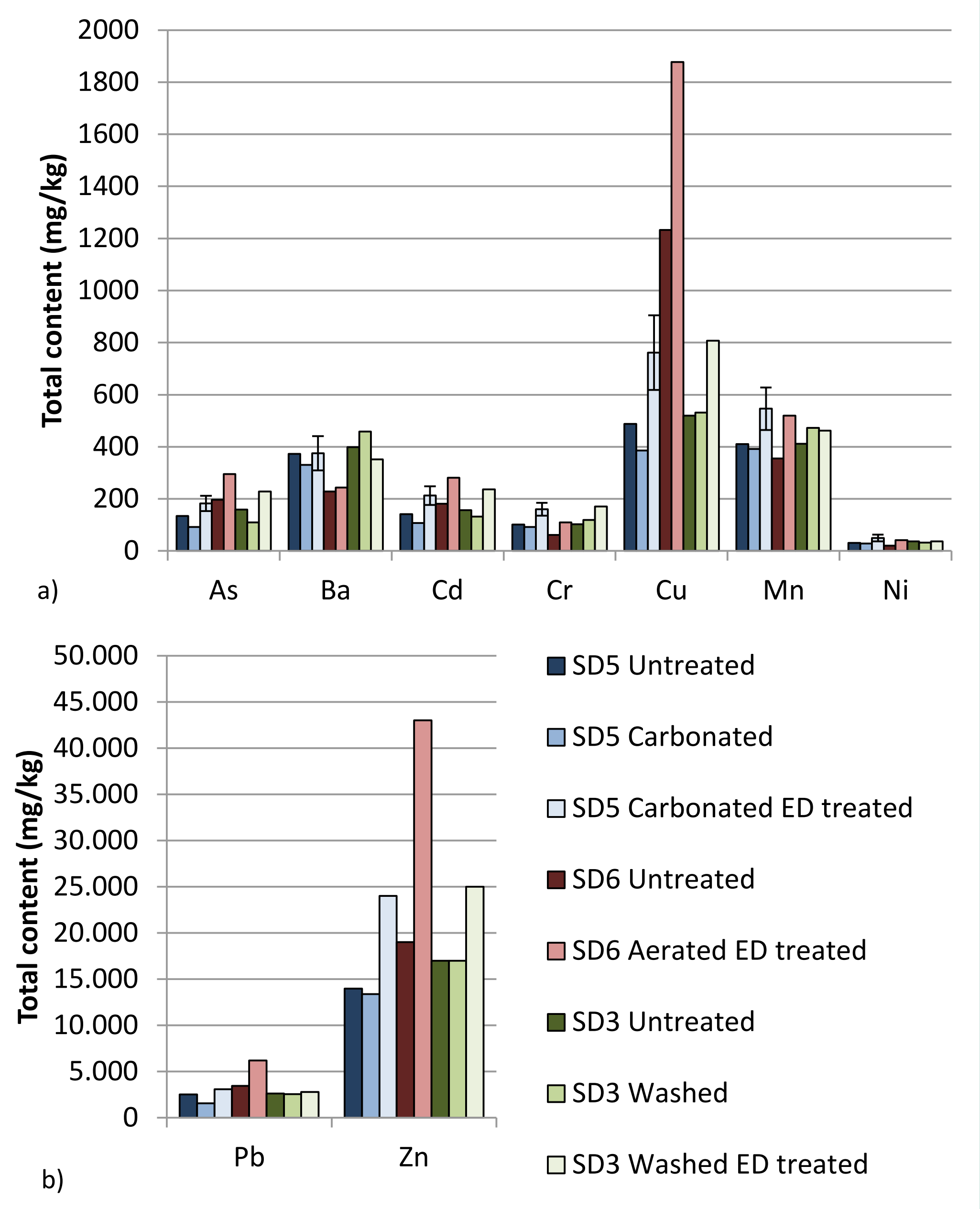

FIGURE 7
a) AND b) TOTAL CONTENTS OF ELEMENTS IN THE CARBONATED (AVERAGE AND STANDARD DEVIATION OF EXPERIMENTS 20 AND 21) AND AIR TREATED (EXPERIMENT 22) MATERIAL PRIOR TO TREATMENT AND AFTER.

3.1.2 Mineralogy and morphology before and after treatments

Table 8 shows the major components as given by XRF analysis of the SD and FA batches before and after ED treatments. It was found that the untreated SD and FA mainly consisted of Ca and Cl. Main components were also K, Na and S. ED treatment and washing resulted in similar changes by reducing the K, Na and Cl contents significantly. Even though only one sample from each batch was analyzed by XRF, it can be seen that the overall trend of major components in the ED treated samples are consistent, and different operational conditions during the experiments seemed not to influence the final composition significantly.

TABLE 8
INITIAL AND FINAL CONTENT OF MAJOR COMPONENTS IN THE SD AND FA BATCHES (% OF DRY MATTER), R = RAW RESIDUE, T= TREATED RESIDUE, NUMBER= EXPERIMENT NUMBER. MnO WAS 0.03-0.09% IN ALL CASES. <* =<0.7.

Batch (%)	**SD1**		**SD3**			**SD3wash**		**SD4**		**SD5carb**		**SD6**	**FA1**	
Exp.	R	3	R	12	15	R	23	R	16	R	21	R	R	18
Al_2O_3	1.2	2.1	2.1	3.0	4.9	2.8	3.6	1.2	1.9	2.1	4.2	1.2	1.8	8.5
CaO	55	48	64	45	39	55	42	57	50	36	43	55	50	36
Fe_2O_3	0.7	1.2	1.0	1.0	1.3	1.0	1.0	0.6	0.7	0.8	1.2	0.4	0.8	1.7
K_2O	4.8	0.6	7.7	1.2	1.6	0.5	1.0	5.4	2.4	3.1	0.6	4.7	5.9	1.7
MgO	0.3	1.5	0.6	1.5	2.2	1.3	1.8	0	1.2	0.3	1.7	0.3	0.7	3.2
Na_2O	5.5	<*	10.2	3.0	2.7	<*	<*	8.2	3.4	7.1	<*	11.2	8.8	<*
P_2O_5	0.2	0.5	0.2	0.7	1.0	0.7	0.8	0.1	0.4	0.1	0.7	0.05	0.2	1.8
Si_2O	2.6	5.3	2.6	5.3	6.4	5.1	6.0	1.3	3.2	3.0	7.3	0.8	2.4	14.5
SO_3	8.2	8.0	6.2	6.2	9.5	8.2	8.7	9.5	9.5	5.2	12.7	10.7	5.2	12.7
TiO_2	0.4	0.6	0.7	0.8	1.0	0.8	0.8	0.3	0.5	0.4	0.8	0.1	0.6	1.8
Cl	12	0.6	24	2.7	3.3	1	2.1	14	4.9	19	2.2	22	19	1.4

The Cl content was higher than what is accepted for CFA (max 0.4%) for all samples, though significantly reduced by treatment and close to an acceptable level for the samples treated by either washing or electrodialysis. In contrast, the SO_3 and CaO contents were around 3 and 30 times higher than acceptable, respectively and none of them were significantly affected by any of the treatments. CaO was indeed found to be the main component of all the materials, and the sum of SiO_2, Al_2O_3 and Fe_2O_3 was found to be nowhere near the required level of minimum 70%. P_2O_5 and MgO met the criteria for all samples. The electrodialytically treated FA was the material approaching an acceptable mineralogical composition the most.

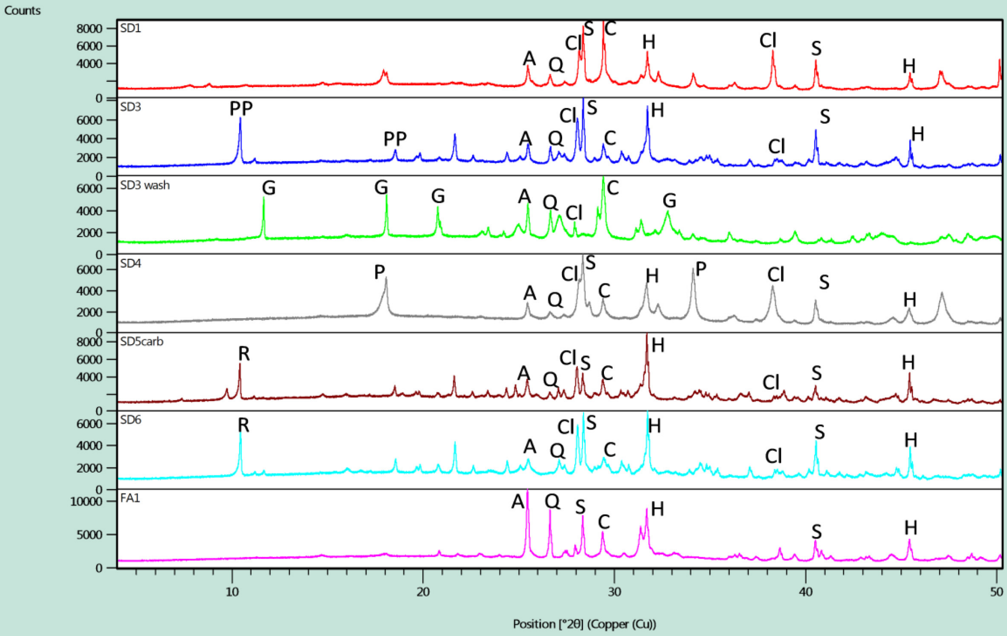

FIGURE 8
XRD DIFFRACTOGRAMS WITH MAIN MINERAL PHASES IN SD AND FA BATCHES BEFORE TREATMENT. A-ANHYDRITE, Q-QUARTZ, S- SYLVITE, C- CARBONATE, H – HALITE, CL – CALCIUM HYDROXYCHLORIDE, R-RICHERITE, PP – POTASSISPARGASITE, G-GYPSUM

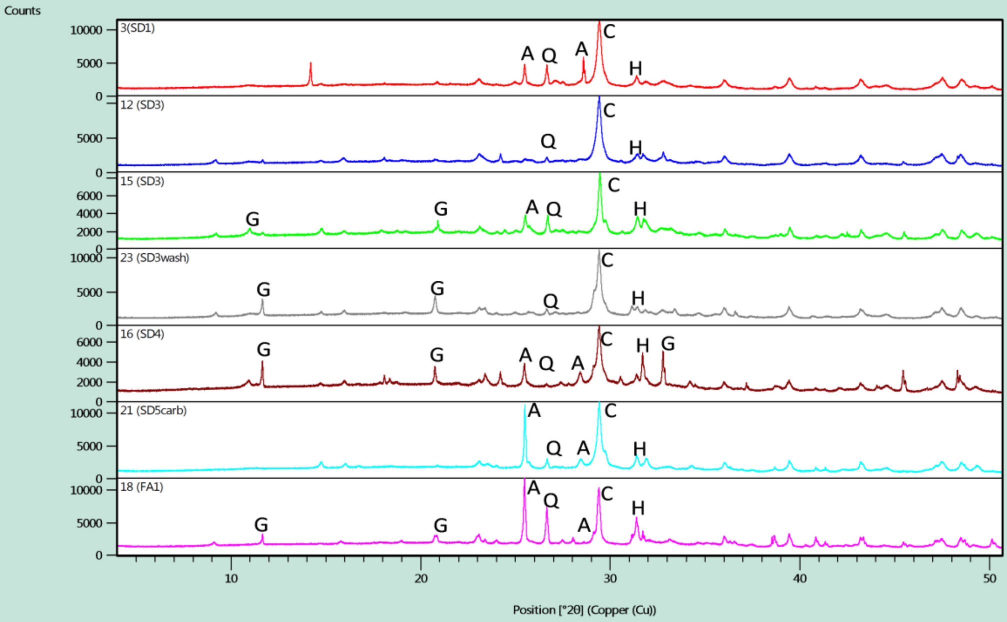

FIGURE 9
XRD DIFFRACTOGRAMS WITH MAIN MINERAL PHASES AFTER ED TREATMENT: A- ANHYDRITE, Q-QUARTZ, C-CARBONATE, H – HALITE, G- GYPSUM

The XRD diffractograms from which the major crystalline phases in the different samples are specified based on interpretation are seen in Figures 8 and 9. The diffractograms for the MSWI residues were noisy due to the complex mineralogy and heterogeneity of the samples. The main soluble mineral compounds identified in the SD and FA residues were sylvite (KCl) and halite (NaCl), which were typically removed in the ED treated samples and the washed SD residue. Flue gas treatment typically results in formation of calcium carbonates, chlorides, hydroxides or sulphates. Accordingly, Ca minerals such as $CaCO_3$, $CaSO_4$, $Ca(OH)_2$, $CaSO_4•H_2O$ and CaOHCl were identified. Calcite ($CaCO_3$) and anhydrite ($CaSO_4$) were present in all the SD and FA residues, portlandite ($Ca(OH)_2$) was identified only in the SD4 batch, Richerite ($Na(CaNa)Mg_5Si8O_{22}(OH)_2$), was a likely mineral phases observed in the SD5 carb and SD6 batches and potassicpargasite ($Ca_2H_2KMg_5O_{24}Si_6$) was a possible mineral in the SD3 batch. Thus, the mineralogy for the untreated SD batches differed, apart from the main phases.

The ED treatment resulted in a slightly more mineralogical homogeneous material consisting of mainly calcite and quartz, because easily soluble minerals were removed and the Ca mineralogy changed. E.g. richerite ($Na(CaNa)Mg_5Si8O_{22}(OH)_2$), which was most likely present in the SD5 carb and SD6 batches, was not seen in the ED treated. The peaks for calcite had higher counts in the ED treated residues which indicate that carbonate did not dissolve during ED treatment. A further carbonation of the residue during ED treatment, which would produce more calcite, is possibly occurring. Also, the total Ca content was at similar or lower in the ED treated residues compared to the untreated. Gypsum ($CaSO_4•H_2O$) was formed by reaction between Ca and SO_4 both during washing (observed in the washed sample SD3) and during ED treatment, where it was seen in all but two samples (exp. 3 and 21) after the ED treatment

In the ED upgraded residues it was clearly seen that the soluble KCl and NaCl salts had been removed by the ED process, which was also observed in other studies where MSWI fly ash was investigated by XRD after EDR [40, 42], and is supported by the XRF results. The final Cl concentrations in the ED treated residues were in the range between 0.6 – 4.9 %. By washing the SD3 residue, the Cl content was reduced from 24 to 1 %. Another study showed much lower Cl content, 0.4-0.7 % using the same pilot scale set-up for ED treatment, but without the test runs with NaCl between the experiments [32]. The results from this study indicates that the test of the stack with NaCl between the experiments influenced the Cl content in the ED treated residues.

3.1.3 Leaching of toxic elements and salts before and after treatment

In table 9 the leaching of the untreated FA, W and SD and pre-treated (washed and carbonized) SD is shown. All regulatory limits, i.e. category 3 limits for use in constructions and limits for landfilling as mineral waste, were exceeded for Cl and Pb in all batches [1, 2]. W, however almost met the regulatory limit for mineral waste for both elements. Further, for Zn and Ba category 3 [1] 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. Thus residue including APC residues from semidry fluegas cleaning appeared more reactive and inappropriate for use than pure FA and residue from wet fluegascleaning. Washing and carbonation clearly reduced leaching of most elements except Cd and Cr.

Leaching of Hg, Mo, Sb, Se, V only exceeded target values slightly in a few instances. F (not shown) only exceeded taget values in SD1 (26.7 g/L) while it was below detection limit in all other analyzed samples (SD3 and W). Potential leaching of these elements, reported for the first time, is thus not anticipated to be the major concern for the use of the material in constructions.

TABLE 9

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 /L]; Ba, Pb, Zn: [mg/L]; Cl, Na AND SO4: [g/L]. < MEANS THAT THE VALUE WAS BELOW DETECTION LIMIT FOR THE APPARATUS. BOLD: CATEGORY 3 [1] VALUES EXCEEDED.

	SD1	SD2	SD3	SD3 wash	SD4	SD 5	SD 5 Carb	SD6	SD average	W	FA
pH	11.8	9.8	11.9	-	12.1	12.0	9.0	11.8	11,5	10,7	12.6
As (µg/l)	<20*	**59**	**<91***	**51**	**94**	**110**	25	**321**	**146±119***	38	<20*
Cd **(µg/l)**	<20*	<20	<20*	<20	<20	22	**1,860**	<20	<22	<20	<20*
Cr (µg/l)	117±128*	128	61±2*	345	25±7*	65	**925**	44	83±58*	432	20±0*
Cu **(µg/l)**	313±84*	592	889±397*	23	339±97*	**2,920**	833	**4,469**	1,551±1,734*	35	23±11*
Hg (µg/l)	0.7	-	0.7	-	2.2	-	**1.8**	1	**1.2±0.7**	-	<20*
Mn **(µg/l)**	<20*	<20	<100*	<20	<20	22	<20	<20	<22	<20	**2024±48***
Mo (µg/l)	577	-	770	370	380	-	-	948	635±288*	-	<20*
Ni **(µg/l)**	<20*	<20	<20	<20	28	25	<20	55	<55	<20	40±2*
Sb (µg/l)	**35**	-	-	**21**	**39**	-	-	**79**	**51±24**	-	**49±40***
Se **(µg/l)**	**265**	-	-	**62**	< 20	**-**	**-**	**114**	**<114**	-	43±55*
V (µg/l)	**680**	18	<20	<20	20	-	-	66	**109±107***	<20	**3.3±1.1***
Ba (mg/l)	**8±2***	**10**	**17±5***	2	**6**	**34**	**17**	**60**	**21±21***	0.7	0.4±0.03*
Pb (mg/l)	**304±24***	**343**	**453±168***	**22**	**441±12***	**535**	**0.6**	**1,107**	**509±107***	**2.6**	<20*
Zn (mg/l)	**7±1***	**18**	**32±10***	**2.3**	**9.3±4.7***	**50**	0.3	**55**	**27±21**	**2.2**	**31±1***
Cl (g/l)	**49±0***	**87**	**87±3***	**15**	**43±25***	**88**	**84**	**100**	**79±20**	**6**	<20*
Na (g/l)	**6±2***	**9**	**13±2***	**1.9**	**4**	**12**	**14**	**12**	**9.1±3.3***	**12**	**14±2***
SO_4 **(g/l)**	1±0*	1	0.9±0*	1.2	1.0±0.2*	1.3	0.7	0.7	0.9±0.5*	**5.3**	9±0.5*

The leaching of SD after ED treatments can be seen in table 10. The values given are those obtained by analyzing leachability after the end of the experiments from material which had been transported and stored in suspension in tanks for days to weeks prior to filtration. In all experiments leaching of As was reduced to below 20 µg/L except from experiment 15, in which it was below 50 µg/L, i.e. still within the category 3 [1] limit for use in constructions and the limit for landfilling as inert waste [2]. Likewise, leaching of Ba was reduced to below 3.500 µg/L in all experiments, except by experiment 16, i.e. in general to below the category 3 limit [1] 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. This shows that the quality of the output material is sensitive to large variations in the quality of the input material. Cd leaching remained below 20µg/L after all treatments, i.e. well below target limits and also below that of leaching from CFA. Cr leaching in general increased slightly by ED treatment of the SD, but remained below target limits and well below the leaching of Cr from CFA in all cases except experiment 6, after which the leaching exceeded the category 3 [1] limit for use in constructions slightly, but not that of leaching from CFA. Cu leaching was reduced to below 120 µg/L after all ED treatments thus well below target limits and only slightly above the leaching of Cu from CFA. Mn leaching remained below 20 µg/L after all treatments, i.e. well below target 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 above the leaching from CFA and the limit for deposition as inert waste. Se leaching exceeded the category 3 [1] limit for use in constructions, and the level in CFA. V also exceeded the leaching from CFA. SO_4 leaching remained below target limits and in most cases below the leaching from CFA. Ni leaching remained below or was reduced to below 20 µg/L by most experiments, however after one experiments (15) Ni leaching increased to exceed the limit for use in constructions and that of leaching from CFA. This behavior seems to have no correlation with initial batch, treatment time or current density, and needs further attention. Hg leaching remained rather unchanged during treatment and thus still exceeded category 3 [1] limits slightly after treatment of residue from which it exceeded the limit prior to treatment.

Leaching of Pb, Zn, Cl and Na was reduced significantly in all experiments irrespective of treatment time, current density and batch of APC residue. In some cases Zn (experiments 14 and 15) and Na (experiments 1-7) leaching was reduced to below target values and even below the leaching from CFA for Zn in experiment 15. In most experiments, however, leaching remained above target values for the two elements, which was also the case for Pb and Cl in all experiments. There was a tendency towards higher Na and Cl leaching in the experiments made in the later phase of the project. At this stage, testing of the stack for malfunctions had been introduced to avoid damage on membranes. The present results bring suspicion about that the NaCl from the tests was not fully removed from the system prior to experiments, and contributed to the leaching from the final product.

TABLE 10

LEACHING FROM SD MSWI APC RESIDUE AFTER ED TREATMENT. *ITALIC*: NO CURRENT APPLIED. **BOLD**: THRESHOLD VALUES EXCEEDED. AVERAGE OF TRIPLICATE ANALYSIS OF ONE SUBSAMPLE EXCEPT: *AVERAGE TRIPLICATES O TWO DIFFERENT SUBSAMPLES OF THE BATCH.

Exp.	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±0.8*	10.2±0.2*	11.9 0.3*
As (µg/l)	< 20	<20	<20	_<20_	<20	<20	<20	<20*	<20	_<20*_	<20*	<20*	<20*	<20*	<20	<20*
Ba (mg/l)	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 (µg/l)	< 20	<20	<20	_<20_	<20	<20	<20	<20*	<20	_<20*_	<20*	<20*	<20*	<20*	<20*	<20*
Cr (µg/l)	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 (µg/l)	23	49	<20	_39_	50	<20	<20	34±21*	40	_63±81*_	67±47*	65±64*	141±3*	83±79*	32	44
Hg (µg/l)	-	-	1.0	-	-	-	-	-	-	-	-	-	-	-	0.8	__1.7__
Mn (µg/l)	<20	<20	<20	_<20_	<20	<20	<20	<20*	<20	_<20*_	<20*	<20*	<20*	<20*	<20*	<20
Mo (µg/l)	-	-	-	-	-	-	-	658	-	_239_	421	219	211±74*	317±225*	708±81*	249±166*
Ni (µg/l)	__307__	<20	<20	_<20_	<20	<20	<20	<20*	<20	_<20*_	<20*	<20	<20	<20	72	<20
Sb (µg/l)	-	-	-	-	-	-	-	__40__	-	___35___	__32__	__33__	__61__	__42__	__58±32*__	__51__
Se (µg/l)	-	-	-	-	-	-	-	__251__	-	___102___	__183__	__117__	25	__104±18*__	__379±441*__	317
V (µg/l)	-	-	-	-	-	-	-	__562__	-	___311___	__490__	__397__	__402__	__540__	__662__	__820__
Pb (mg/l)	__13__	__12__	__14__	___23___	__24__	__12__	__62__	__18__	__6__	___11±2*___	__14±5 *__	__11±3*__	__21±4 *__	__1.5__	__1.0__	__149 ±23*__
Zn (mg/l)	__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 (g/l)	__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__
F (g/l)	-	-	-	-	-	-	-	1.3	__11.7__	_2.4_	1.6	__6.3__	0.8	1.0	-	-
Na (g/l)	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 (g/l)	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*

Leaching of target elements before and after ED treatment and additional treatments (washing, aeration and carbonization) is illustrated in table 11 and figure 10 for the three different residues by average of final values (after wet storage) of all treatments with standard deviations shown. For most of the constituents reported in figure 10, the standard deviation on results after ED treatment was higher than before treatment. This may result from more samples having been analyzed after the multiple treatment experiments, but may also signal that the parameters varied among the experiments (time and current density) influenced the results. This is investigated later in this section.

For Cr, leaching increased by any treatment, however exceeding regulative limits only for FA and W, while not for SD, after ED treatment. After carbonation, leaching from SD, however, also exceeded legislative limits.

Pb leaching was reduced by ED treatment, but there was no significant difference between the average Pb leaching after ED treatment and the reference experiments with no current applied, also the average leaching after ED treatment had not been reduced more than by simple washing. Combinations of ED with carbonation, aeration or washing, however, reduced Pb leaching significantly beyond what was obtained by washing or other co-treatments alone. The best result was obtained after carbonation. There was an indication of better reduction when applying aeration, as the Pb leaching was reduced to a slightly lower level from an initially higher level by this treatment than by ED or washing alone. This may suggest that the simultaneous aeration during ED induces carbonation into the residue with ED. Target levels were met after combined carbonization and ED as well as after ED of the W residue. For the residue from Vestforbrænding, it seemed that mixing the FA with scrubber sludge prior to ED improves leaching reduction of Pb as compared to treating the FA alone.

Zn leaching appeared to behave very similarly to Pb leaching. Like for Pb, combinations of treatment by ED with carbonation, aeration and washing improved results beyond what could be obtained by any of the treatments alone. And also for this element, the best treatment was obtained by combination of carbonation and ED.

In contrast combined treatments had no effect on Cl leaching. Cl leaching remained at more or less the same level after any treatment, far above levels feasible for use as substituent in construction materials. Finally, SO_4 leaching was high only in the W and FA residues, and from those it decreased to acceptable levels by the ED treatment. No significant effects could be monitored from the combined treatments or the application of current to the SD residue, which had a relatively low SO_4 leaching from the start.

TABLE 11
LEACHING AFTER ED TREATMENT OF APC RESIDUE 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/L]; BA, PB, ZN: [mg/L]; CL, NA AND SO4: [g/L]. 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	8.9±0.1	10.1±0.1	11.9±0.4	10.6	11.5±0.6	10.5	10.8±0.2
As (μg/l)	37	<20	<29	<20	<20	**58**	<20
Cd (μg/l)	20	<20	<20	<20	31	<20	<20
Cr (μg/l)	**1838**	**991±234**	341±146	410	**974**	105	482±183
Cu (μg/l)	<20	37±14	28±25	26	<20	28	57±23
Mn (μg/l)	16	<20	<20	<20	<20	<20	<20
Mo (μg/l)	-	704±76	497±16	-	-	400	691±22
Ni (μg/l)	<20	**<193**	<47	<20	<20	<20	<37
Sb (μg/l)	**118**	**337±136**	94±58	-	-	**225**	<40
Se (μg/l)	**344**	**<56**	<20	-	-	<20	**<204**
V (μg/l)	-	**135±177**	**264±339**	-	**418**	21	**<527**
Ba (mg/l)	0.5	0.8±0.9	2.6±0.1	0.9	0.6	1.3	1.8±0.6
Pb (mg/l)	0.1	**1.8±2.2**	**18±11**	<0.020	0.038	**1.3**	**0.40±0.35**
Zn (mg/l)	0.4	0.2±0.0	**3.5±2.8**	0.1	0.08	0.8	0.12±0.07
Cl (g/l)	**5.8**	**14±11**	**20±7**	**14**	**7.1**	**9.5**	**12±0**
F (g/l)	-	-	-	-	-	-	1.3
Na (g/l)	**2.8**	**3.6±1.1**	**3.1±0.6**	1.3	-	1.4	**1.8±0.1**
SO_4 (g/l)	1.6	1.9±0.4	1.0±	1.0	0.9	1.0	0.9±0.0

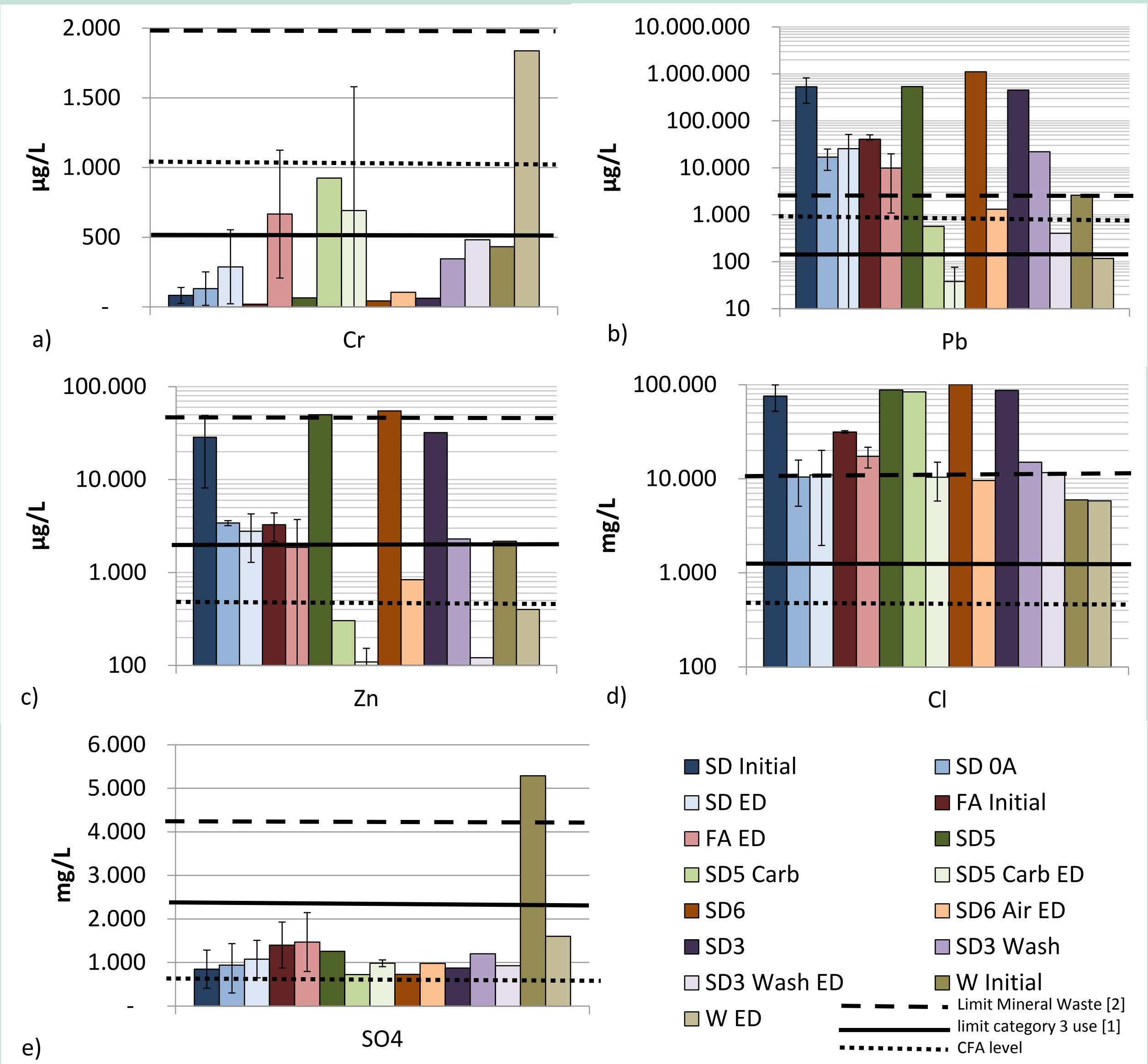

FIGURE 10

AVERAGE LEACHING AND STANDARD DEVIATION BEFORE AND AFTER ED TREATMENT: SD INITIAL: AVERAGE OF SD BATCHES 1-6. SD 0A: AVERAGE OF EXPERIMENTS 4 AND 10. SD ED: AVERAGE OF EXPERIMENTS 1-3, 5-9, 11-16. FA INITIAL: AVERAGE OF FA BATCHES 1-2. FA ED: AVERAGE OF EXPERIMENTS 17-19. SD5 CARB: LEACHING FROM SD5 AFTER CARBONIZATION, CARB ED: AVERAGE OF EXPERIMENTS 20-21. SD 6 AIR ED: LEACHING AFTER EXPERIMENT 22.

3.1.4 Leaching as a function of time and current density

Leaching of Pb, Zn, Cr, Cl and SO4 is illustrated in figure 11 as a function of time for experiments 8-12. In these figures, the results are those of samples which have – most of them - been filtrated immediately after having been taken i.e. without wet storage. The procedure has, however, not been 100% consistent, as the time of storage prior to filtration was not anticipated to impact results, thus some samples, and in particular those taken by the end of the experiment were not filtered immediately.

The figure shows that Pb leaching was reduced from 334 mg/L to around 10 mg/L during the first 0.4h almost independently of current density (figure 5a). This effect must primarily be an effect of the dissolution 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. The leaching reduction was however a bit higher than by mere washing (by which leaching was reduced to 22 mg/L – see table 8) except for the 4A experiment after which the leaching was reduced to a similar level as by washing, thus an added effect of the application of dialysis may be seen. There was no visible difference between the 0A experiment and the 1A experiment. The 2A experiment however seemed to have a bit higher reduction. Thus the main effects must be 1) washing, 2) dialysis and 3) the effect of the current application is only tertiary. Even beyond the first 0.4 h, no significant difference in the development between experiments with different current densities was observed. Only a weak tendency of improved reduction for the 1A experiment, which apparently dropped to 1 mg/L after 2.7 h, was observed. Apart from that, Pb leaching remained rather constant around 5-10 mg/L in all experiments. Leaching increased again during post experimental storage of the diluate, particularly for the 0A, 1A and 2A experiments to 16-18 mg/L (results not shown in figure), while the reduced leaching seemed to be more permanent in the 4A and 6A experiments, after which it remained at approximately 13 and 6 mg/L respectively. Thus the short treatment at 6A resulted in lower permanent leaching than longer treatment at lower current densities. Leaching, however still exceeded the legislative limit (category 3 [1]) by 60 times.

Zn leaching also reduced significantly during the first 0.4h of the experiments from 25 mg/L to around 1-4 mg/L (figure 5b), which was the same level as obtained by washing. The development for Zn seemed, however, to be more dependent on current density, with the lowest reduction obtained in the 0A and 1A experiments. Further, no significant change in leaching during post experimental storage was observed for Zn. Although somewhat unstable during time, the highest reduction was obtained in the 2A experiment, which at several points was below the legislative limit of 1.5 mg/L, and which also had the lowest permanent reduction to 2.6 mg/L.

In contrast to Pb and Zn, Cr leaching (figure 5c) increased significantly during the first half hour of treatment from 63 µg/L to 600-1,000 µg/L, which was a markedly higher increase than observed after washing (table 8). 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 (63-96 µg/L after all five experiments).

Cl leaching reduced during the first 0.8h of the residence time in all experiments (figure 5d) to levels approximately 10 times lower than what was observed after washing. Like Zn, also Cl reduction appeared to depend on current density as the highest reduction was obtained in the 4A experiment, followed by the 6A experiment. The only experiment which reached a leaching below the regulatory limit was the 4A experiment after 0.3 and 0.8h, 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/L for the 0-2A experiments, while it remained at 8 g/L in the 4A experiment. The lowest permanent leaching was obtained after the 6A experiment: 5 g/L: well below the initial value, the level obtained by washing and just above the legislative value of 3 g/L (category 3) [1], however still several size orders higher than leaching from CFA.

Like Cr leaching, SO4 leachability increased during the first half hour of the experiments, and then remained rather constant during all experiments at 1000-1400 mg/L, almost identical to what was obtained by washing. The post treatment storage of the diluate, though, caused SO4 leachability to decrease further to levels as low as 3-8 mg/L.

The changes in leaching behavior due to post treatment storage are not fully understood and should be studied further. It is however evident that the final product after ED is not a stable product, but changes properties while in contact with water and atmospheric air. This finding may be a severe constraint to the use of the material in construction materials, as such must be able to persist and show unchanged environmental performance in humid conditions. A further statistical analysis could potentially highlight which treatment worked better, and therefore we decided to make Multivariate Analysis to reveal any correlations.

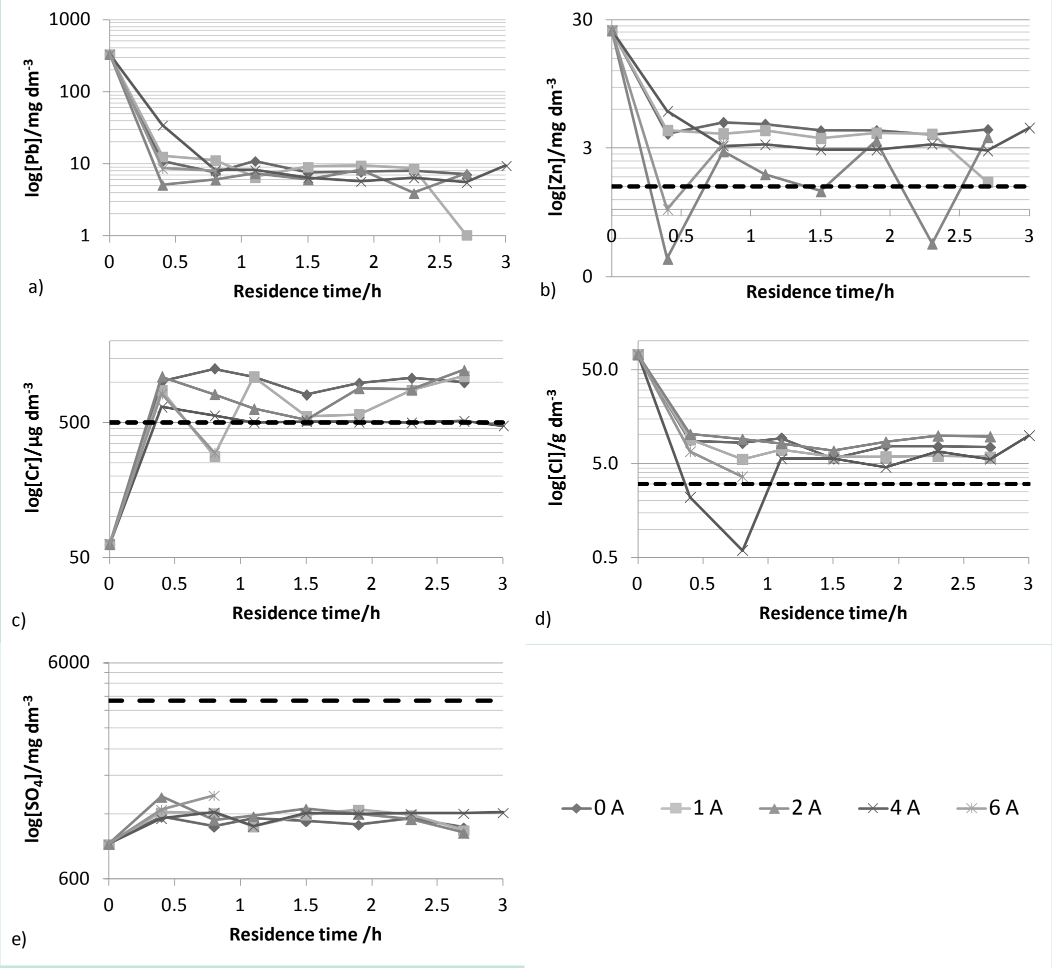

FIGURE 11
LEACHING OF PB, AND ZN, CR, CL AND SO4 AS A FUNCTION OF TIME AND CURRENT DENSITY (EXPERIMENTS 8-12).

3.1.5 Multivariate analysis

In general PLS calculations which included Na and Cl final concentrations yielded poor models (R2Y<0.3; Q2=0) and it was decided not to proceed with evaluating the influence of variables on the results of these two elements, since this may lead to misinterpretations of the data.

The PLS models that included the results of Pb, Zn and SO_4 were fairly good and although the R2Y values were in the lower range, and caution was made in the evaluations of the model, it was possible to observe some general trends. Since the data included more than two settings in the discrete variable ‘treatment prior to ED’, the PLS models were calculated in three blocks:

1. Experiments with no additional treatment to ED, to evaluate the influence of initial concentrations of salts and heavy metals, current density and retention time on ED.
2. Testing the influence of wet storage with experiments with no additional treatment as reference. The influence of initial concentrations, current density and retention time was also evaluated.
3. Evaluating the influence of pre-washing with the experiments of no prior treatment as reference. The influence of initial concentrations, current density and retention time was included in the PLS model.

For each block, PLS models of all elements (total model) as well as of each element (individual models) were calculated. Not enough data existed to statistically evaluate the influence of carbonation and aeration.

3.1.5.1 Influence of variables in experiments with no additional treatment

A weight plot, illustrating the contribution of each variable in the X matrix to the description of the systematic variation in the Y space, reveals that Pb and Zn are located close to one another indicating similar trends in variable importance and settings for Pb and Zn (see figure 12). SO_4 is located opposite Pb and Zn with regards to the first axis indicating opposite trends in variable settings. These primary conclusions are further supported in the VIP and coefficient plots of the individual models (figure 13-14).

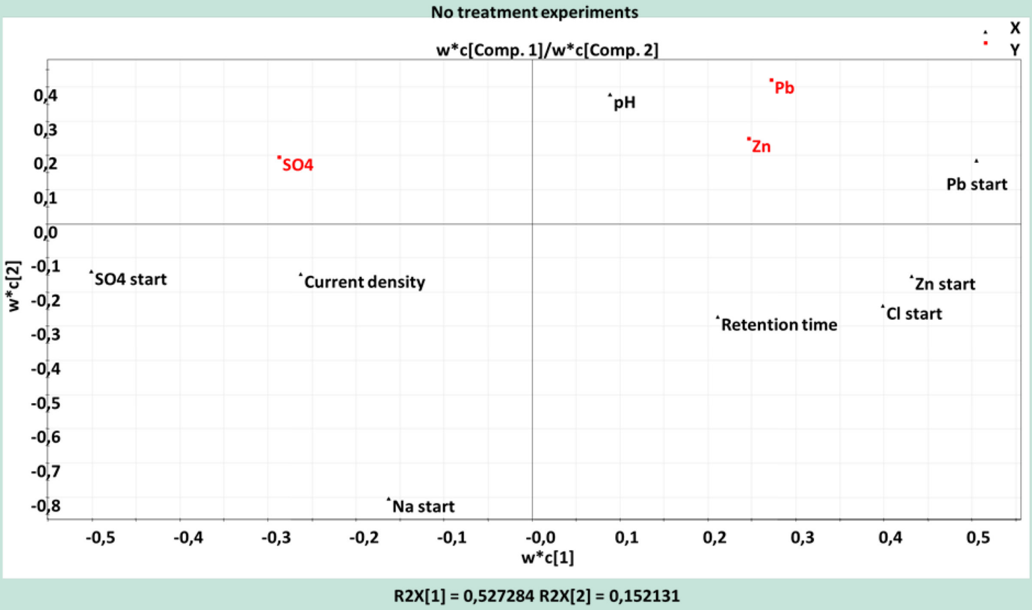

FIGURE 12
WEIGHT PLOT FOR EXPERIMENTS WITHOUT PRIOR TREATMENT. VARIABLES LOCATED CLOSE TO ONE ANOTHER HAVE SIMILAR VARIATION IN THE MULTIVARIATE SPACE.

The VIP plots (figure 13) for Pb, Zn and SO_4 illustrate that the initial concentrations of salts and heavy metals are far more important for the leaching concentrations than current density and retention time during ED. Interestingly, the coefficient plots (figure 14) for the three individual models illustrate that opposite settings for the two heavy metals and SO_4 are necessary to achieve low final leaching concentrations. Low initial concentrations of Pb, Zn and Cl thus results in low final leaching concentrations of Pb and Zn and high final leaching concentrations of SO_4. Opposite settings of current density and retention time will also lead to low leaching concentrations of heavy metals and SO_4.

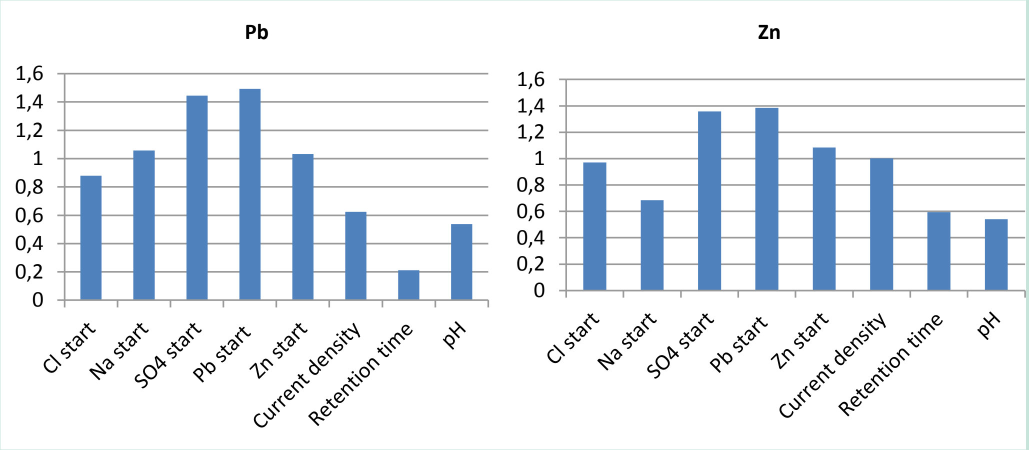

FIGURE 13
VIP PLOTS FOR Pb AND Zn BASED ON INDIVIDUAL MODELS. HIGH VIP VALUES HAVE THE HIGHEST INFLUENCE (POSITIVE OR NEGATIVE) ON THE EFFICIENCY OF ED.

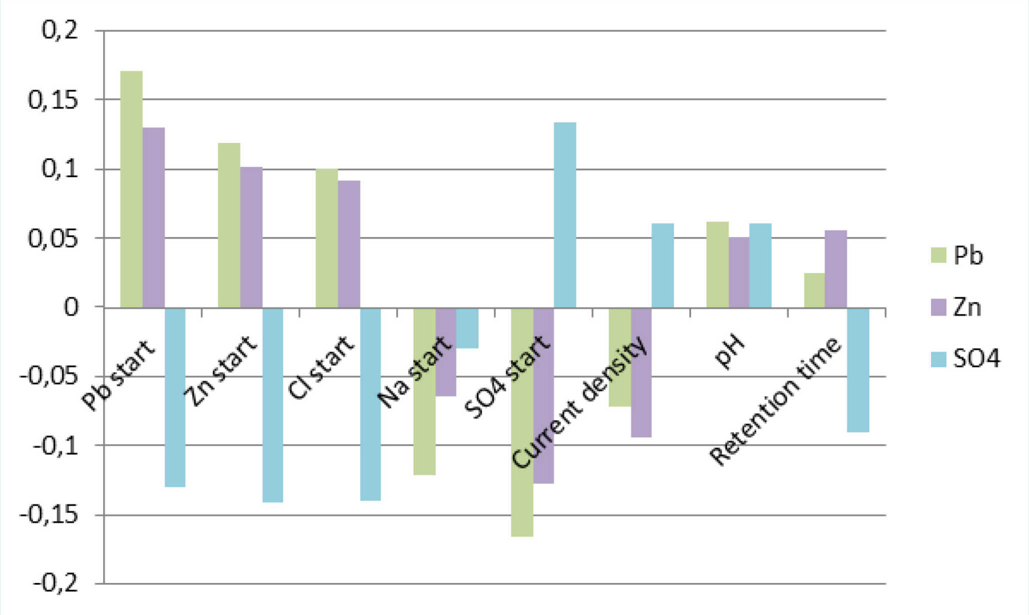

FIGURE 14
COEFFICIENT PLOTS OF THE INDIVIDUAL PLS MODELS.

3.1.5.2 The influence of wet storage

The VIP plots of the individual PLS models (figure 15) based on the second block of data, illustrate that the initial concentrations of heavy metals and salts have the highest influence on the efficiency of the ED treatment. The influence of wet storage is small in comparison. The coefficient plots in figure 16 reveal the same trend as above that similar settings decrease the final leaching concentrations of Pb and Zn, while opposite settings decrease the leaching concentrations of SO_4.

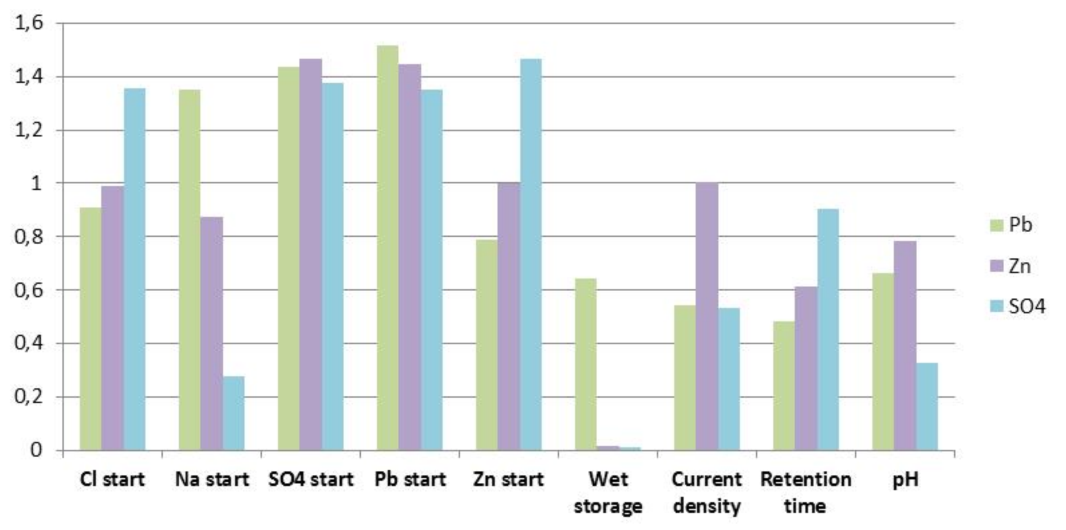

FIGURE 15
SUMMARY OF THE VIP PLOTS FOR THE THREE INDIVIDUAL PLS MODELS.

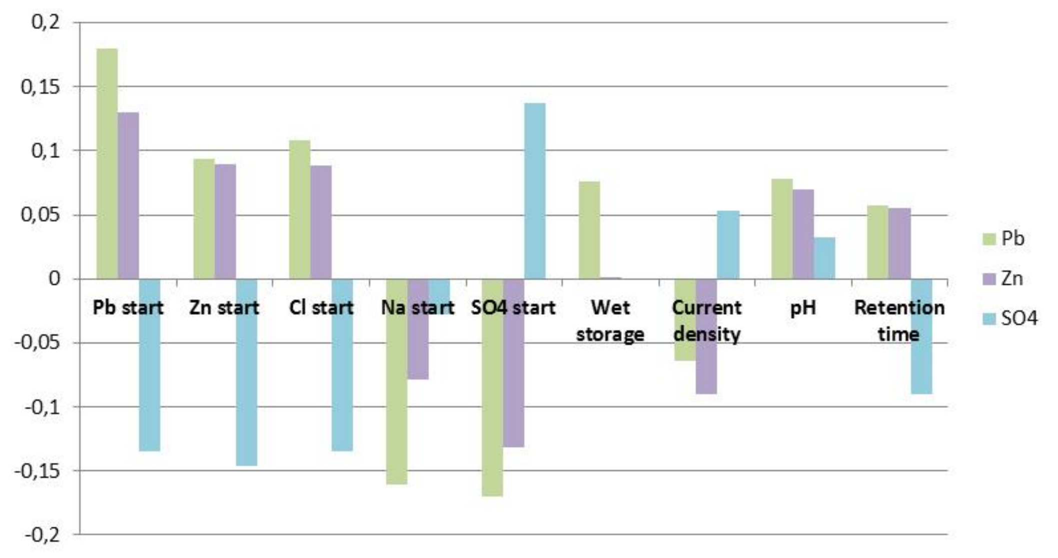

FIGURE 16
COEFFICIENT PLOTS OF INDIVIDUAL PLS MODELS.

3.1.5.3 Influence of washing

The individual PLS models of the third data block (figure 17) reveal that pre-washing has the highest influence on the efficiency of ED in comparison to the initial concentrations in the batches as well as in comparison to the experimental variables current density and retention time. The coefficient plot (figure 18) illustrates that pre-washing decreases the final leaching concentrations of all three components.

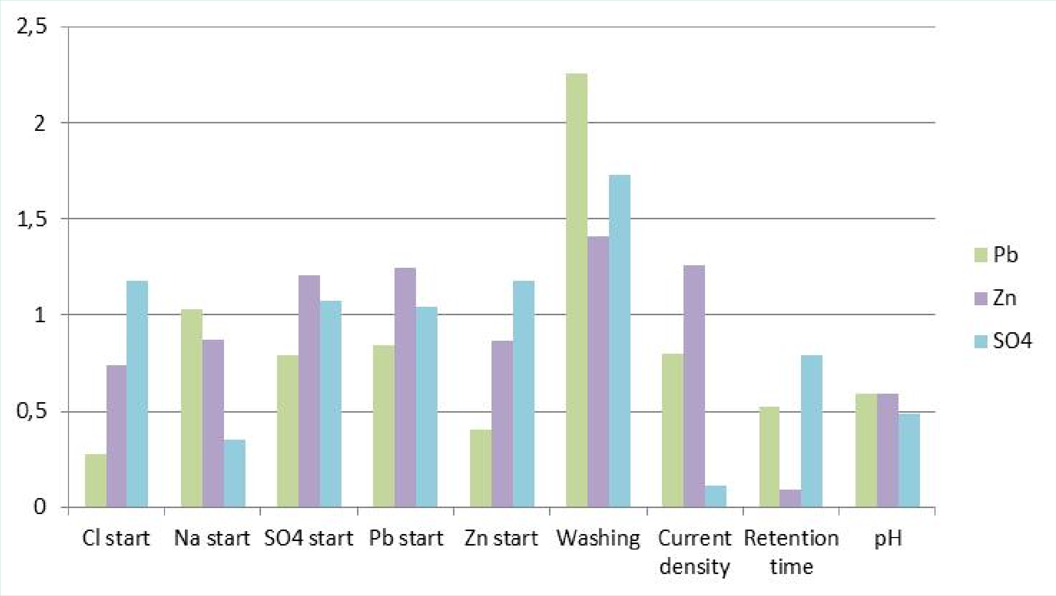

FIGURE 17
SUMMARY OF VIP PLOTS IN INDIVIDUAL PLS MODELS EVALUATING THE INFLUENCE OF PRE-WASHING.

FIGURE 18
COEFFICIENT PLOTS OF INDIVIDUAL PLS MODELS EVALUATING THE INFLUENCE OF PRE-WASHING

In conclusion the pilot scale experiments showed that although it was possible in single experiments to reduce leaching of all elements to levels close to or beneath target values, it was not possible to reduce leaching off all target elements by adjusting current density, treatment time: Experimental conditions and pre-treatments affected different target elements differently. Final pH was observed to be a major factor for the leachability of several target elements. Initial leaching significantly in general affected final leaching, thus as leaching was in general lower from raw FA and W than from raw SD, this was mirrored in lower leaching obtained after ED treatment of FA and W compared to SD. Combining pre-washing, aeration and in particular carbonation with ED reduced leaching from SD significantly more than any of the treatments alone. Further development should be made with combined treatments of FA and W, while it is recommended not to use semidry air pollution control systems if the residue is intended for any kind of use. The observed effect of combined ED and aeration is interesting and should be further investigated.

3.2 Laboratory scale experiment

Two sets of laboratory experimental investigations were made 1) to reveal any influence of the membrane type used (reported in section 3.2.1); 2) to reveal any influence of the experimental setup used (reported in section 3.2.2.).

3.2.1 Treatment with different membrane types

During the ED remediation with one of the membranes (Excellion), liquid flows between the compartments were observed. After contacting the manufacturer, it was determined that the membranes were degraded by the use of nitrate solutions in the electrolyte compartments (I, II and IV). Specifically, a water permeability as high as 0.01327 mL/(min·cm^2·psi) was detected (the normal value would be below 0.0005 mL/(min·cm^2·psi)). The lack of function when subject to contact with nitrates renders this membrane brand unsuitable for the ED remediation of APC residues. Therefore, Excellion results are not analyzed further in this report.

Table 12 shows the leaching results of SD and FA after ED treatment with the other membranes. Leaching values reduced after the ED treatment regardless of the membrane used, except for Cr for which it consistently increased; and SO_4 for SD, which showed a slight increase. There was a significant difference between the results obtained with different membranes for Cr, Pb and Zn for SD, while opposite for Cl and SO_4 for the FA. For the SD the best reduction was obtained with the Ionics and Neosepta membranes for Pb and Zn, and with the Neosepta and Ralex membranes for Cr. Significantly lower Pb leaching was observed from the SD after the laboratory scale experiments with Ionics and Neosepta membranes than from the pilot scale. This difference, however, cannot be explained by the influence of the membranes, as the Neosepta membranes were the ones used in the pilot scale. As the laboratory scale experiments were run with similar retention time and current density as the pilot scale experiments these variables do also not explain the difference. It may be speculated that more efficient circulation of the residue in the treatment unit could be an explanation, but this needs further investigations to verify. Nevertheless the laboratory scale results suggest that leaching reduction approaching target values may be obtained by redesign of the treatment unit. How exactly this should be done is beyond the scope of this project.

Even more so, the results for FA support this hypothesis by showing significantly lower leaching for Cr, Pb, Zn and Cl despite membrane type than what was observed in pilot scale. Again this cannot be explained by the difference in membrane type used or experimental setting, as these parameters were identical to the pilot scale experiments, thus a redesign of the treatment unit may improve the technology significantly.

TABLE 12
METAL AND SALT LEACHING FROM FA ACCORDING TO DS/EN 12457-1 (MEAN VALUE±STANDARD DEVIATION)
VALUES EXCEEDING CATEGORY 3 [1] LIMITS IN BOLD.

Compound (Units)	Ionics	Neosepta	Ralex	ANOVA: Mean values different?
SD After treatment				
pH	**12.1**	**12.1**	**12.1**	-
Cr (µg/L)	**1,240±45.2**	**757±39.5**	**881±77.3**	Yes
Pb (µg/L)	**3,960±27.7**	**3,510±813**	**13,600±1,260**	Yes
Zn (µg/L)	**4,480±132**	**4,380±445**	**5,990±406**	Yes
Cl (mg/L)	**8,280±250**	**8,870±264**	**8,690±363**	No
SO_4 (mg/L)	1,340±30.1	1,320±7.14	1,330±33.6	No
FA After treatment				
pH	11.1	11.1	11.1	-
Cr (µg/L)	430±43.7	482±49	461±46.2	No
Pb (µg/L)	**473±742**	**132±127**	34±6.11	No
Zn (µg/L)	568±257	460±130	269±18.6	No
Cl (mg/L)	1,360±24.9	1,370±20.5	1,560±56.2	Yes
SO_4 (mg/L)	1,630±3.49	1,660±34.9	1,810±35.9	Yes

3.2.2 Leaching before and after treatment in different cell setups

The heavy metal leaching before and after the electrodialytic experiments in relation to pH measured in the leachate is shown in Fig. 19 along with limiting values category 1 [1] (C1) and category 3 [1] (C3). The results confirm those of the pilot scale experiments (chapter 3.1.3) and the membrane study (chapter 3.2.1) in that leaching form FA is lower than from SD, and that leaching could be reduced more from FA than from SD. In contrast to the pilot scale experiments, the leaching limiting value C3 was successfully met for both Cd, Cr, Cu, Pb and Zn in several of the experiments (FA-2-0.1-7D, FA-3-1-7D, FA-3-0.1-14D and FA-3-0.1-7D) where the leachate pH was between 10.5 and 11.5. For the SD APC residue the C3 values for heavy metal leaching was also met in one experiment (SD-3-0.1-14D) at leachate pH 10.5. Clearly a connection between pH and leaching is found, which is in accordance with what was observed in the pilot scale experiments – here the lowest leaching of Pb and Zn from SD was observed after treatment by experiment 15 (though not meeting C3 requirement for neither Pb, Cr or Cl), after which pH of the residue was 10.2, while pH was 11 and above after all other experiments.

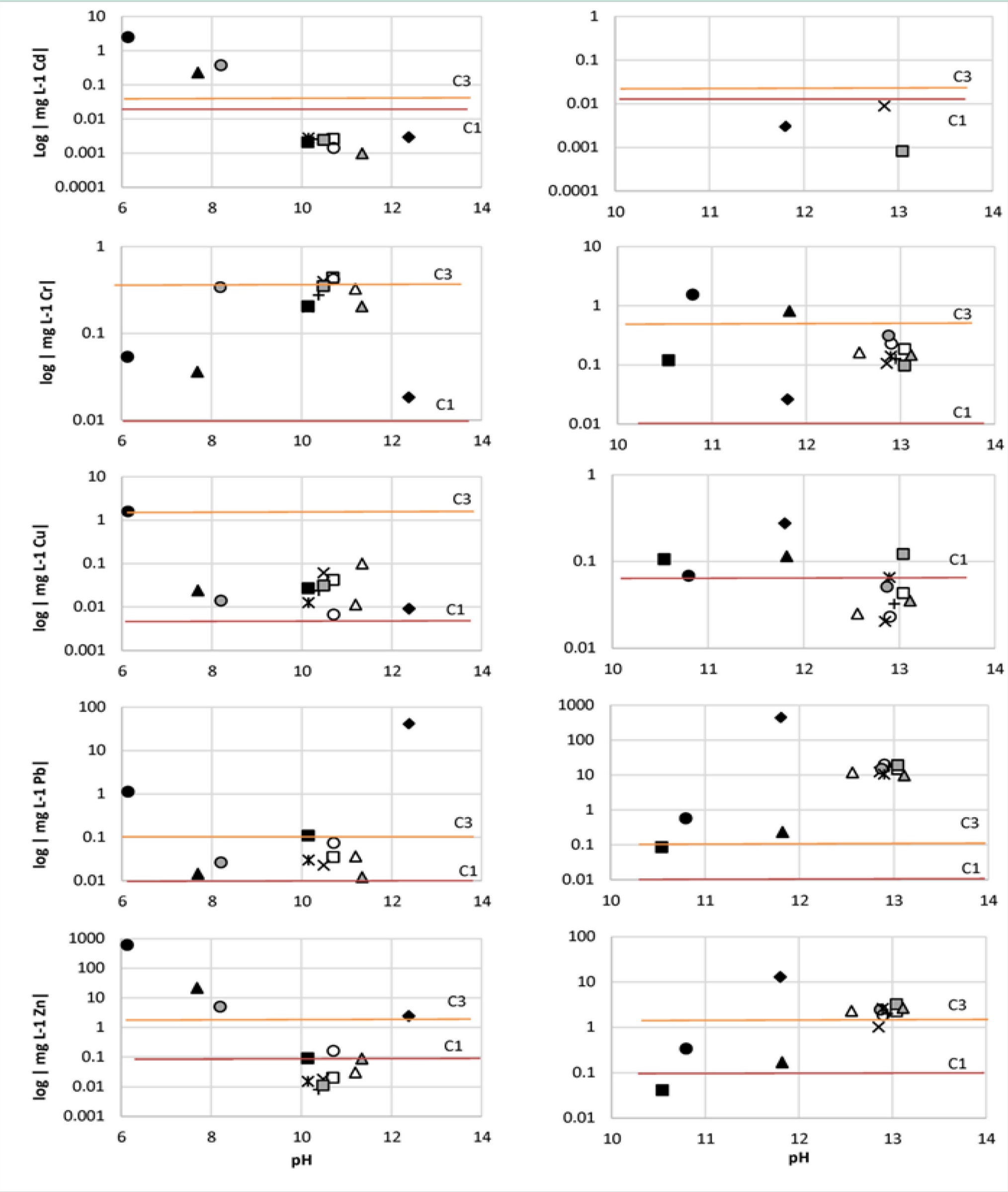

FIGURE 19
LEACHING OF HEAVY METALS BEFORE AND AFTER ELECTRODIALYTIC REMEDIATION FOR FA (COLUMN 1) AND SD (COLUMN 2). C1 AND C3 ARE LEGISLATIVE LIMITS TO MEET RESTPRODUKTBEKENDTØRELSEN [1] FOR CATEGORY 1 AND CATEGORY 3 USES, RESPECTIVELY.

The concentration of leached chloride after the electrodialytic experiments is shown in Fig. 20, together with the C1 and C3 values for chloride. Contrarily to the heavy metals, chloride leaching was not pH dependent but availability controlled. The chloride leaching was significantly reduced in all the electrodialytic experiments for both the MSWI residue types and for both cell types. For the fly ash, which had the lowest initial chloride content, the chloride leaching was reduced to below C3 in all experiments, which means that for four experiments, both the measured heavy metals and chloride leaching levels complied with the regulative limits C3. The Cl limiting value for C3 was fulfilled for two of the experiments (SD-3-1-7D and SD-3-1-14 D), but the heavy metal leaching was not below the limit for these two experiments. For Cl leaching there seems to be a difference between the two cell types, with generally lower final leaching of Cl from the residues when using the 3 compartment cell. The amount of Cl in the suspension liquid at the end of the ED experiments was higher in the experiments with the APC residue than with the fly ash (results not shown). There was a general tendency for a higher amount of Cl in the suspensions with the 2 compartment cell, which means that the oxidation of chloride directly at the anode is not as efficient as electromigration for removal of Cl from the suspension.

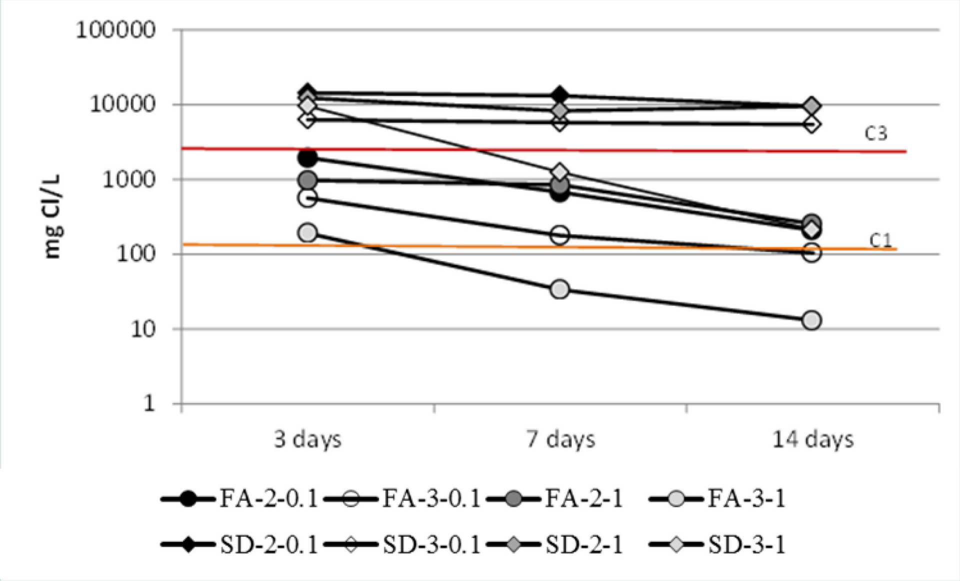

FIGURE 20
CHLORIDE LEACHING IN THE MSWI RESIDUES AFTER THE ED EXPERIMENTS. C1 AND C3 ARE LEGISLATIVE LIMITS TO MEET RESTPRODUKTBEKENDTØRELSEN [1] FOR CATEGORY 1 AND CATEGORY 3 USES, RESPECTIVELY.

3.3 Use of MSWI APC as substituent in mortar

3.3.1 SEM/EDX

The morphology of the raw and ED upgraded APC residue is visualized by SEM/EDS images in Fig. 21. A visual analysis of incineration residue can itself give an indication of the efficiency of combustion, as well as any process required to give the material a final destination. Figure 21 shows that the APC residues particles are mostly of a small shape, of two different types: particles of type (X) have a spherical shape. They are formed in the combustion chamber and composed of aluminosilicate matrices. Particles of type (Y) appear highly polycrystalline from the processes of condensation as the gases cool down. According to Quina (2005) [43] the smaller particles are composed of Si and Al, intermediate particles are fewer in number and comprises Pb and Hg, and the larger particles contain higher amounts of Fe, Cr and Ni. Iretskaya et al. (1999) [44] observed that by leaching the microporosity of the particles increased, due to the removed salts. They also noted that small particles could remain adsorbed on the surface of the largest particles. Furthermore, Le Forestier & Libourel (1998) [45] observed particles from different origins (scrubbers, for instance) and found various forms such as flakes, prisms, needle shaped, sintered pellets and spheres. Eighmy et al. (1995) [46] found out that after leaching processes existence of spherical particles was evident which were composed of aluminum silicates, deposited on volatile elements such as Cl, K, Zn, Na, S and Pb. In Fig. 21 changes are clear from the form of raw residue to upgraded residue. The largest changes in shape occurred for experiences with 2C cell design (Fig. 21 c, d, e and f).

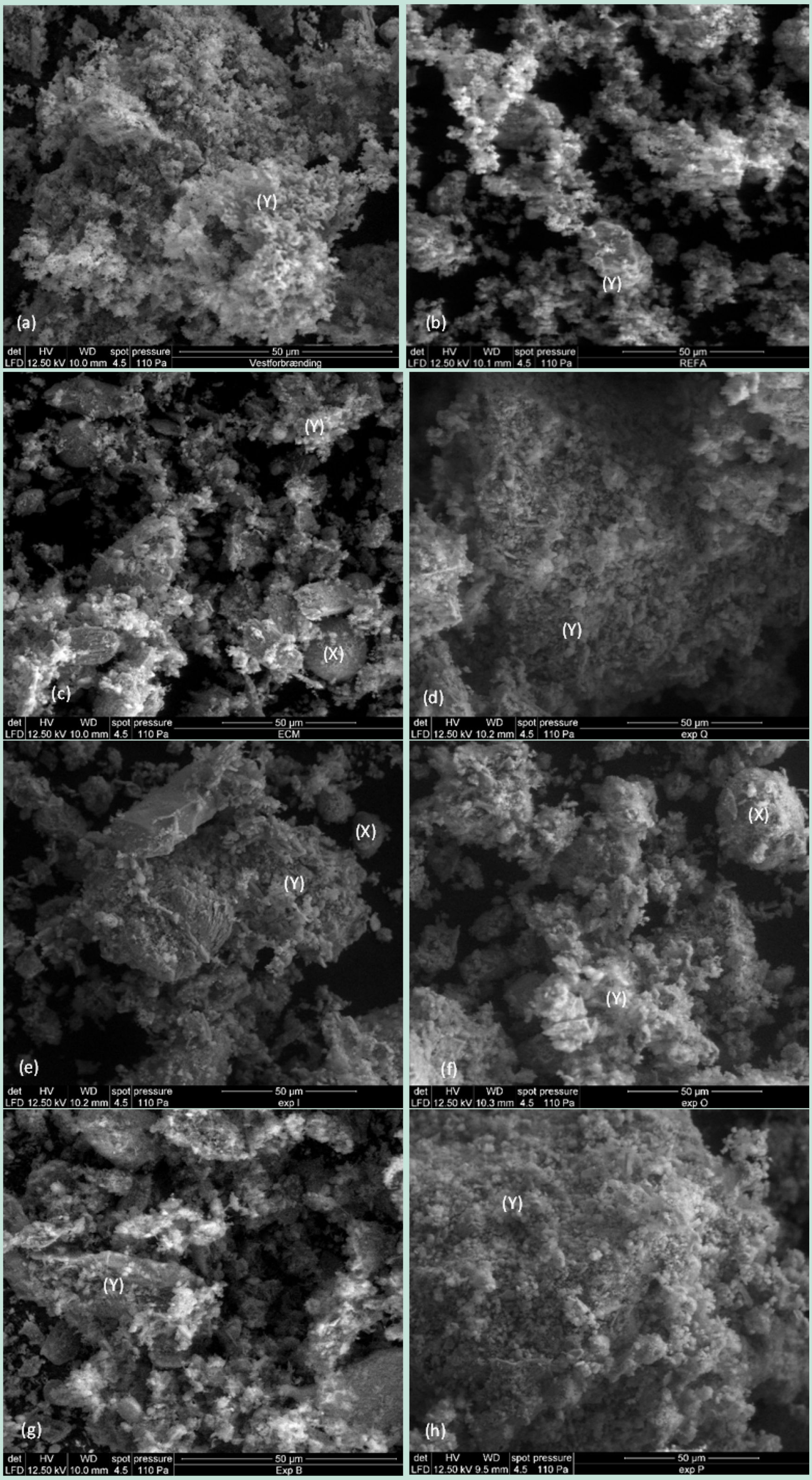

FIGURE 21

IMAGES OF SEM BEFORE ED TREATMENT: (a) RAW FA, (b) RAW SD3; AFTER ED TREATMENT (7 DAYS OF DURATION TIME): (c) FA-2-0.1-7, (d) SD-2-0.1-7, (e) FA-2-1-7, (f) SD-2-1-7, (g) FA-3-0.1-7, (h) SD-3-0.1-7. MAGNIFICATION: 1000X; (X) - GLASS PARTICLES, (Y) - POLYCRYSTALLINE PARTICLES.

3.3.2 Porosity and density and compressive tests

Table 13 presents the porosity and density values obtained for the tests on mortar bars after 28 days of curing time. Compared to the reference mortar without APC residues the porosity increases slightly when substituting with APC residues. Porosity is directly related to the amount of water. Thus, having an increased amount of water will increase the porosity. The increase in porosity may be explained by the heterogeneity of the waste in relation to the cement particles. The porosity will increase when the particle size of ash is higher than the dimensions of the voids created by the bars particles, thus not fulfilling the existing voids and increasing porosity. The results indicate that the results are more similar to the reference with substitution of cement for FA substitution than with SD.

TABLE 13
POROSITY AND DENSITY OF SPECIMENS: REFERENCE; SUBSTITUTION 5% OF RAW AND UPGRADED APC RESIDUES FA AND SD3 AS CEMENT. ρ_d = TOTAL DENSITY , ρ_f = SOLID MATTER DENSITY.

Mortar sample	M_{Ref}	M_{FA}	$M_{FA-2-0.1}$	M_{FA-2-1}	$M_{FA-3-0.1}$	M_{FA-3-1}	M_{SD}	$M_{SD-2-0.1}$	M_{SD-2-1}	$M_{SD-3-0.1}$	M_{SD-3-1}
Porosity (%)	16	18	17	17	18	18	18	18	18	18	17
ρd (kg m^{-3})	2146	2085	2113	2118	2119	2109	2115	2133	2110	2102	2129
ρf (kg m^{-3})	2558	2544	2541	2579	2547	2557	2553	2592	2571	2574	2587

Both the total and the solid matter densities were very close to the densities of reference concrete which are 2100 and 2650 kg/m^3, respectively.

Compressive strength of the mortar after 28 days is illustrated in figure 22. It can be seen that when substituting cement with raw FA, the compressive strength drops, while in general, the compressive strength was not affected if the FA had been subject to ED treatment prior to substitution. The opposite is the case for SD: the compressive strength was not affected by substituting cement with raw residue, but it was significantly reduced, if the SD had been ED treated. As compressive strength above 12 MPA is acceptable (according to EN 206-1) for concrete depending on the use, all the tested mixtures are acceptable for some uses and most of them even for the most critical uses which require 40 MPa as to what regards this parameter. Replacement of cement by FA can be seen to result in lower loss of strength than by replacement with SD.

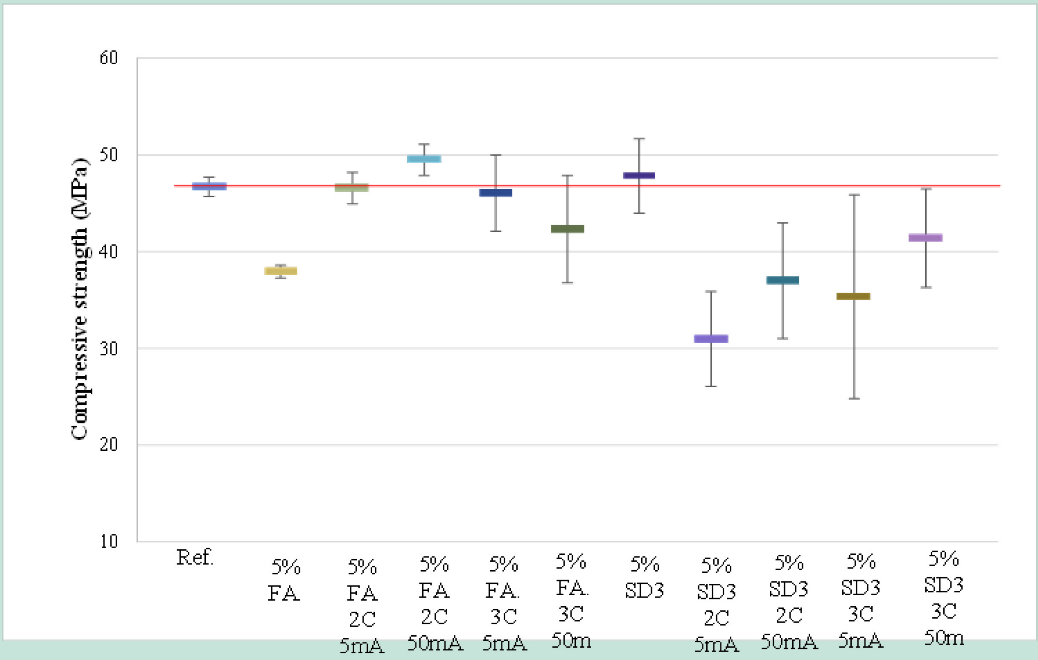

FIGURE 22
COMPRESSIVE STRENGTH OF SPECIMENS AFTER 28 DAYS CURING FOR MORTAR SAMPLES: REFERENCE; SUBSTITUTION OF 5% CEMENT >BY RAW AND UPGRADED APC RESIDUES (MEAN VALUES ± STANDARD ERROR). RED LINE = REFERENCE LEVEL.

3.3.3 Leaching behaviour

Table 14 presents the values of leached heavy metals for the reference, raw APC residues and the upgraded APC residues. Cd leachability was below detection limit (0.02mg/L) for all samples. For upgraded SD residue, leaching of metals seems to increase, with some exceptions; while for FA it seems that the leaching remains at the reference level with few exceptions – in particular for Cr for which leaching does indeed seem to increase also for FA.

TABLE 14
HEAVY METALS LEACHABILITY FROM CRUCHED MORTAR SAMPLES; EXPERIMENTAL DATA OBTAINED BY PREN 12457-1 ON MORTAR: REFERENCE; SUBSTITUTION 5% OF RAW APC RESIDUES AND UPGRADED APC RESIDUES FROM VESTFORBRÆNDING AND REFA AS CEMENT.

	mg/L	FA					SD3				
	M_{Ref}	M_{FA}	$M_{FA-2-0.1}$	M_{FA-2-1}	$M_{FA-3-0.1}$	M_{FA-3-1}	M_{SD}	$M_{SD-2-0.1}$	M_{SD-2-1}	M_{SD-}	M_{SD-3-1}
Cr	0.04	0.03	0.03	0.03	0.09	0.07	0.05	0.09	0.08	0.07	0.06
Cu	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.01
Pb	0.08	0.05	0.04	0.05	0.15	0.02	0.03	0.01	0.04	0.02	0.07
Zn	0.03	0.02	0.01	0.01	0.06	0.02	0.05	0.07	0.10	0.09	0.05
pH	12.4	12.4	12.4	11.6	12.4	11.1	12.4	12.4	12.3	12.4	12.7

3.3.4 Chloride

The chloride ion promotes the oxidation of iron in the form of rust, causing not only a reduction of the section of the armature, but also an expansion due to iron oxide formation, which ultimately result in the disintegration of concrete, accelerating the corrosion process. Table 15, shows the chloride contents in the reference and in the specimens previously described. The results are in conformity with EN-206-1, European Standard for Concrete – Specification, performance, production and conformity, section 6.2.7 expressing the percentage of chloride ions by mass of cement. The amount of chloride increased after substituting 5% of the cement for APC residue, but the values for upgraded FA were very close to the reference. For upgraded SD the values were higher, with one exception.

TABLE 15
EN 206-1 EUROPEAN STANDARD FOR CONCRETE; AMOUNT OF CHLORIDE IN MORTAR: REFERENCE; SUBSTITUTION 5% OF RAW APC RESIDUES AND UPGRADED APC RESIDUES FROM VESTFORBRÆNDING AND REFA AS CEMENT.

%	FA					SD3				
M_{Ref}	M_{FA}	$M_{\text{FA-2-0.1}}$	$M_{\text{FA-2-1}}$	$M_{\text{FA-3-0.1}}$	$M_{\text{FA-3-1}}$	M_{SD}	$M_{\text{SD-2-0.1}}$	$M_{\text{SD-2-1}}$	$M_{\text{SD-3-0.1}}$	$M_{\text{SD-3-1}}$
0.2	0.4	0.2	0.2	0.2	0.2	0.7	0.7	0.3	0.3	0.2

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Electrodialytic upgrading of MSWI APC residue from hazardous waste to secondary resource

The aim of this project was to contribute to the development of electrodialytic treatment technology of air pollution control residues (APC) from municipal solid waste incineration (MSWI) to obtain maximal leaching reduction by optimization of treatment time and current density for different types of MSWI APC residues. The concept idea was in a pilot scale unit to reduce the mobility of toxic elements and salts by electrodialytic treatment enough for the residual product to constitute an environmentally safe resource for substitution of virgin resources in construction material e.g. for substitution of cement or fillers in concrete.

In general leaching could not be reduced by optimizing current density and treatment time in the pilot scale stack treatment unit, as hypothesized, even though there was evidence of dependency on current density for e.g. zinc, this was not true for most elements, and it was clear that experimental conditions and pre-treatments affected different target elements differently. Statistical analysis of the results revealed that the final pH was the major parameter determining leachability.

The robustness of the stack setup proved to be very limited. At several occasions during the project, the diluate spacers clogged, and areas with high resistance and heat development evolved. Membranes burned and had to be changed.

Because the results of the pilot scale stack experiments did not give the anticipated results and tools for optimized up-scaling, instead laboratory investigations were made on the influence of different membrane brands and influence of different experimental setups.

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