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## Electrodialytically Treated MSWI APC Residue as Substitute for Cement in Mortar



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### ABSTRACT

Air pollution control (APC) residues from municipal solid waste incineration (MSWI) are considered hazardous waste and need pre-treatment prior to possible reuse. Here, two MSWI APC residues, from which the most mobile fraction of heavy metals and salts has been removed by carbonation and/or electro-dialytic remediation, were used in Portland cement mortar. Mortar bars with 15 % weight replacement of cement by APC residues showed compressive strengths up to 40 MPa after 28/32 days. Heavy metal and salt leaching from both crushed and monolithic mortars with APC residues was generally similar and comparable to both the reference mortar and mortar with coal fly ash. These results indicate that electro-dialytic remediation could be used a pre-treatment method for MSWI APC residues prior to reuse in mortar.

**Keywords:** electrokinetic remediation, mortar, leaching, fly ash, heavy metal

## 1. INTRODUCTION

In Denmark municipal solid waste incinerators (MSWI) have air pollution control (APC) systems which generate residues with a high content of salt and leachable heavy metals. Currently, MSWI APC residue is classified as hazardous waste and stabilized and disposed of abroad. Current practice in other countries are either temporary disposal until a treatment method has been found or permanent disposal in hazardous waste landfills, often with pre-treatment (solidification, stabilisation or extraction) of the APC residue [1].

Contrarily to the MSWI APC residue, fly ash from coal combustion is considered a valuable resource to be used in production of cement and as a supplementary cementitious material (SCM) in mortar and concrete. Mortar consists of binder (cement), water and fine aggregate (sand) at a given ratio and is the basis for concrete which is a mix of mortar and coarse aggregate. Up to 5 % of the total global anthropogenic CO<sub>2</sub> is emitted by Portland cement production and the replacement of Portland cement by other binders such as industrial by-products have gained increasing interest [2]. MSWI fly ash or APC residues could potentially be used as binder in mortar and concrete [3], but the content of heavy metals restricts/limits this possibility, mainly due to their mobility [4]. Only a few studies have been made where MSWI APC residue is tested for direct reuse in mortar and concrete, most studies report results for fly ash, without the APC products [1].

Pre-treatment of MSWI APC residues prior to reuse has shown to be difficult, as the method should be able to keep the desired material characteristics and treat the contaminants. Generally two approaches are considered when treating heavy metals in MSWI APC residues prior to potential reuse: stabilization or extraction of heavy metals. Stabilization methods include carbonation, thermal treatments or chemical stabilizations, such as stabilization with phosphates, chelating agents or ferrous compounds. In stabilization, the material characteristics are only altered slightly and the heavy metals are still present in the same quantity but are less available [1, 4]. Extraction techniques include different washing and chemical extraction methods. Acid washing is efficient for removing heavy metals, but drastically alters the pH and material characteristics [1, 4].

An electro-dialytic (ED) upgrading method, where the mobile fraction of heavy metals is removed by an electric current at the MSWI APC residues' original alkaline pH, has shown potential for reducing heavy metal and salt leaching and keeping an alkaline pH in the MSWI APC residue both bench [5] and pilot scale [6]. The principle of electro-dialytic (ED) upgrading is illustrated in Fig. 1.

ED is widely used e.g. for desalination of solutions in industrial scale, but not for suspensions of solid matter. MSWI APC residues in suspension (up to 10% DM) have been subjected to ED. The ED system consists of an ED stack with multiple concentrate compartments (concentrate) and compartments containing the APC residue suspension (diluate). The concentrate and the diluate are pumped through the ED stack and the compartments are separated by ion exchange membranes and anions and cations from the diluate are removed to the concentrate by the applied current. Dewatering is required prior to reuse of the upgraded APC residue as a constituent in construction materials.

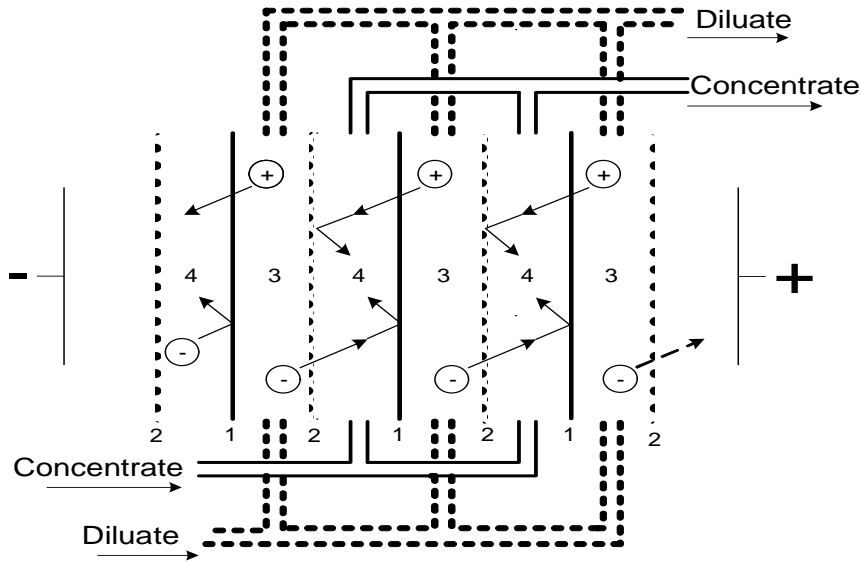


Figure 1 – Principle of electro-dialytic upgrading of APC residue. 1/2- ion exchange membranes, 3- diluate compartments, 4- APC residue suspension (diluate) compartments

ED differs from another treatment set-up developed by the same research group by aiming at lower final metal leaching while maintaining the alkaline pH instead of obtaining the highest possible heavy metal removal. The latter may be time-consuming and take weeks [7, 8] and result in high matrix changes by either acidification of the residue [9] or by the addition of chemical complexing agents. Although few studies of the electro-dialytic method have focused on reducing heavy metal leaching instead of the total content, those that exist indicate that this can be achieved with treatment times in the order of hours, simultaneously reducing the salt concentration significantly [5, 6]. This last approach was recently also recommended by Lima et al. [10].

In this paper, the properties of MSWI APC residues after electro-dialytic upgrading were studied to evaluate if the residues can qualify as secondary resources and if the electro-dialytic upgrading method has potential as a pre-treatment method prior to reuse. Focus was on the technical and environmental properties of the electro-dialytically upgraded residue as a secondary raw material that could partly replace Portland cement in mortar.

## 2. MATERIALS AND METHODS

### 2.1 Experimental APC residue

Five experimental APC residues were used in this study:

- Coal: coal fly ash from Dong Energy A/S, Avedøreværket blok 1.
- Raw: raw semi-dry MSWI APC residue. The residue was collected after a semi-dry flue gas cleaning process from a Danish waste incineration plant, REFA I/S.
- Carb: raw MSWI APC carbonized by letting it react with atmospheric CO<sub>2</sub> under humid conditions.
- EDU: raw MSWI APC residue upgraded in electro-dialytic pilot scale experiments according to Kirkelund et al. [6]

- EDUcarb: carbonized MSWI APC residue upgraded in an electrolysytic pilot scale experiment according to Kirkelund et al. [6].

## 2.2 Analytical procedures

Total heavy metal and minor element concentrations (Al, As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Zn) in the APC residue were measured by ICP-OES (induced coupled plasma – optical emission spectrometry) after pre-treatment by DS259 [11] where 1 g of APC residue and 20 ml 7.3 M HNO<sub>3</sub> were heated at 200 kPa (120°C) for 30 min. The liquid was subsequently separated by vacuum filtration through a 45 µm filter and diluted to 100 ml. The units used in this paper are mg/kg for concentrations in dry matter. Major oxide composition was estimated from semi-quantitative analysis by X-ray fluorescence (XRF) on powder samples. Loss on ignition was measured after heating at 550°C for one hour. The pH was measured in 1 M KCl at a liquid-to-solid ratio (L/S) of 5 and after 1 hour of agitation, pH was measured by a Radiometer Analytical pH electrode. The amount of water soluble APC residue was estimated as mass reduction when mixing 1 g APC residue with 20 ml distilled water, agitated for 24 hours.

Leaching experiments were made according to DS/EN 12457-3 part 1 [12] at L/S 2, mixing 40 g APC residue and 80 ml distilled water. The suspension was shaken for 6 hours on an end-over shaker before vacuum filtration through a 45 µm filter and the filtrate was divided into two subsamples. One subsample for analysis of anions (Cl, SO<sub>4</sub>) by ion chromatography (IC) and the other subsample was acidified by addition of concentrated HNO<sub>3</sub> before analysis of heavy metals and minor elements on ICP-OES.

Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses for main morphology were performed on the samples. For the SEM/EDX analysis, a small subsample of the residue (<0.5 g) was placed directly on carbon tape. No further pre-treatment of the samples was made. The accelerating voltage of the SEM was 30 keV with large field detector (and X-ray cone). Different areas of the samples were investigated by SEM and the element distribution was examined by element mapping using EDX on unpolished samples. Residue mineralogy was studied by X-ray powder diffraction (XRD), for identification of major crystalline phases. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu K $\alpha$  radiation with a 2 $\theta$  X'Celerator detector. The samples were scanned in the range of 4-100 2 $\theta$  within 8 hours. The diffractograms were interpreted using the ICDD PDF-4 database for minerals.

## 2.3 Mortar

For preparation of mortar, low alkali sulphate resistant cement (CEM I 42.5 N) from Aalborg Portland and 0/4 mm quartz sand of class E from RN Sten & Grus, Hvidovre, Denmark were used. The mortar was mixed according to EN 196-1 [13] at a water/binder-ratio of 0.5 and a sand/cement ratio of 3 (reference mix). The cement was substituted 15 % by weight with APC residue, which is within the acceptable replacement range between 5-25 % from previous studies [10, 14, 15]. Six experimental mortars were made, five with substitution of the different APC residues and a reference mortar without APC residue. The 6 cm · 12 cm cylindrical mortar bars were cast in PEH molds and demolded after 1 day. The mortars were cured in separate water baths to avoid cross contamination.

Compressive strength was tested after 7 and 28 days at 20°C on mortars prepared and cured according to DS/EN 12390-3 [16] in triplicate for each mortar, except for the raw and EDU which was tested after 32 and 56 days. Adiabatic heat development was measured after DS 423.37 [17] with slight modifications on reference, coal, raw, EDU and EDUcarb mortars continuously during 7 days after mixing. For simple workability assessment, slump tests by using a 75 mm cone were made on the reference, raw, EDU and EDUcarb mortars according to Bartos [18].

Leaching experiments were made on crushed and monolithic (ca. 3 cm · 3 cm) samples of the mortar cured for 28/32 days following the same procedure as for the APC residues. Leaching of the crushed samples represents the worst case scenario if the material is disposed of after its service life and monolithic samples represent leaching that could occur during service life time [15]. The mortars were stored in sealed bags at room temperature until the leaching experiments were made.

### **3. RESULTS AND DISCUSSION**

#### **3.1 APC residue characteristics**

APC residue characteristics for the five residues are shown in Table 1. The minor element concentrations in the MSWI APC residues were generally higher than in the coal residue. This was expected due to the different fuel conditions during incineration. Up to 50 % of the residue was water soluble. This explains why the metal concentrations in the ED upgraded residues were higher than in the untreated: when the residues are mixed with water, soluble salts dissolve and are removed; and even though parts of the metals are removed by the electro-dialytic treatment, the total concentration increases due to the larger decrease in total mass.

The results for major elements confirmed the difference in composition between the coal fly ash and the APC residues. The APC residues, as also seen by other authors consist mainly of Ca and Cl [19, 20], which is due to addition of lime during the acid gas cleaning. Also, the Ca concentration was 10 times higher in the MSWI residues than the coal fly ash and almost half of the content of what is to be found in cement [15]. The sulfate content increased when the APC residues were electro-dialytically treated and the Na, K and Cl content decreased. The Cl content in the ED upgraded residues were, however, still a factor 10 higher than in the coal residue. High chloride content in MSWI APC residue is considered a limiting factor for reuse as Cl can cause corrosion in reinforced steel [21]. The limit for reuse in mortar according to DS/EN 450 [22] is a chloride content below 0.1 %, which could be met for the upgraded MSWI APC residues by adjusting the electro-dialytic treatment process [6].

Due to the carbonation processes, pH in the Carb and EDUcarb samples was two pH units lower than in the coal, raw and EDU residues, which is due to the introduction and further reaction of H<sub>2</sub>CO<sub>3</sub> in the residue [23]. Despite the carbonization and electro-dialytic upgrading, all residues were alkaline. The loss on ignition (LOI) of the carbonized residues were higher than of the raw, probably due to bound lattice water in the carbonized residues, as the LOI results would be expected to be in the same range as the raw and EDU samples. Lattice water is removed when heating a sample between 450-600 °C [24] and will not be removed by the temperature used for drying (105°C) prior to LOI analysis. The limit value for LOI is maximum 9% according to DS/EN 450 [22], which was met by the coal, Raw and EDU samples.

Table 1 – Characteristics of the different APC residues.

|                               | Parameter                      | Coal   | Raw    | Carb   | EDU    | EDUcarb |
|-------------------------------|--------------------------------|--------|--------|--------|--------|---------|
|                               | LOI (%)                        | 1.6    | 0.7    | 8.1    | 0.9    | 9.5     |
|                               | Water solubility (%)           | 11     | 42     | 50     | 20     | 13      |
|                               | pH <sub>KCl</sub>              | 12.5   | 12.2   | 10.0   | 12.4   | 9.9     |
| Minor element content (mg/kg) | Al                             | 26,450 | 23,450 | 14,050 | 22,650 | 20,000  |
|                               | As                             | 24.3   | 127    | 138    | 192    | 257     |
|                               | Ba                             | 1,100  | 370    | 349    | 448    | 299     |
|                               | Cd                             | 1.5    | 170    | 190    | 245    | 287     |
|                               | Cr                             | 45.7   | 93     | 96     | 150    | 196     |
|                               | Cu                             | 31.7   | 575    | 572    | 807    | 744     |
|                               | Mn                             | 198    | 411    | 372    | 664    | 603     |
|                               | Ni                             | 31.7   | 32     | 30     | 47     | 142     |
|                               | Pb                             | 19.1   | 2,200  | 3,150  | 2,150  | 4,400   |
|                               | Zn                             | 87.7   | 14,650 | 20,200 | 21,600 | 32,400  |
| Major oxide content (%)       | CaO                            | 7.0    | 64.4   | 36.4   | 40.6   | 43.4    |
|                               | Na <sub>2</sub> O              | 1.8    | 10.2   | 7.1    | 0.7    | 0.7     |
|                               | K <sub>2</sub> O               | 2.9    | 7.7    | 3.1    | 0.4    | 0.4     |
|                               | SO <sub>3</sub>                | 1.3    | 6.2    | 5.2    | 12.5   | 10.2    |
|                               | Al <sub>2</sub> O <sub>3</sub> | 22.7   | 2.1    | 2.1    | 3.0    | 3.8     |
|                               | Si <sub>2</sub> O              | 53.5   | 2.6    | 3.0    | 7.1    | 7.7     |
|                               | Fe <sub>2</sub> O <sub>3</sub> | 7.6    | 1.0    | 0.8    | 1.2    | 1.6     |
|                               | MgO                            | 2.2    | 0.6    | 0.3    | 1.4    | 1.3     |
|                               | MnO                            | 0.05   | 0.06   | 0.04   | 0.08   | 0.09    |
|                               | P <sub>2</sub> O <sub>5</sub>  | 0.7    | 0.2    | 0.1    | 0.7    | 0.8     |
|                               | TiO <sub>2</sub>               | 1.0    | 0.7    | 0.4    | 0.8    | 1.0     |
|                               | Cl                             | 0.01   | 24     | 19     | 0.7    | 0.4     |

Leaching of heavy metals and salts from the different residues is shown in Table 2, together with the Category 3 values for leaching and these values represent the maximum allowed values for reuse of waste materials in construction [25]. The results from leaching and the discussion on the effect of the carbonization and the electrodynamic treatment have been presented previously [6]. The conclusions from this study regarding leaching, which is also apparent in Table 2, are:

- Carbonization leads to increased Cd, Cr and Cu leaching but a reduces leaching of other heavy metals, especially Pb and Zn
- Electrodynamic upgrading of both the raw and carbonized APC residue significantly reduces the leaching of most heavy metals, except Cr which increases.

- Cl leaching is drastically reduced due to electrodiolytic upgrading

Table 2 – Element leaching from the residues. *N.m.* – not measured. <sup>a</sup>[6].

| Element                | Coal  | Raw <sup>a</sup> | Carb <sup>a</sup> | EDU <sup>a</sup> | EDUcarb <sup>a</sup> | Category 3 [25] |
|------------------------|-------|------------------|-------------------|------------------|----------------------|-----------------|
| pH <sub>leachate</sub> | 12.3  | 12.0             | 9.0               | 12.3             | 8.3                  | -               |
| Al (mg/l)              | 2.6   | n.m              | 3.0               | n.m              | 0.4                  | -               |
| As (µg/l)              | <25   | 110              | <25               | <25              | <25                  | 50              |
| Ba (mg/l)              | 0.7   | 34               | 17                | 0.45             | 0.1                  | 4               |
| Cd (µg/l)              | 1.2   | 22               | 1,860             | 0.1              | 0.7                  | 40              |
| Cr (mg/l)              | 1.0   | 0.06             | 0.9               | 0.24             | 1.6                  | 0.5             |
| Cu (µg/l)              | 7.0   | 2.9              | 833               | 15.3             | 8.8                  | 2000            |
| Mn (µg/l)              | <25   | <25              | <25               | <25              | <25                  | 1000            |
| Ni (µg/l)              | <25   | <25              | <25               | <25              | <25                  | 70              |
| Pb (µg/l)              | 31    | 535,300          | 586               | 3,780            | 27                   | 100             |
| Zn(µg/l)               | 77    | 49,800           | 303               | 1,660            | 160                  | 1500            |
| Ca (g/l)               | 1.2   | 36               | 26                | 1.6              | 0.9                  | -               |
| Na (g/l)               | 0.3   | 11.5             | 13.9              | 0.3              | 0.6                  | 1.5             |
| Cl (g/l)               | 0.003 | 88               | 84                | 2                | 1.3                  | 3               |
| SO <sub>4</sub> (g/l)  | 0.04  | 1.3              | 0.7               | 1.1              | 1.8                  | 4               |

Leaching of Cr increased significantly in both upgraded residues compared to the raw residues. This suggests a shift from Cr (III) to Cr (VI), the latter which is more mobile at alkaline conditions. Cr leaching in the coal residue also exceeded the values of category 3. Thus, according to the Category 3 guidelines none of the residues comply with the values regarding leaching. However, at the final pH of the ED treated compared to the untreated (Table 1), the difference in leaching could not be equally reduced just by pH alone, which could be seen from pH-dependent leaching experiments by Kirkelund et al. [6] for the same raw and carb APC residues. Gao et al. [26] found higher leached concentrations in waterwashed fly ash than was seen here for the EDUcarb, both samples which were similar in pH. This shows that the electrodiolytic treatment is beneficial for reducing the leachability of heavy metals. Leaching behaviour of electrodiolytically treated harbour sediments showed similar pH dependent leaching patterns before and after electrodiolytic treatment, even if up to 95 % of heavy metals were removed, despite matrix changes of the sediment and a significant change of pH due to electrodiolytic treatment [27]. Thus, further changes in the pH of the electrodiolytic treated APC residues could change the leaching properties.

Scanning electron microscopy analysis (SEM) of the coal, raw, carb and EDU APC residues showed different morphology. Typical SEM images of the APC residues are shown in Fig. 2.



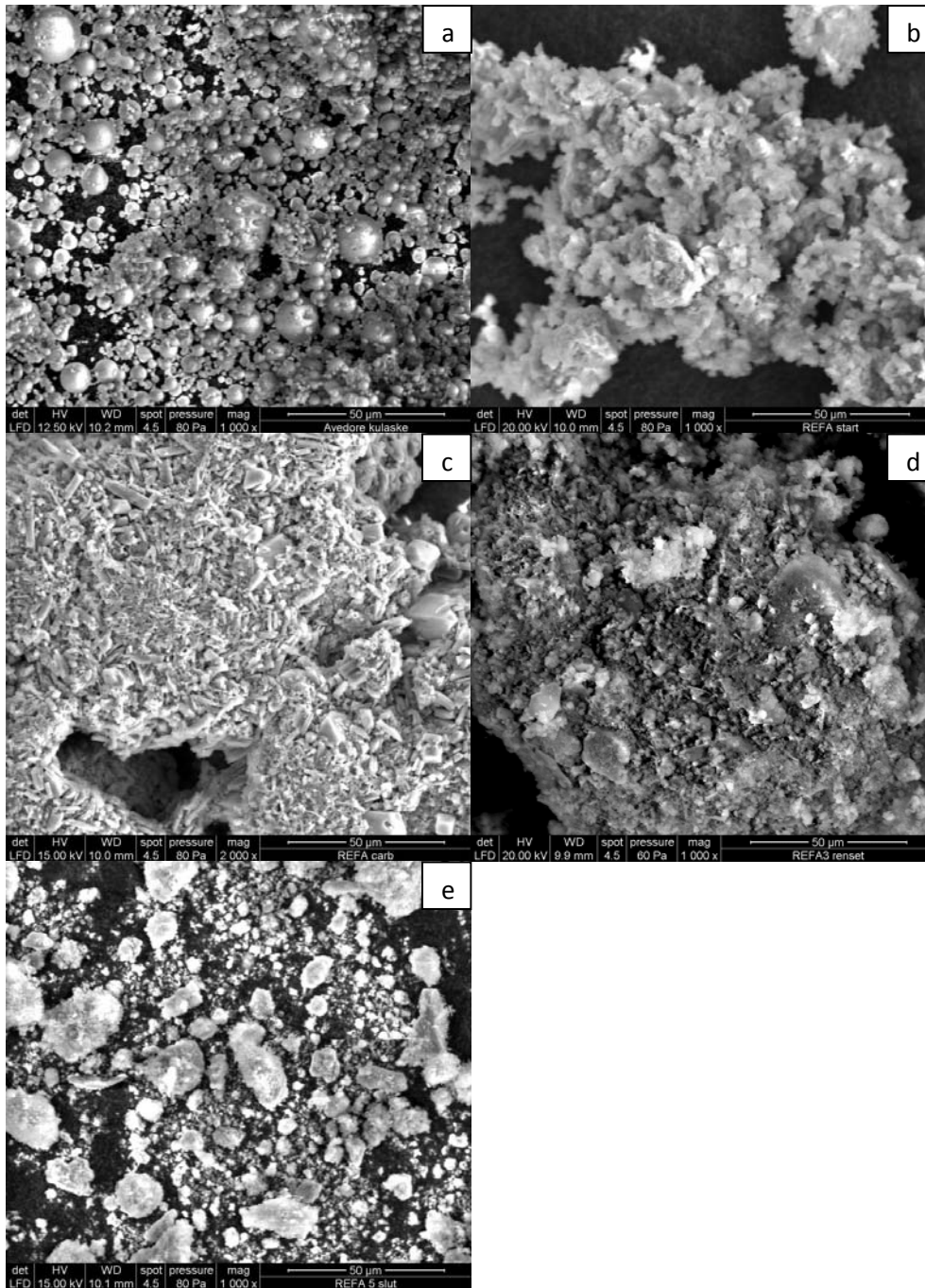


Figure 2 – SEM images of the APC residues, a) coal, b) raw, c) carb, d) EDU, e) EDUcarb

In the coal APC residue (Fig. 2 a) the typical spherical fly ash particles dominated. This finding was also seen by e.g. Brown et al. [28] who also showed that the elemental composition of the fly ash particles is dependent on coal feed and incineration temperature. The raw and the carbonated APC residue both consisted of particles of different sizes; however, agglomerates dominated the samples. The elemental mapping by SEM/EDX (results not shown) showed that the major constituents found in the raw and carbonized APC residue were O, Cl and Ca; while Ca, O and S were most abundant in the ED treated residues, which was also seen by the XRF analysis. The only distinct element overlap was seen in the raw and carb sample, by Na and K together with Cl. No clear overlapping patterns were found for heavy metal speciation. Fig. 2 b) shows a more granular and porous surface of the raw sample, with what looked like salts

between the grains, which changed to a more crystalline and less porous surface of the carbonated sample (Fig. 2 c). A similar change was also observed by Jiang et al. [29], where the crystallinity was caused by reaction products from the carbonization reaction. Both the raw and carbonized APC residue changed when electrodiagnostically upgraded. The EDU residues lost some of the granularly and crystalline appearances, which could be due to the removal of soluble salts.

The XRD diffractograms are seen in Fig. 3. from where the major crystalline phases in the different APC residues are specified based on interpretation.

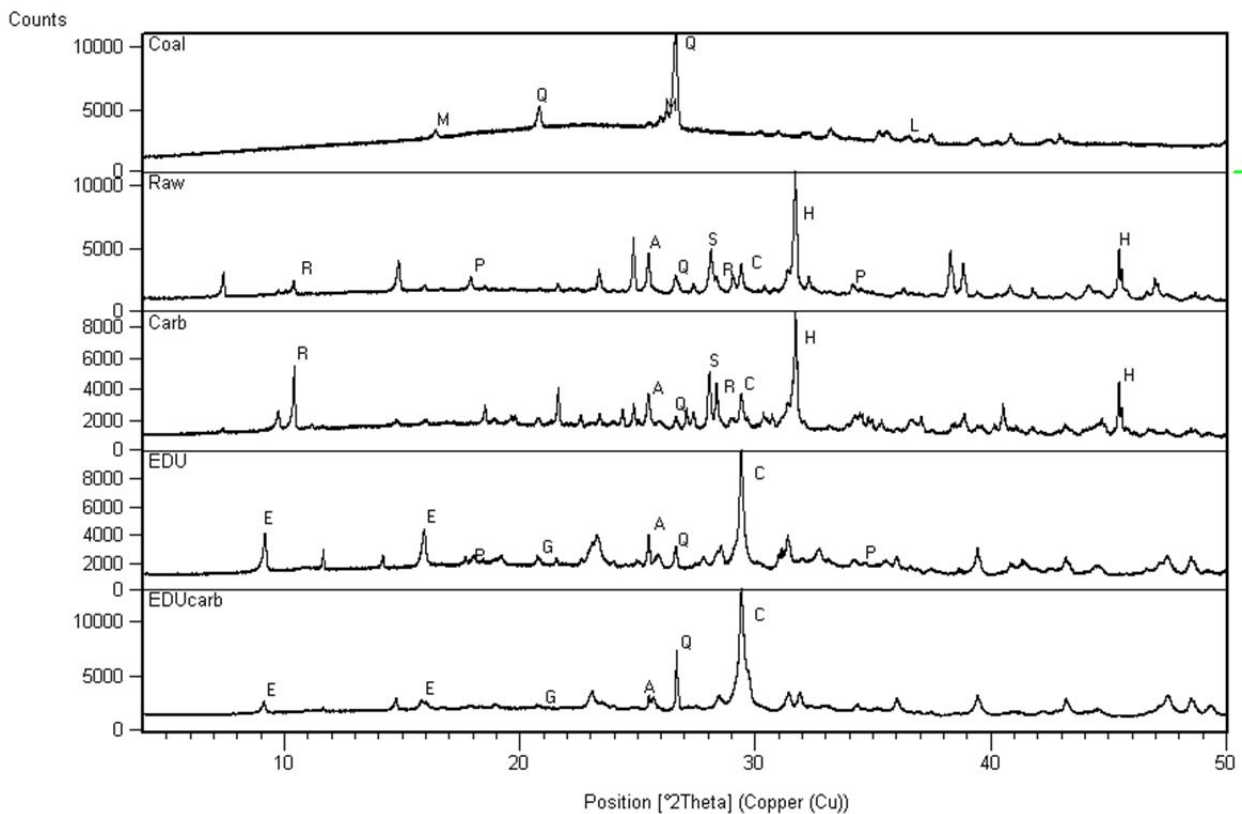


Figure 3 – XRD diffractograms with main minerals. M-mullite, Q-quartz, L-lime, R-richterite, P-portlandite, A-anhydrite, S-sylvite, C-calcite, H-hallite, E-ettringite, G-gypsum

The diffractograms for the MSWI residues were noisy due to the complex mineralogy and heterogeneity of the samples. The main minerals in the coal residue were identified as quartz, lime and mullite, which are typical minerals in coal fly ashes [28]. The main mineral compounds in the raw and carbonated residues were sylvite (KCl) and halite (NaCl) which were not identified in the ED upgraded residues. Contrarily to the coal APC residue, CaO was not identified as a Ca mineral in the MSWI residues, which was also expected as the acid gas treatment typically results in calcium carbonates, chlorides, hydroxides or sulphates. Thus, Ca minerals such as  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{Ca(OH)}_2$  and  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  were identified. Calcite ( $\text{CaCO}_3$ ) and anhydrite ( $\text{CaSO}_4$ ) were present in all the four MSWI residues, portlandite ( $\text{Ca(OH)}_2$ ) was present only in the non-carbonized residues, and gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) only in the EDU treated residues. The peaks for calcite had higher counts in the ED upgraded residues which indicate

that carbonate was not dissolved during ED treatment. A further carbonation of the residue during ED treatment is also possible, which would produce more calcite. Also, the total Ca content was at similar level in the ED upgraded residues compared to the untreated. Richerite ( $\text{Na}(\text{CaNa})\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ ) was most likely present in the raw and carbonated residues, but was not seen in the ED upgraded. Indications of formation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ ) were seen after ED treatment and ettringite has been shown to effectively immobilize oxyanions such as Cr (VI) [30]. However, Cr was not stabilised by the ED treatment as the Cr leaching was higher in the residue after ED. This may suggest that ettringite could not immobilize Cr as seen by the other authors.

In the ED upgraded residues it was clearly seen that the soluble KCl and NaCl salts were removed by the ED process, which was also seen in another study where MSWI fly ash was investigated by XRD after EDR [31] and also corresponds with the reduced leaching. The final obtained Cl concentrations in the ED treated residues were lower (0.3 – 0.5 %) than what has been reported for simply washing MSWI fly ash by water (1.3 – 1.8 %) [26, 32]. Thus, ED treatment enhanced removal of chloride from MSWI APC residues compared to washing.

Water solubility of up to 20 % of the electrodiallytically treated APC residue was seen, despite the significant removal of soluble minerals such as sylvite and halite. On the other hand, 11 % of the coal fly ash was also soluble. This suggests that there could be soluble phases also in the amorphous phase of the fly ash and APC residues, which could not be determined by the SEM/EDX.

### 3.3 Mortars

#### *Compressive strength, heat development and workability*

All the mortars containing APC residue exhibited lower compressive strength than the reference mortar (Table 3).

*Table 3 – Compressive strength and slump test of mortars.*

| Mortar sample | Compressive strength (MPa) |         |         |         | Slump (mm) |
|---------------|----------------------------|---------|---------|---------|------------|
|               | 7 days                     | 28 days | 32 days | 56 days |            |
| Mref          | 35 ± 1                     | 45 ± 3  |         | 56 ± 1  | 12.0       |
| Mcoal         | 29 ± 2                     | 42 ± 2  |         | 44 ± 2  |            |
| Mraw          | 27 ± 2                     |         | 41 ± 0  | 41 ± 10 | 11.0       |
| Mcarb         | 27 ± 1                     | 26 ± 0  |         |         |            |
| MEDU          | 34 ± 1                     |         | 40 ± 2  | 45 ± 1  | 7.5        |
| MEDUcarb      | 31 ± 5                     | 41 ± 6  |         |         | 4.5        |

The results showed a larger strength increase from 32 to 56 days for the reference mortar, but limited strength change for the mortars containing carb and EDUcarb residue. The compressive strength for the mortars with EDU, EDUcarb and coal residue were similar during the whole period and only slightly higher than the compressive strength of the mortar with raw residue. The only mortar which showed significantly lower strength after 28 days was the Mcarb mortar.

During the mortar mixing, it was observed that the workability decreased when MSWI APC was added. These observations were also confirmed by the slump test, see results in Table 3. The decrease in workability is most likely linked to the porosity of the APC residues, as was also observed to be higher in the MSWI residues than in the coal residue in the SEM analysis (Fig. 2). Porous particles will adsorb water in the mortar mix and reduce the workability, which should be compensated for by adding water or superplasticizer [28]. The workability of the mortar pastes increased when adding coal residue to the paste compared to the reference mortar paste without APC residues. Other factors than porosity influencing the workability could be the particle size, shape and surface characteristics. The circular shape of the coal APC residue was significantly different than the granular shape of the MSWI residues. The EDU residue showed higher workability than the EDUcarb residue, which also appeared more porous (Fig. 2d).

Metallic Al and sulphate in MSWI APC residue is regarded as important factors to lower compressive strengths when added in mortars due to crack formation [15]. However, the compressive strengths in this study are similar to what has been observed in other studies [10, 14, 15]. Contrary to Geiker et al. [14] no visible crack formation was observed in the mortars in this study. To make a contribution to reducing the CO<sub>2</sub> emissions from the concrete industry, it is necessary that the residues are substituting the cement and not the aggregate, even if aggregate substitution has shown better compressive strengths compared to reference, for untreated MSWI fly ash (e.g. [10]).

The heat development of the mortars is illustrated in Fig. 4.

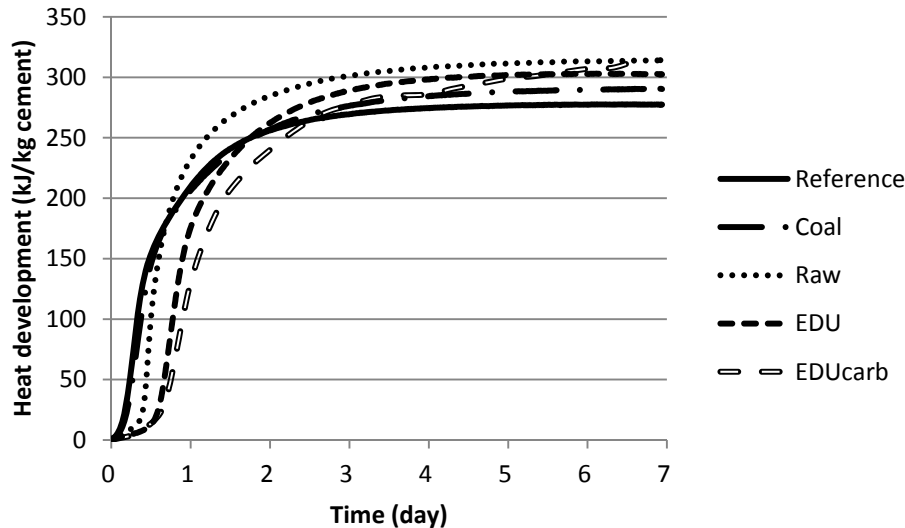


Figure 4 – Adiabatic heat development in mortars with and without fly ash and APC residues

The initial hydration was delayed in the mortars containing APC residue compared to the reference, but the highest heat acceleration period for all mortars occurred within the first days. The cumulative heat development measured within the first seven days was higher for all the mortars containing APC, which indicates that the APC either acted pozzolanic or induced a possible filler effect.

The initial setting times were found from the heat development curves, as the time where the extension of the linear part of the curve in acceleration period crosses the abscissa and found to be: reference (3 h); coal (3 – 4 h); raw (9 h), EDU (13 h) and EDUcarb (18 – 19 h). The initial setting times were delayed when adding APC residue to the mortar, however to a lesser extent than a similar study with MSWI APC residue from a wet process [14]. This indicates a dependence on the composition of the APC residue. Taylor [33] claims that salts of Pb and Zn as well as phosphates can cause hydration retardation. Soluble Zn can be a hydration retarder because it can form amorphous layers on cement grains and Pb has been observed to coat cement grains and precipitate on silicate surfaces [34]. It was seen that the observed setting times increased with increasing total Zn and Pb content. However, for the MSWI APC residues, the raw APC residue with the highest leachable amount of Zn showed the shortest delay of the two, which suggests that the formation of  $Zn(OH)_2$  is not the controlling mechanism. Addition of Cl to mortars can act as an accelerator or retarder depending on the concentration for the initial hydration and according to Brough et al. [35] as an accelerator at concentrations below 4 %. Here, the contrary occurred; adding the upgraded MSWI APC residue with a low Cl content (0.4 – 0.7 %) retarded hydration compared to the raw MSWI APC residue with high Cl content (24 %). At present the combined effect of soluble components on the setting time is not well described.

#### *Leaching from mortars*

Leaching from mortars cured for 28/32 days are shown in Table 4. For most elements leaching from the crushed samples was higher than from the monolithic, except for Ca and Na. Substitution of cement by APC residues did not significantly increase metal leaching. The Danish legislation for the maximum leaching concentrations for disposing inert waste [36] is also seen in Table 4.

*Table 4 – Element leaching ( $\mu\text{g/l}$ ) from mortars cured for 28<sup>1</sup>/32<sup>2</sup> days. A-Mref, B-Mcoal, C-Mraw, D-Mcarb, E-MEDU, F-MEDUcarb*

| Element   | Crushed        |                |                |                |                |                | Monolithic     |                |                |                |                |                | Inert waste |
|-----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|
|           | A <sup>1</sup> | B <sup>1</sup> | C <sup>2</sup> | D <sup>1</sup> | E <sup>2</sup> | F <sup>1</sup> | A <sup>1</sup> | B <sup>1</sup> | C <sup>2</sup> | D <sup>1</sup> | E <sup>2</sup> | F <sup>1</sup> |             |
| pH        | 12.6           | 12.6           | 12.6           | 12.6           | 12.5           | 12.6           | 12.6           | 12.6           | 12.5           | 12.5           | 12.5           | 12.5           |             |
| Al        | 195            | 241            | 311            | 65             | 91             | 142            | 148            | 261            | 250            | 194            | 459            | 187            | -           |
| As        | 5              | 5              | 9              | 6              | <5             | <5             | <5             | 14             | 11             | <5             | <5             | 6              | 50          |
| Ba        | 1,700          | 2,100          | 900            | 4,900          | 500            | 3,100          | 1000           | 1,100          | 600            | 2,600          | 400            | 1,600          | 3500        |
| Cd        | <5             | <5             | <5             | <5             | <5             | <5             | <5             | <5             | <5             | <5             | <5             | <5             | 15          |
| Cr        | 28             | 18             | 20             | 6              | 41             | 14             | 33             | 21             | 17             | 7              | 31             | 12             | 100         |
| Cu        | 16             | 13             | 28             | <5             | 27             | 12             | 22             | 14             | 12             | 10             | 18             | 6              | 450         |
| Mn        | <5             | <5             | <5             | <5             | <5             | <5             | <5             | 12             | <5             | 17             | <10            | 6              | -           |
| Ni        | 7              | 7              | <5             | 14             | 9              | 7              | 6              | <5             | <5             | 7              | 7              | 10             | 100         |
| Pb        | 58             | 53             | 159            | 92             | 69             | 209            | 58             | 49             | 90             | 59             | 76             | 128            | 100         |
| Zn        | 38             | 46             | 101            | 55             | 44             | 153            | 26             | 37             | 155            | 34             | 65             | 76             | 1000        |
| Ca(mg/l)  | 750            | 690            | 1,370          | 1,184          | 747            | 753            | 701            | 716            | 978            | 1,111          | 734            | 775            | -           |
| Na(mg/l)  | 97             | 11             | 134            | 201            | 42             | 136            | 48             | 48             | 95             | 121            | 37             | 45             | -           |
| Cl (mg/l) | 23             | 25             | 1,484          | 1,216          | 66             | 26             | 26             | 21             | 948            | 744            | 49             | 11             | 275         |
| SO4(mg/l) | 18             | 11             | 52             | 7              | 60             | 5              | 3              | 3              | 47             | 5              | 57             | 6              | 280         |

Only four mortar samples exceeded the threshold values for heavy metals. This indicates that the heavy metals are incorporated in the mortar matrix with time or water soluble metals are released during curing. The EDUcarb residue showed the highest leaching from the mortar compared to the initial amount available for leaching from the residue, which is most likely due to the increased pH in the mortar that changes the heavy metal leachability. Comparing the MEDU and MEDUcarb to the Mcoal samples, similar leaching levels were observed, even though the total concentration of Pb and Zn in the EDU samples was a factor 100 and 1000 higher respectively.

The pH in the mortar was generally higher than in the residues and at a level where the heavy metals are expected to be stable in the matrix [7]. The slight increase in Cr leaching in the upgraded residues (Table 2) suggests a shift from Cr (III) to Cr (VI) during ED treatment. Higher Cr leaching was also seen from the mortars with upgraded residues compared to raw, which was also seen in the leaching of the APC residues alone. When comparing the amount of leached heavy metals from the APC residues to the amount leached from the mortars, it can be seen that the mortars generally incorporates the heavy metals. This also includes Cr, where 14 and 1 % of the total leachable Cr in the APC residues is leached from the mortars containing EDU and EDUcarb, respectively. Cr leaching was high in the reference mortar, which has also been seen in other studies [10, 15]. The Cr leaching from mortars containing EDU samples were lower than leaching from the reference and coal mortar. This is an improvement to what was seen by Aubert et al. [15] where a higher Cr leaching was seen from mortars with MSWI fly ash compared to a reference sample and also exceeded the limits for inert waste disposal. A study where concrete samples containing fly ash with a higher Cr content than cement were carbonated, did not show increased leaching of Cr compared to reference samples [37]. Contrarily, the same concretes with fly ash subjected to NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions increased Cr leaching compared to reference concrete.

This suggests that the choice of final application for concrete containing waste incineration residues should be carefully considered. As MSWI APC residue is considered hazardous waste in most countries, direct reuse will probably not be allowed, so even if the metal leaching from the mortars with untreated and upgraded residue were similar, this would probably not be an argument that would promote reuse of untreated APC residue. Most importantly, the total Cl concentration and the Cl leaching decreased significantly when introducing electrodiolytic upgrading. Regarding long term leaching of metals it would be expected that in mortar samples containing untreated residue the leaching would increase due to the higher water solubility of the residue.

#### **4. CONCLUSION**

Two electrodiolytically (ED) treated MSWI APC residues were evaluated for use in mortar as Portland cement replacement, i.e. a potential alternative use of these residues compared to disposal in hazardous waste disposal sites. One of the residues was carbonated followed by electrodiolytic treatment. The carbonated ED treated residue shows lower leaching of heavy metals compared to the only ED treated residue before use in mortar. However, when the carbonated ED treated residue is incorporated in mortar, the heavy metal leaching increases due to a higher pH in the mortar than in the residue itself. The heavy metal leaching from the mortars with ED treated MSWI APC residues is similar to reference mortar without added APC residue. Mortars with ED treated residues show similar compressive strengths compared to

mortars with coal fly ash, where the compressive strengths are up to 45 MPa, but lower than the reference mortar. The initial setting times are delayed with up to 16 hours in mortar with ED treated residues compared to reference mortar and the workability also decreases in these mortars, which should be considered for application of such mortar. The high salt content suggests that the ED treated MSWI APC residues are most applicable to unreinforced concrete.

From an environmental and mechanical point of view, electro-dialytic upgrading has potential as a pre-treatment method prior to reuse of APC residue. Carbonation of the APC residue prior to ED does not improve the quality of the residue neither for technical nor environmental performance in mortar. There seems to be a potential for using electro-dialytically upgraded APC residue in mortar, however, long term leaching and the durability should be investigated further.

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