



Licenciada em Ciências de Engenharia do Ambiente

Cátia Joana Costa Magro

Electrodialytic remediation of two types of air pollution control residues and their applicability in construction materials

Dissertação para obtenção do Grau de Mestre em
Engenharia do Ambiente

Perfil de Engenharia de Sistemas Ambientais

Orientador: Professora Doutora Alexandra de Jesus Branco
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Ao paizinho e à mãezinha.

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Sumário

Os resíduos de controlo de poluição do ar (CPA) provenientes da incineração de resíduos sólidos urbanos são classificados como resíduos perigosos. No entanto, os mesmos podem conter potenciais recursos. Tendo em conta os diferentes sistemas de limpeza de gases de combustão utilizados (húmido ou semi-seco), os resíduos apresentam características químicas e físicas diversas, que por sua vez irão influenciar o sucesso da remediação e a sua possível reutilização. O processo electrodiálítico (ED) foi aplicado a dois tipos de resíduos de CPA visando a sua possível remediação. Foram estudadas as características iniciais destas duas cinzas e aplicadas diferentes condições experimentais (célula electrodiálítica de 2 e 3 compartimentos, 5 ou 50 mA de corrente elétrica e 3, 7 e 14 dias de tratamento). Os resultados obtidos mostram que a remediação neste tipo de resíduos é bastante difícil, mas que a utilização de uma corrente contínua de baixa intensidade promove a imobilização de metais pesados presentes nos resíduos. A lixiviação do Pb, no resíduo do sistema húmido foi anulada, em algumas das experiências, enquanto que as restantes apresentaram valores abaixo da legislação dinamarquesa, com algumas exceções. Este resultado foi bastante distinto dos resultados obtidos em estudos anteriores. Apesar da dificuldade em remover os metais pesados estudados, as melhores eficiências de remoção foram obtidas após 14 dias: 84% de Cd, 67% de Pb, 67% de Zn, 30% de Cu e 21% de Cr. Após a remediação das cinzas, foi estudado a sua possível reutilização em materiais de construção, nomeadamente em barras de argamassa. Assim, 5% de Cimento Portland Comum foi substituído por resíduos de CPA com e sem pré-tratamento. A qualidade do material produzido foi avaliado tendo em conta os seguintes parâmetros: porosidade, densidade, resistência mecânica, lixiviação de metais pesados e quantidade de cloretos. Os resultados obtidos permitem concluir que, para o sistema húmido, promover um pré-tratamento antes da reutilização em materiais de construção parece ser a melhor opção, já que os valores de metais ficam menos lixiviáveis e os testes de resistência mecânica são comparáveis ao material sem incorporação de cinzas. Todavia, para o sistema de limpeza semi-seca, um pré-tratamento parece piorar os resultados de remediação, sendo portanto, uma opção fazer a incorporação do resíduo em bruto. Em conclusão, os resultados deste estudo sugerem possibilidade de reutilização de resíduos CPA, o que apresenta grandes vantagens na gestão de resíduos, bem como na conservação.

Palavras-chave: *Resíduos de controlo de poluição do ar, processo electrodiálítico, barras de argamassa, metais pesados*

Abstract

Air pollution control (APC) residues from municipal solid waste incineration are classified as hazardous waste and disposed of, although it contains potential resources. Due to the different fuel gas cleaning system designs (wet or semi-dry), the APC residues present distinct chemical and physical characteristics that influence the remediation success and their possible reuse. Electrodialytic (ED) process was applied to two types of APC residues aiming their remediation. The characteristics of raw residues and upgraded APC and a broad range of ED experimental conditions were studied (ED cell with – 3 and 2 compartments; 5 or 50 mA of direct current; 3, 7 and 14 days of remediation time). Obtained results showed that remediation was very difficult but the use of low level direct current promoted the immobilization of the heavy metals. The leaching behaviour, for instance, of Pb was avoided in wet system, while the remaining values were kept below the Danish regulation thresholds, with a few exceptions. Still, after 14 days of ED process the best removal rates achieved were: 84% of Cd, 67% of Pb, 67% of Zn, 30% of Cu and 21% of Cr. Thus, 5% of Ordinary Portland Cement was replaced by APC residues in mortars, with or without ED pre-treatment. Porosity, density, compressive strength, heavy metals leaching and chloride were tested. After analysing the parameters, it is possible to say that for the wet gas cleaning systems use a pre-treatment before the reuse in building materials is the best option, since the values for heavy metals leaching tests decrease after, and compressive strength are comparable to material without residue. However, for semi-dry cleaning gas systems, the heavy metals leaching after pre-treatment appears to increase, so for this type of APC it is thus possible to aggregation only of the raw residue. The results of this study suggest new possibilities for this APC waste reuse, presenting great advantages in the waste management system as well as for resource conservation.

Keywords: *Air pollution control residues, electrodialytic process, mortar bars, heavy metals*

Abstrakt

Røggasrensningssaffald (RGA) fra affaldsforbrænding er klassificeret som farligt affald og deponeres, selv om RGA indeholder potentielt brugbare ressourcer. Forskellige røggasrensningssystemer (våd eller semi-tør proces) resulterer i RGA med for meget forskellige kemiske og fysiske karakteristika som har betydning for eventuel behandlingsmetode og genbrug. Elektrodialytisk rensning (ED) ble brugt til at oprense de to forskellige typer RGA. Karakteristik af rå og elektrodialytisk rensset RGA samt flere elektrodialytiske rensningsforsøg (ED- celle med 3 eller 2 kamre; 5 eller 50 mA strømstyrke; 3,7 eller 14 dages rensningstid) blev udført. Resultaterne fra de elektrodialytiske rensningsforsøg viste at oprensningsgraden var lav, men at strømmen kunne bruges til at immobilisere tungmetaller i RGA. Udvaskningsforsøg viste at for våd RGA, var Pb udvaskning meget lav og for de fleste andre tungmetaller blev de danske grænseværdier overholdt. Den højeste oprensning blev opnået efter 14 dages rensning hvor 84% af Cd, 67% af Pb, 67% af Zn, 30% af Cu og 21% af Cr blev fjernet. Derefter blev 5 % af Portland cement erstattet af enten rå eller elektrodialytisk rensset RGA til brug i mørtelprøver. Porøsitet, densitet, trykstyrke og tungmetal og klorid udvaskning blev testet på mørtelprøverne. For våd RGA, er det en fordel med elektrodialytisk rensning i forhold til erstatning i mørtel, da tungmetaludvaskningen minimeres samt at trykstyrken for mørtel er sammenlignelig med referenceprøver uden RGA. Modsat, for semi-tør RGA bliver udvaskningen af tungmetaller højere af elektrodialytisk rensning, på denne baggrund vil rå semi-tør RGA være mere fordelagtig til mørtel. Resultaterne fra dette projekt åbner for nye muligheder for RGA genbrug, som vil kunne føre til store fordele i affaldshåndteringssystemer og ressourceforvaltning.

Søgeord: Røggasrensningssaffald, elektrodialytisk rensning, mørtelprøver, tungmetaller

Abbreviations and symbols

2C - Two compartments
3C - Three compartments
3D - Three days
7D - Seven days
14D - Fourteen days
AN - Anion-exchange membrane
APC - Air pollution control
CAT - Cation-exchange membrane
DC - Direct current
DK - Denmark
ED - Electrodialytic
EDR - Electrodialytic remediation
FA - Fly ash
IC - Ion chromatography
ICP-OES - Inductively coupled plasma – optical emission spectroscopy
L/S - Liquid-to-solid
LOI - Loss on ignition
MSW - Municipal solid waste
MSWI - Municipal solid waste incineration
PAH - Polycyclic aromatic hydrocarbon
PCB - Polychlorinated biphenyl
PT - Portugal
REFA – I/S REFA, Waste-to-energy incineration plant
S/S - Solidification/stabilization
SEM/EDS - Scanning electron microscope/energy dispersive X-ray spectroscopy
Vest – I/S Vestforbrænding, Waste-to-energy incineration plant

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1. Introduction

Air Pollution Control (APC) residues are one of the waste products from flue gas cleaning in the incineration facilities. There are different APC residues, depending on the design of the plant. They are considered hazardous due to their contaminants content, namely heavy metals, salts and/or dioxins. Due to their hazardousness and instability, APC residues constitute an environmental problem and, consequently, stabilization prior disposal is required. In Portugal the APC residues are mixed with cement to its inertization, and disposed of in landfills, in Denmark these residues are not allowed to be landfilled due to the risk of groundwater contamination. They are exported to Germany or Norway, where they are either backfilled into mines (Germany) or deposited in an old calcite quarry at an Island in the Oslo Fiord – Langoya - after being mixed with sulphuric acid (Jensen, 2014). The methodology is dependent on the soil characteristics of each country.

Although APC residues are considered hazardous waste, they have features that can be further reused, if the contaminants are successfully removed they can be a valuable resource. For instance in the production of concrete. Nevertheless, the reuse of such a waste should always be in accordance to the precautionary principle and the uncertainty of the contaminants behaviour over time.

Objectives and research

Q₁ - Is the Electrolytic (ED) process an appropriate pre-treatment for APC residues?

Q₂ - Can APC residues be incorporated in building materials, after ED process?

Within these main questions, there will be other targets such as, understand how two different gas cleaning systems influence the overall characteristics of the generated APC residues and how they affect heavy metals and salts removal. Electrolytic remediation (EDR) was applied to two types (wet and semi-dry system) of APC residues and different conditions were tested. Two EDR cells were used: one with three compartments and a recently patented cell with two compartments (Ottosen *et al.*, 2014). After, the ED process, the ashes were submitted to a stabilization/solidification (S/S) technique. These APC residues were further studied and defined to be suitable and stable (porosity and density, compressive strengths, leaching behaviour and chloride content) for reuse in building materials. Legislation was used to verify if the residue were in conformity, both for leaching of heavy metals and for anions.

Dissertation structure

This work is organized in 8 chapters:

1. Introduction - work scope and relevance, main objectives and structure;

2. Literature review - description of the central theme and relevant terms and previous work developed;
3. Materials and methods - description of materials used, characterization analysis, identification and data treatments methods;
4. Results and discussion- presentation of results, hypothesis formulation and their discussion;
5. Conclusions – main outcomes;
6. Future developments;
7. References;
8. Annexes.

2. Literature review

2.1 Waste management in Europe

Municipal solid waste (MSW) remains a major problem in modern societies, despite the significant efforts to prevent, reduce, reuse and recycle it. Municipal solid waste normally contains a mixture of organic wastes, fabrics, paper, oil, rubber, plastics, metal, glass, and wood, among others. Figure 2.1 shows the composition of MSW in different countries. In this figure is evident the difference between different proportions of waste composition, showing that even if the technologies for management of waste are equal, the waste will differ from country to country.

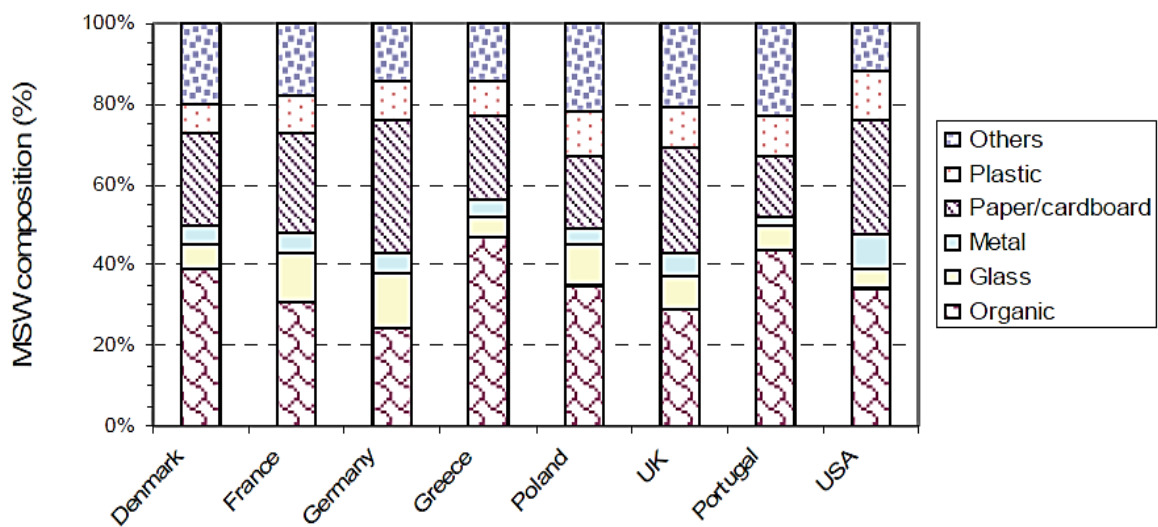


Figure 2.1. Composition of MSW (Adapted from Gentil *et al.*, 2009 in Quina *et al.*, 2011)

In Europe-27 Stat Members, MWS production in 2012 was 492 kg year⁻¹ *per capita*, with an annual decrease since 2003 (Eurostat, 2012). Although Portugal had a *per capita* production of 453 kg MWS in 2012, the production of MWS in some countries was much higher, as in Denmark or Switzerland: 668 kg year⁻¹ *per capita* and 694 kg year⁻¹ *per capita*, respectively (Eurostat, 2012).

Since 1997 Portugal has been applying Strategic Plans of Urban Solid Wastes (Plano Estratégico para os Resíduos Sólidos Urbanos - PERSU) which allow the country to give fundamental steps in waste policies. In December 28, 2006, the Strategic Plan for MSW for the period 2007-2016 (PERSU II) was approved. This plan aims at continuing the waste management policy taking into account the new requirements formulated at national and community level. These new requirements were thought to ensure diverting biodegradable municipal waste from landfill and recycling/recovery of packaging waste while seeking to overcome the limitations of implementing PERSU I. In 2005, 21% of Portuguese solid

waste was incinerated, very near to the established value of 22% (Ministério do Ambiente, do Ordenamento do Território e do Desenvolvimento Regional, 2007). The Portuguese Government has decided to review the plan before the next Community Support Framework 2014-2020. As goals, PERSU 2020 provides increased uptake of recyclable waste through selective collection (Ministério do Ambiente, Ordenamento do Território e Energia, 2014). PERSU 2020 will distinct, for the first time, goals for the 23 systems of waste management in the country, by population density and socio-economic parameters of the region in which systems are inserted (Ministério do Ambiente, Ordenamento do Território e Energia, 2014).

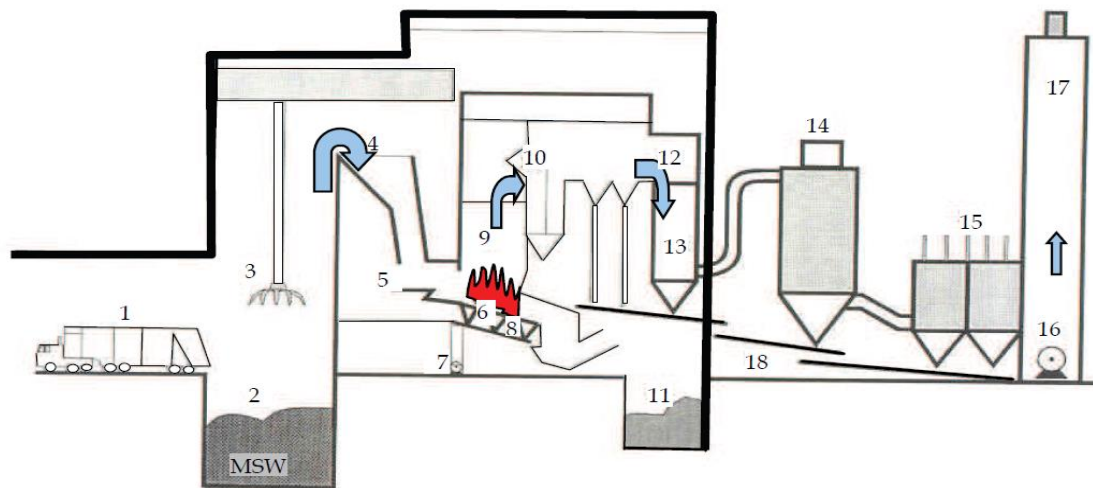
Nowadays modern systems embrace different methodologies aiming as much as possible to achieve sustainable global solutions for waste management. Life Cycle Assessment tools have been used to assess the potential environmental burdens of different waste management strategies from the environmental, energetic and economic point of view (Quina *et al.*, 2011). These calculations have shown that landfilling, even if gas is recovered and leachate is collected and treated, should be avoided, due to the fact that resources in the waste are inefficiently utilized (Sundqvist, 2005). Environmental sound alternatives include incineration, material recycling, anaerobic digestion or composting (Lima, 2008).

2.1.1 Incineration

According to Directive 2000/76/EC of the European Parliament and Council, incineration plants *correspond to any stationary or mobile technical unit dedicated to the thermal treatment of wastes with or without recovery of the combustion heat generated. This includes the incineration by oxidation of waste as well as other thermal treatment processes such as pyrolysis or gasification in so far as the substances resulting from the treatment are subsequently incinerated.* This description includes the site and the entire incineration plant counting:

- Waste reception and handling (storage, on site pre-treatment facilities);
- Combustion chamber (waste-fuel and air-supply systems);
- Energy recovery (boiler, economiser, etc.);
- Facilities for clean-up gaseous emissions, on-site facilities for treatment or storage of residues and waste water, stack;
- Devices and systems for controlling incineration operations, recording and monitoring;
- Incineration conditions.

Figure 2.2 presents a scheme of a typical mass burning MSW incinerator, which includes the above referred facilities.



- | | | |
|-----------------------------|------------------------|----------------------------|
| 1- waste collection vehicle | 7- forced-draft fan | 13- economiser |
| 2- waste storage pit | 8- undergrate air zone | 14- dry scrubber |
| 3- waste handle crane | 9- furnace | 15- fabric filter baghouse |
| 4- feed hopper | 10- boiler | 16- induced-draft fan |
| 5- feeder | 11- bottom ash bunker | 17- stack |
| 6- grate | 12- superheater | 18- APC residues conveyor |

Figure 2.2. Simplified scheme of a MSW incinerator (adapted from IAWG, 1997)

It is important that the gases produced after energy recovery, mostly occur in the boiler (10), superheater (12) and economiser (13). The amount of gases produced during combustion contain air pollutants that are harmful for the environment and, consequently, must comply with the stringent regulatory limits (Quina *et al.*, 2011). Thus, depending on the desired cleaning degree, different APC systems may be used. As an example, in Figure 2.2, a dry scrubber (14) and fabric filters (15) are used. In these units, APC residues are produced and further transported through a conveyor (18) for a silo (not represented). Most of the modern incinerators treat APC residues before disposal in monofills. Finally, by using an induced-draft fan (16), the cleaned flue gas is released by the stack. Concerning air pollution, it is important to note that combustion includes very fast reactions (fractions of seconds) that take place in the gas phase, and self-supporting combustion is possible if heat value of the waste and oxygen concentration are sufficient (Quina *et al.*, 2011).

The Directive 2000/76/EC, on the incineration of wastes aims *to prevent or to limit as far as practicable negative effects on the environment, in particular pollution by emissions into air, soil, surface water and groundwater, and the resulting risks to human health, from the incineration and co-incineration of waste*. This Directive, known as Waste Incineration Directive, states that continuous measurements of NO_x, CO, total dust, Total Organic Carbon, HCl, HF and SO₂ should be carried out, and at least twice a year for heavy metals (Cd, Tl, Hg, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V), dioxins and furans.

Municipal solid waste incineration (MSWI) in waste-to-energy can be considered an environmentally friendly solution and a common alternative to landfilling, while allowing to recover a large part of the energy contained in MSW (Lima, 2008). Besides several advantages, this process also presents some disadvantages that are reported in Table 2.1.

Table 2.1. Advantages and disadvantages of MSWI (Quina *et al.*, 2011)

Advantages	Disadvantages
<ul style="list-style-type: none"> ▪ Handle waste without pre-treatment ▪ Reduce landfilling demand for MSW ▪ Reduce waste volume by 90% ▪ Reduce waste weight by 70% ▪ Possibility of recovering energy (electricity or heat) ▪ If well managed, low air pollution is released ▪ Destroys potential pathogens and toxic organic contaminants ▪ Can be located close to the centre of gravity of MSW generation ▪ Reduce cost of waste transportation ▪ Require minimum land ▪ Stack emissions are odour-free ▪ Reduce organic materials mainly to CO₂ instead CH₄ and other volatile organic compound 	<ul style="list-style-type: none"> ▪ Originates hazardous waste (APC residues), that require safe disposal ▪ Originates slags (bottom ashes) ▪ Originates huge volume of flue gases ▪ High investment and operating costs ▪ High maintenance costs ▪ Requires suitable composition for auto-combustion ▪ Negative public perception

2.1.2 Air pollution control residues

Municipal solid waste incineration is a highly efficient technique for waste management, as it significantly reduces the volume of waste (Quina *et al.*, 2011). However, MSWI may cause environmental problems, mainly related to the disposal of the produced fly ash (FA) considered hazardous by CEN prEN 14899. There are different types of ash residues that result from cleaning emissions from MSW incinerators, and it is important to differentiate between FA and APC residues. Fly ash is the finer fraction of the particulate (< 200 µm) which is entrained in the flue gas and subsequently trapped in an electrostatic precipitator filter before any further treatment of the gaseous effluents. Fly ash can be recovered separately from the gas stream, or they can be incorporated into the APC residues (Zacco *et al.*, 2014).

Since APC residues include the particulate matter captured after the acid gas treatment units, the waste may be a solid or a sludge, depending on the type of APC equipment used (dry, semi-dry or wet processes), and is generally characterized by high concentrations of salts, heavy metals and trace organic pollutants (Quina *et al.*, 2007).

The composition of MSW varies over time and from country to country, due to the differences in lifestyle and waste recycling process seasons. Also, chemical and physical characteristics of the FA depend on the composition of the raw MSW, the operational conditions, the type of incinerator and APC system design (Zacco *et al.*, 2014). As the APC residues that will be further on studied are respectively from an incinerator with a semi-dry system and another one with a wet system, is given an enlarged description (Astrup, 2008):

- **Semi-dry residue systems** – Slaked lime is injected into the gas, either in dry form or as a slurry. This aims to neutralize acidic components in the flue gas, and is typically done before removing the FA from the flue gas. Fly ash, reaction products, and unreacted lime is typically removed in fabric filters. Activated coal may be injected for dioxin removal and removed together with the FA. Dry and semi-dry systems typically generate a single residue;
- **Wet residue systems** – Fly ash is typically removed before neutralizing acidic components. After this, the flue gas is scrubber in one, two or multistage arrangement of scrubbers. The scrubber solutions are then treated to produce sludge and gypsum. Wet systems typically generate more than one residue.

These different methods will produce very distinct APC residues, and in order to select the most appropriate method of treatment or application for any residue, its main characteristics, and particularly chemical properties should be known. In some cases, some physical characteristics may also be very important. The major elements present in the APC residues are Si, Al, Fe, Ca, Mg, K, Na and Cl⁻. Regarding heavy metals, Cd, Cr, Cu, Hg, Ni, Pb and Zn are the most frequent, with Zn and Pb being generally found in the largest amounts (Quina *et al.*, 2007). Table 2.2 presents typical rates of heavy metals and chloride in different residue components: FA, dry, semi-dry and wet processes.

Table 2.2. Typical ranges of heavy metals and chloride in different residue components (Chandler *et al.*, 1997)

Content of APC (mg kg ⁻¹)			
Elements	FA	Dry	Semi-dry and wet
Cd	50 - 450	140 - 300	150 - 1400
Cr	140 - 1100	3 - 570	80 - 560
Cu	600 - 3200	16 - 1700	440 - 2400
Pb	5300 – 26 000	2500 – 10 000	3300 – 22 000
Zn	9000 - 70 000	7000 - 20 000	8100 - 53 000
Cl⁻	29 000 – 210 000	62 000 – 380 000	17 000 – 51 000

Trace quantities of very toxic organic compounds are also usually present in these residues, namely polycyclic aromatic hydrocarbons (PAH), chlorobenzenes (CB), polychlorinated biphenyls (PCB) and polychlorinated dibenzo-p-dioxins (PCDD) and furans (PCDF) (Quina *et al.*, 2007). Whenever the treatment, utilization or disposal of APC residues is considered, both Pb and Cl⁻ are of particular concern due to their leaching behaviour. Consequently, the natural pH of these residues is usually very high (12-13 pH), which may constitute a problem for some applications. It should be noted that 12.5 is the pH value of a saturated solution of Ca(OH)₂ (Quina *et al.*, 2007).

Due to the high concentration of several heavy metals, the reuse of APC residues as a secondary material is forbidden in many countries, with the ever more stringent legislation. Therefore, taking into account the potential environmental impact of these residues, the main problems that have to be solved concern toxic heavy metals (e.g., Pb, Zn, Cd, Cr, Cu, Ni, Hg), the high concentration of soluble salts (e.g. NaCl, KCl, salts of Ca), and organic micropollutants (e.g., dioxins, furans) (Quina *et al.*, 2007). Consequently, a technical remediation process is required before providing possible reuses to the APC residues. There are two alternative ways of handling APC residues: landfilling after adequate treatment or recycling as a secondary material after suitable inertisation

2.1.2.1 Possible applications

Appropriate treatments for APC residues, specifically regarding heavy metals, can be grouped into three classes (Zacco *et al.*, 2014):

- i. Separation processes, for instance, electrochemical process;
- ii. Solidification/stabilization process, for example cement based;
- iii. Thermal methods, like microwave treatment.

A combination between separation processes and S/S processes will be further considered for this study. Electrodialytic method will be explained in section 2.3, the S/S processes are considered in the following paragraphs.

The S/S processes use additives or binders in order to physically and/or chemically immobilize hazardous components initially present in waste (Wiles, 1996). Solidification involves the transformation of a liquid or a sludge into a solid, and may not lead to a chemical interaction of the constituent of concern with the solidifying agent. The process reduces the mobility of the contaminants in the treated material through encapsulation, as a consequence of the reduced surface area and lower permeability (Quina *et al.*, 2007). On the other hand, the main goal of stabilization is to convert the contaminants into less soluble or less toxic forms, with or without solidification (Quina *et al.*, 2007). In

practice, the best approach to S/S technology involves initial chemical stabilization and then solidification of the waste. Inorganic materials, such as cements or pozzolanic materials are the most common binders (Quina *et al.*, 2007). Solidification/stabilization methods consist of mixing the binders with the waste and water, and sometimes with chemical additives (e.g. sodium silicate or soluble phosphates). The quantities involved are optimized as a function of the performance required for the final product (leaching behaviour, compressive strength, setting time, etc.), which may be either solid massive (monolithic) or granular (Quina *et al.*, 2007).

Van de Laar *et al.* (1994) show that with the exception of chlorides, the immobilization of most toxic elements is possible through S/S processes. According to Quina *et al.* (2007) the most dynamic research area is in the field of solidification with binders, using in particular Portland cement. In practice, at the industrial level in Europe, this is indeed the most important method for treatment of APC residues (Quina *et al.*, 2007). Thus, to better understand the process, when water is added to cement a hydration reaction takes place. The hydration products crystallize and create a three-dimensional structure that binds together all the substances present into a hard mass. The reactions that occur are the basis for the S/S process, applied world-wide for the treatment of hazardous waste. The 3-dimensional structure formed, which comprises hydration products, water, small bubbles of air, and particles of sand or stone, can also include small particles (< 150 µm). Air pollution control residues particles have a small grain size and they could fill these spaces and become encapsulated inside the concrete matrix (Ferreira *et al.*, 2003a).

When Portland cement or similar binders are employed, the product is monolithic and a significant increase in weight (almost double) and volume may occur, which affects shipping and landfill costs (Ferreira *et al.*, 2003a). Environmental costs should also be considered as resources such as soil and raw materials are used. Another disadvantages of treatment with cement are related with low retention of salts, which may leach out in the short term, the possible release of heavy metals in the medium to long term, and finally the problem of the monolith formed at the landfill site that will hardly ever be used again (Ferreira *et al.*, 2003a). The main advantages come from the fact that this technology is well established and low cost. According to Ferreira *et al.* (2003a) it is advisable to remove the salts before adding the binders, whenever possible.

2.2 Heavy metals

Some metals that potentially exist in higher concentrations in APC residues may have a damaging action to the environment. Like in nature, the incineration process does not destroy or form heavy metals. The total quantity of metal entering the combustion chamber is just redistributed in the process effluent

(Quina, 2005). In literature, there are many studies about the behaviour of metals in the combustion chamber incineration processes (Fernandez *et al.*, 1992; Wey *et al.*, 2001; Ferreira *et al.*, 2003b). One way to reduce the amount of heavy metals in MSW is the selective separation, mainly of batteries, electronic components and plastics, which has been gaining importance particularly during last decade.

The potential negative effect to the environment of a metal is determined by its oxidation state, its chemical form and its concentration. The possible toxic effects in humans are the occurrence of acute toxicity effects, skin and eyes irritation, allergic reactions, systemic toxicity, organ toxicity, carcinogenic, mutagenic and eventually teratogenic (reproductive toxicity) (Quina, 2005). According to Evans (1989) the toxicity in plants and in animals can vary considerably but it still can be sorted as follows:

Hg, Cd, Ag, Tl > Cu, Pb, Co, Sn, Be > In, Ba > Cr, Mn, Zn, Ni, Fe > Y, La > Sr, Sc > Cs, Li, Al

The main route through which metals can damage humans are inhalation and ingestion of liquids or solids where they exist. Since the APC residues result from a thermal process, it is appropriate to classify the various metals based on their volatility (Fernandez *et al.*, 1992):

- Non-volatile - elements with a high boiling point and hardly volatilize in the combustion zone: Al, Ba, Be, Ca, Co, Fe, K, Mg, Mn, Si, Sr, Ti, Cu, Cr, Ni;
- Semi-volatile - elements that volatilize during combustion and can condense on the surface of the particles as the gas cools Pb, Cd, Se, Sb, Zn, In, As;
- Volatile - Elements that can be released into the gas phase: Hg, Cl, Br.

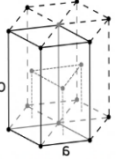
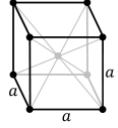
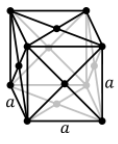
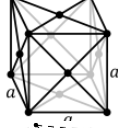
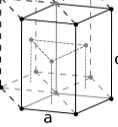
The leaching process is one of the main mechanism by which the residue can damage the environment, and humans in particular. In solution, metals can be found as free ions and/or complexed with organic or inorganic compounds. There is a huge number of ligands that can cause metal complexes, in form of soluble complexes generally connected to Cl⁻, OH⁻ or organic matter, or many of which are conjugate bases of weak acids (Quina, 2005). The extent of complexation mainly depends on the amount of metal ions, complexing ligands and pH in solution. Thus, the total metal content of a solution is the sum of free metals plus the sum of all the metal species that may form (Quina, 2005). Furthermore, the chemical forms in which one element is in solution (speciation) can be decisive for the mobility in the environment, bioavailability and ability to participate in reactions of precipitation and adsorption/absorption (Kot & Namiesnik, 2000).

Youcai *et al.* (2002) reported that the concentration of metals in the FA is highly correlated with the temperature of the boiling and melting points of the oxides, sulphates and chlorides, thus, lower these temperatures lead to higher heavy metals concentrations at the ash. According to Sabbas *et al.* (2003),

the relevant metals to consider in waste incineration are: As, Al, B, Ba, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, Zn, and in terms of anions are the following: Br⁻, Cl⁻, CN⁻, F⁻, NH₄⁺, NO₃⁻, NO₂⁻, SO₄²⁻.

The chemical and physical characteristics that influence the behaviour of heavy metals during the pollution control in incineration processes are of utmost relevance. Table 2.3 presents some characteristics of Cd, Cr, Cu, Pb and Zn.

Table 2.3. Some chemical and physical characteristics of Cd, Cr, Cu, Pb and Zn (<https://www.ncbi.nlm.nih.gov/pccompound/?term=Iron>)

GENERAL PROPRIETIES			PHYSICAL PROPRIETIES			ATOMIC PROPRIETIES		
Crystal structure	Element category	Thermal conductivity (W m ⁻¹ K ⁻¹)	Melting point (K)	Boiling point (K)	Heat of vaporization (kJ mol ⁻¹)	Oxidation states	Ionization energies (kJ mol ⁻¹)	Electro negativity (Pauling scale)
	Transition metal	96.6	305	1040	99.87	2, 1 (mildly basic oxide)	1st: 867.8 2nd: 1631.4 3rd: 3616	1.69
	Transition metal	93.9	2173	2915	339.5	6, 5, 4, 3, 2, 1, -1, -2 (strongly acidic oxide)	1st: 652.9 2nd: 1590.6 3rd: 2987	1.6
	Transition metal	401.1	1356	2868	300.4	+1, +2, +3, +4 (mildly basic oxide)	1st: 745.5 2nd: 1957.9 3rd: 3555	1.90
	Poor metal	35.3	601	2013	179.5	4, 3, 2, 1 (Amphoteric oxide)	1st: 715.6 2nd: 1450.5 3rd: 3081.5	1.87
	Transition metal	116	693	1180	123.6	+2, +1, 0 (amphoteric oxide)	1st: 906.4 2nd: 1733.3 3rd: 3833	1.65

Specifying for the incineration process:

Cadmium

The percentage of Cd present in the FA from MSWI mostly comes from the batteries that still arrive at municipal systems (Quina, 2005). Verhulst *et al.* (1996) reported that Cd is easily volatilized as chlorides ($\text{CdCl}_2(\text{g})$), even in oxidizing conditions, like Cd(g) if temperatures are high ($> 700\text{ }^\circ\text{C}$). The formation of sulphate ($\text{CdSO}_4(\text{g})$) is also possible but it will be a dominant phenomenon for low temperatures ($< 700\text{ }^\circ\text{C}$). In the S/S methods, for instance with cement, a strong reduction in the amount of leached Cd can be observed due to the dilution effect element and incorporation of the mineral phase. The Cd can be effectively adsorbed onto the surface of the iron oxide (Zacco *et al.*, 2014).

Chromium

Chromium may come from several materials, and the major sources are glue, matches, scrap metal and building materials (Abbas & Steenari, 2001). The behaviour of this element in the combustion chamber is conditioned by the fact that both in the metallic form and in the form of various Cr compounds they have a relatively low vapour pressure and it is consequently difficult to volatilize. However, Cr(VI) is more likely is the oxidation state since it is solid and oxidized at high pH (Cai *et al.*, 2003). In terms of treatment, the Cr(III) is easier to treat as it is more immobile than Cr(VI). Additionally, the form (III) and (VI) may be soluble in an alkaline medium, with the predominance of one form over the other depending on the redox potential (Quina, 2005).

Copper

In the combustion chamber of the incineration processes it is thermodynamically possible that the total volatilization of Cu occurs in the form of $\text{CuCl}(\text{g})$ and $\text{Cu}_3\text{Cl}_3(\text{g})$ or in complex oxides ($\text{CuO}\cdot\text{Fe}_2\text{O}_3$, $\text{CuO}\cdot\text{Al}_2\text{O}_3$ and silicates). In practical terms, volatilization of Cu is normally low, and very dependent on the chamber reduction conditions and amount of existing chlorides (Verhulst *et al.* 1996). Also the volatilization in the form of sulphates is significant only at low temperatures ($< 700\text{ }^\circ\text{C}$).

Lead

When there is no pre-sorting, the source of Pb can be any of the materials on which it is employed. However, the materials with larger contribution are batteries, welding, wiring (Pb in metallic form), crystal, fluorescent bulbs, paints and pigments present in several different materials (Quina, 2005). These materials can provide about $120\text{ g of Pb t}^{-1}\text{ MSW}$, with a higher transfer to 33% for particles entrained by the gases (Quina, 2005). Verhulst *et al.* (1996) stated that Pb easily volatilized as chlorides ($\text{PbCl}_2(\text{g})$ $\text{PbCl}(\text{g})$), even in oxidant conditions, as well as $\text{PbO}(\text{g})$ and $\text{Pb}(\text{g})$, if the temperatures are higher ($> 700\text{ }^\circ\text{C}$). The sulphates formation ($\text{PbSO}_4(\text{g})$) is also possible but it will be a dominant phenomenon only at low temperatures ($< 700\text{ }^\circ\text{C}$). The Pb amount present depends on the particle size

distribution (Yuan *et al.*, 2005). In terms of treatment of these wastes, Pb can be separated and recovered (Pedersen, 2002b), stabilized through chemical additives and treated by S/S using, for example cement (Zacco *et al.*, 2014).

Zinc

Verhulst *et al.* (1996) referred that Zn partially volatilizes in the form of chloride ($ZnCl_2(g)$), even in oxidizing conditions, as well as $ZnO(g)$ and $Zn(g)$. To volatilize Zn, reducing conditions and excess chlorides are favourable. The formation of sulphates ($ZnSO_4 \cdot 2H_2O(g)$) is also possible but will be a dominant phenomenon for low temperatures ($< 500\text{ }^\circ\text{C}$). In the combustion chamber it can also form stable compounds with Zn ($ZnO \cdot Fe_2O_3$, silicates, silicoaluminates), significantly reducing its volatility. The S/S treatments are generally suitable for this metal but it should be taken into account that Zn exhibits amphoteric behaviour that, in some treatments, may unexpectedly lead to increased leached amounts. Since the Zn concentrations are significant in waste incineration, some studies show that this metal can be recovered (Pedersen, 2002b).

Anions (Cl^- , SO_4^{2-})

Chloride has a considerable relevance in incineration processes, particularly at the level of the chemical compounds formed during the process of APC. In fact, the MSW can contain significant amounts of chloride, being its main source the plastics fraction (Quina, 2005). The presence of the chloride has environmental disadvantages since HCl is its volatilization primarily form. The $Cl_2(g)$ formation is thermodynamically unstable at more than $150\text{ }^\circ\text{C}$ (Verhulst *et al.*, 1996). In addition, the presence of a high amount of chloride significantly increases the volatilization of most metals (Marani *et al.*, 2003).

This high chloride content in the waste is damaging at many levels, because it is easily leached and it is poorly retained in the S/S treatment which after makes unfeasible to use this residue in material production (Zacco *et al.*, 2014). Giordano *et al.* (1983) showed that high concentrations of chloride in the ash promote metals mobility in the soil since it works as an anion complexing agent. The CaOHCl develops during the neutralization of HCl by excess lime, according to the reaction 2.1:



The sulphates may be formed in the combustion of the incineration chamber from the sulphur present in the MSW, and it can also influence heavy metals volatilization, although the effect is much smaller than for chlorides (Quina, 2005).

Once the APC residues that will be further studied (section 4), will be also reused in future building materials, it is important to understand how the metal leaching occurs and which are the factors that influence it. The leaching processes are the main exposure ways for ecosystems and living beings. They involve the contact a liquid with a solid material, resulting in a partial dissolution of particular components. Leaching is the result of the occurrence of more or less complex chemical reactions, being the chemical species mobilized by the processes of diffusion and/or convection (Quina, 2005).

According to Quina (2005), there are several physical, chemical and biological factors that may influence the leaching processes. The most relevant factors are the physical size of particles subject to leaching, the mineral phases homogeneity, the process time, the flow of leaching agent, the temperature, the porosity of the solid matrix, the geometric shape and size of the material, the permeability matrix and the hydrogeological conditions (Quina, 2005). The most important chemical factors are the chemical equilibrium kinetics, the material pH, the possibility to occur complexation, redox conditions, adsorption processes, ion exchange, surface complexation and electrostatic attraction (Quina, 2005). The biological action may also impact the leaching processes that is directly related to the living beings' ability to affect some of the physical and chemical aspects above mentioned (Quina, 2005).

Among all the factors that may affect the leaching processes, the pH is a decisive parameter for all the phenomena involved. Thus, the metals leaching should always be indexed to the pH value present in the solution. There are several processes that can have a strong influence in the leached amount. For example, complexation with organic matter Dissolved Organic Carbon or Cl⁻, that can increase the amount leached in the alkaline pH range (pH > 7) (Quina, 2005). In terms of pH, it should be distinguished whether if the system is open or closed to the atmosphere, considering that in open systems that variable can be strongly affected by absorption of CO₂ from the air (Quina, 2005).

Summarizing up, the amount of metals may vary several orders of magnitude depending on the pH range. In general, at less than pH 4, a plateau is reached that must be relatively close to the potentially leachable amount (Quina, 2005).

2.3 Electrodialytic process – A remediation technique

The theoretical principle of electrokinetics has been studied throughout the years, since 1809 Reuss (Lima, 2008), until recent journal publications, e.g. Suzuki *et al.* (2014). The ED process is a combination of the electrokinetic principle with the use of ion-exchange membranes. The enhanced electrochemical remediation technique was developed at the Technical University of Denmark (patent PCT/DK95/00209) in 1990s for Ottosen & Hansen (1992), Hansen (1995) and Ottosen (1995).

However, the introduction of membranes to an electrochemical process was tried before by Carr *et al.* (1962 in Lima, 2008).

The ED process has proved its efficiency on the removal of heavy metals from soil (Ottosen, 1995; Ottosen *et al.*, 1997; Hansen *et al.*, 1997; Ribeiro & Mexia, 1997; Ribeiro, 1998; Ribeiro *et al.*, 2005; Ribeiro & Rodríguez-Maroto, 2006; Jensen *et al.*, 2007; Sun, 2013), as well as from quite a few other solid matrices with high removal efficiencies, such as harbour sediments (Nystroem, 2005), impregnated waste wood (Ribeiro *et al.*, 2000; Christensen *et al.*, 2006), mine tailings (Hansen *et al.*, 2005), sludge (Ottosen *et al.*, 2007) or different ash residues (Ferreira, 2005; Lima, 2008; Lima *et al.*, 2012; Kirkelund *et al.*, 2013). Table 2.4 presents advantages and disadvantages of ED process.

Table 2.4. Advantages and disadvantages of ED treatments (adapted from Gardner, 2005)

Advantages	Disadvantages
<ul style="list-style-type: none"> ▪ There are currently no other viable <i>in-situ</i> methods for treating contaminants in porous media simultaneously; ▪ Ionic contaminants are absorbed to sediment particles and are often not available for removal by the simple flushing action of water. The pH shift produced by the electrolysis of the water effectively desorbs contaminating ions; ▪ The process is competitive in cost and remediation effectiveness to other methods currently in use; 	<ul style="list-style-type: none"> ▪ The ED process is limited by the solubility of the contaminant and contaminants desorption from the soil matrix. Heavy metals in metallic states are difficult to dissolve and separate from soil samples. The process is also not efficient when the target ion concentration is low and non-target ion concentration is high; ▪ Acidic conditions and corrosion of the anode may create difficulties in in-situ efforts.

2.3.1 Transports mechanisms

The ED process is a remediation technique, applied to contaminated porous matrices being particularly suitable for the remediation of fine-grained soils, due to the presence of diffuse double layer. The main principle used in the EDR is that ions (including heavy metal ions) move under the influence of an electric field. When an electric field is applied to, e.g., a water saturated soil matrix, the current is carried by ions in the soil pore water that move according to their charge (Christensen, 2004). A low level direct current (DC) is applied to the cross section of the soil or other matrix between a pair (or multiple pairs) of electrodes, producing a current density in the range of mA cm⁻² (Ribeiro & Rodríguez-Maroto, 2006).

When the electric field is created, EDR has three main transport mechanisms taking place: electromigration, electroosmosis and electrophoresis. Diffusion is also important since the concentration gradient is built up by material transport. These transport processes are schematized in Figure 2.3.

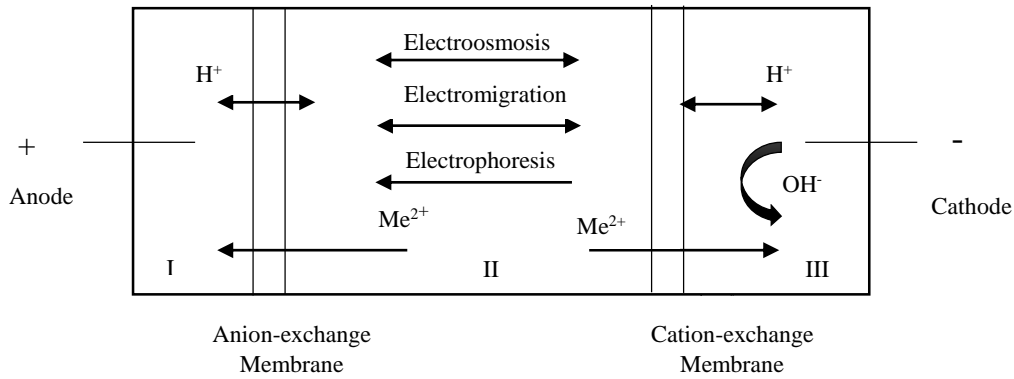


Figure 2.3. Schematic presentation of the EDR principle in an experiment cell (3 compartments). I – anode compartment; II – central compartment; III- cathode compartment (adapted from Nyström, 2001)

Electromigration

Electromigration is the physical transport mechanism that is mainly responsible for moving ions through water or moist soil by an applied DC field (Kelsh, 1996). The electrical current tends to go where the electrical resistance is lower. In soil, the resistance is lower in the diffuse double layer, where the ions are accumulated but not specifically adsorbed. Consequently, it is expected that the electrical current passes along the surface of soil colloids and micropores (Ottosen, 1995).

The current efficiency of electromigration of one specific ionic specie is expressed as the proportion of electrical charge carried by the species of interest, relative to the amount of charge carried by all charged species in solution (Acar & Alshwabkeh, 1993; Ribeiro, 1998; Ribeiro & Rodríguez-Maroto, 2006; Lima, 2008). The electromigration transport, J_m , is given by:

$$J_m = -u * c \phi_e \quad (2.2)$$

Where:

u^* and c – ionic mobility and concentration of species;

ϕ_e - gradient of electric potential.

When applying an electric current to a moist porous material, the ions flow naturally to the opposite charged electrode (electromigration) (Lima, 2008). Electromigration is the most important transport mechanisms for ions in porous media and the electromigration flux is dependent on the ionic mobility, tortuosity factor, porosity of the material, and charge of ions (Acar & Alshwabkeh, 1993).

Electroosmosis

Electroosmosis is the movement of the pore water under the influence of an electric field (Ottosen, 1995). The removal of uncharged species or weakly dissociated organic contaminants, like phenols, is predominant, where the soil has a finite zeta potential (Ribeiro *et al.*, 1999). The flow-direction of electroosmosis is, in the most cases, towards the cathode, but at low pH-values charge reversal of the soil may occur, and cause of electroosmotic flow to change direction (Jensen, 2005). The electroosmotic flux, J_{eo} , is described by the following equation:

$$J_{eo} = -k_e c \phi_e \quad (2.3)$$

Where:

k_e – electroosmotic permeability of soil

c - concentration of species

ϕ_e - gradient of electric potential.

Electroosmotic flow differs from flow caused by a hydraulic gradient because it is mainly dependent on the porosity and zeta potential of the soil, rather than pore size distribution and macropores (Sun, 2013). The electroosmosis is efficient in fine-grained soils (Acar & Alshawabkeh, 1993). The electroosmotic mobility ($k_e c$) is generally 10 times lower than the ion mobility during electromigration ($u^* c$) (Lageman *et al.*, 1989).

Electrophoresis

Electrophoresis is the opposite of electromigration and is the movement of larger units, as protein molecules or colloidal particles, under a potential gradient. The charged particles are electrostatically attracted to one of the electrodes and repelled by the other, where negatively charged clay particles move towards the anode (Ribeiro, 1998). Electrophoresis is generally of limited importance in compacted soil system (Probstein & Renaud, 1987 in Sun, 2014), and the process is rarely encountered in EDR (Jensen, 2005), but can be significant if an electric field is applied to a slurry (Acar & Alshawabkeh, 1993), as well as in unconsolidated soils, the electrophoresis may play a role in their cementation (Ribeiro, 1998).

Diffusion

Diffusion is the movement of ionic species under a chemical concentration gradient. In free solutions, is usually expressed by Fick's law and in porous media as well. In the latter case, the effective diffusion coefficient must be obtained correcting the diffusive coefficient, to take into account the porosity and

the tortuosity effects, which can decrease this transport in more than one order of magnitude (Ribeiro & Rodríguez-Maroto, 2006). The diffusive flux in soil can be obtained by:

$$J_d = -D^*\nabla c \quad (2.4)$$

Where D^* is the effective diffusion coefficient and ∇c is the concentration gradient. In general, in the usual conditions for the electrokinetic treatment this is a secondary transport and can be important only in some areas of soil where gradients are especially high, e.g., acid and basic fronts. (Ribeiro & Rodríguez-Maroto, 2006).

Electrodialysis

Ion-exchange membranes are membranes made of polymers with charged surfaces that promote high permselectivity, low electric resistance, good mechanical/form stability and high chemical and thermal stability (Strathmann, 2004). Two types of membranes are the key to EDR: the cation-exchange membrane and the anion-exchange membrane. The surface will attract dissolved ions, with the opposite charge (counter-ions) from the pore water of the membranes. The counter-ions will be transported through the membrane due to the electrical current and the co-ions (with the same charge as the surface of the membrane) will be rejected (Figure 2.4).

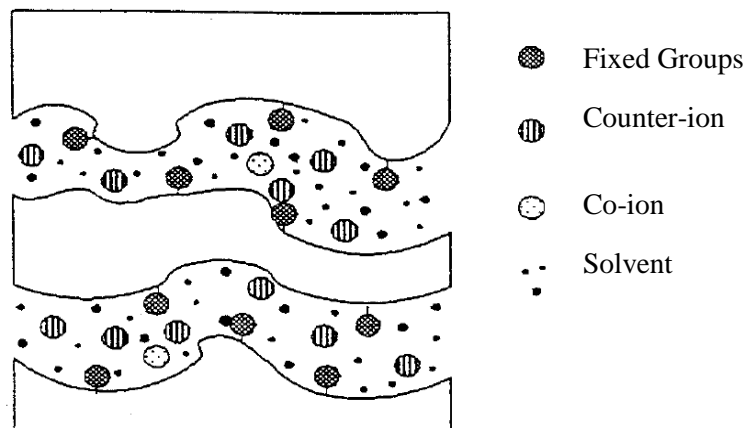


Figure 2.4. Sketch of an ion-exchange membrane (Hansen, 1995)

However, ion-exchange membranes are not be 100% effective, which means that some co-ions can pass the membrane together with the counter-ion, Hansen (1995) presents several advantages of the use of membranes:

- Allow the passage of ions from polluted media to the electrode compartments;

- Prevent/prohibit the passage of ions from electrode compartments (I and III – Figure 2.3) back to the contaminated media (II - Figure 2.3);
- Maintain the ions removed from compartment II in the electrolytes (in compartments I or III);
- Prevent the produced acid and base at the anode and the cathode, respectively, to enter into the soil and be transported through the soil, thus saving energy.

The membranes allow the regulation of the ion fluxes, thus selecting the ions that reach the electrode compartments. A concentration gradient is therefore essential for the flow of ions and water throughout the system (Hansen, 1995).

Electrode reactions

In compartments (I) and (II) of the ED cell (Figure 2.3) the electrolytes are kept re-circulating in order to avoid the build-up of concentration gradients in the vicinity of the electrodes and, at the same time, remove the gasses produced by the electrode reactions (Lima, 2008). The pH in these solutions is varying during the EDR, mainly due to the electrode reactions. Inert electrodes made of carbon, platinum or titanium are used in ED soil remediation because they do not take part in the electrode reactions (Nystrøm, 2001). The applied current leads to electrolysis of water at the electrodes, where the primary reactions are the following:



Thus, acid is produced at the anode and base is produced at the cathode. When the metal concentration in the electrolytes increase, precipitation of the metal at the electrode surface can occur:



If chlorides are present in the electrolyte (anolyte), chloride gas is produced:



Adjustments can be made to the earlier established ED cell treatment purpose depending on the final objective. For example, the number of compartments can be reduced to two compartments and introduce

the anode directly into matrix compartment. This cell design was recently developed at Technical University of Denmark and patented (Ottosen *et al.*, 2014) by Lisbeth Ottosen, Pernille Jensen, Gunvor Kirkelund and Benjamin Ebbens and, till now, no data has been published using this cell design. This new approach uses the acid produced in the anode to promote the electromobilization of heavy metal complexes from a liquid suspension to the cathode compartment, where they are concentrated. This new approach primarily aims to increase the efficiency in mobilizing and separating heavy metals and other elements in a 2C ED cell setup, opposed to a 3C setup.

2.3.2 Electrodialytic treatment of FA and APC residues from MSWI

The removal of heavy metals from MSWI fly ashes using ED treatment was first applied by Pedersen (2002a), with a conventional ED cell. Difficulties during these initial experiments, like the precipitation in electrolytes, poor control of the pH or long remediation times, revealed the need to agitate the matrix in the cell. Pedersen *et al.* (2002a) introduced a stirring rod in the central cell compartment. After the introduction of the stirrer, several studies about EDR of FA from MSWI were made, and the assisting agents were introduced to further enhance the process. Beside the assisting agents, water was also used for acidification.

Table 2.5 summarizes different removal rates obtained by several authors. The differences removal are mainly due to two different reasons: the types of ash and the final pH of treated sample.

Table 2.5. Electrodialytic treatment of FA and APC residues from MSWI reported in literature (adapted from Ferreira, 2005)

Type of ash	Current Density (mA cm ⁻²)	Number of ED cell compartments	Time of treatment (week)	Assisting agent	Removal rates (%)	Refs.
Fly ash: Collected electrostatic precipitator before exposure to flue gas cleaning additive. From: Nuuk, Greenland.	0.8	3	10	0.5 M ammonium citrate in 2.5% NH ₃	Cd 44 Cr 2-3 Cu 18 Pb 8 Zn 73	(Pedersen, <i>et al.</i> , 2001)
	0.8	3	10	0.5 M ammonium citrate in 2.5 NH ₃	Cd 40 Cr 2-3 Cu 31 Pb 2.5 Zn 24	(Pedersen, <i>et al.</i> , 2001)
	0.8	3	3	0.25 M ammonium citrate in 1.25 NH ₃	Cd 70	(Pedersen, <i>et al.</i> , 2001)
Fly ash: Collected on the electrostatic precipitator and not exposed to any flue gas cleaning additive. From: Vestforbraending, Denmark.	0.8	3	2	2.5% NH ₃	Cd 100 Cr 7 Cu 49 Pb 3.5 Zn 42	(Pedersen, 2002b)
	0.8	3	2	Water	Pb 12 Zn 25	(Pedersen, 2002b)
	0.8	3	2	0.25 M Na-citrate	Cd 15 Cr 15 Cu 37 Pb 12 Zn 39	(Pedersen, 2002b)
	0.8	3	2	0.25 M ammonium citrate in 1.25 NH ₃	Cd 62 Cr 20 Cu 59 Pb 6 Zn 39	(Pedersen, 2002b)
	0.8	3	3	Water	Cd 4 Cu 5 Pb 5 Zn 4	(Ferreira <i>et al.</i> , 2004)
Air pollution control residues: Collected in semi-dry air pollution control equipment. From: Valorsul, Portugal	0.8	3	3	3% Na-gluconate	Cd 2 Cu 3 Pb 2 Zn 3	(Ferreira <i>et al.</i> , 2004)
	4.0	3	3	22% Na-gluconate	Cd 5 Cu 2 Pb 3 Zn 3	(Ferreira <i>et al.</i> , 2004)
	4.0	3	3	22% Na-gluconate	Cd 10 Cu 5 Pb 6 Zn 6	(Ferreira <i>et al.</i> , 2004)
	0.8	3	2	3% Na-gluconate	Cd 2 Cu 0.2 Pb 1 Zn 2	(Ferreira <i>et al.</i> , 2004)

Table 2.5. (cont.) Electrodialytic treatment of FA and APC residues from MSWI reported in literature (adapted from Ferreira, 2005)

Type of ash	Current Density (mA cm ⁻²)	Number of ED cell compartments	Time of treatment (week)	Assisting agent	Removal rates (%)	Refs.
Fly ash: Incinerator. From: Valorsul, Portugal	0.8	3	2	Water	Cd 86 Cr 44 Cu 81 Pb 20 Zn 62	(Pedersen <i>et al.</i> , 2005)
	0.8	3	2	Water	Cu 90 Pb 41	(Ottoen <i>et al.</i> , 2006)
Fly ash: Mixture of residue collected from boiler, APC devices and sorbents (e.g. lime). From: Valorsul, Portugal.	0.8	3	2	Distilled Water	Cd 7.4 Pb 22.6	(Lima <i>et al.</i> , 2008a)
	0.8	3	2	0.25 M ammonium citrate in 1.25 ammonia	Cd 40.1 Pb 3.7	(Lima <i>et al.</i> , 2008a)
Air pollution control residues: Results from the complete flue gas treatment at the incineration unit – injection of ammonia for NOx removal in the boiler; addition of lime in the scrubber; collection of all the formed particulates (both electrically and non-electrically chargeable) in filters. From: Valorsul, Portugal	0.8	3	2	Distilled Water	Cd -17 Cu -82 Pb -17	(Lima <i>et al.</i> , 2010a)
	0.8	3	2	0.25 M ammonium citrate in 1.25 ammonia	Cd 57 Cu 45 Pb 21	(Lima <i>et al.</i> , 2010a)
Air pollution control residues: Collected after treatment of flue gas in electrostatic filters. From: Illulissat, Greenland.	1	3	1	Distilled Water	Cd < 0.01 Cr < 0.1 Cu < 0.01 Pb 2 Zn < 0.1 ^(a)	(Kirkelund <i>et al.</i> , 2013)
	1	3	2	Distilled Water	Cd 1 Cr < 0.1 Cu 1 Pb 4 Zn 1 ^(a)	(Kirkelund <i>et al.</i> , 2013)

^(a) values read from graphics

Air pollution control residues, are a more complex FA, which results from the complete flue gas treatment at the incineration unit. Air pollution control includes, in some cases, activated carbon, added in the scrubber for adsorption of heavy metals. The activated carbon is an adsorption agent, and can “hold” strongly to the metals (Ferreira, 2005). The final ash pH is a significant factor and the pH drop that occurs during the ED process promotes the dissolution of oxides, hydroxides and carbonates, and

helps to solubilise the heavy metals (Ferreira, 2005). After, that, metals can be mobilised under the electric field and transported away from waste, more acidification better removals rates (Ferreira, 2005).

3. Material and methods

For a better understanding of the experimental work, Figure 3.1 presents the materials and methods used in the work, initial characterization, ED experimental conditions, mortar bars conditions, performance machines and which legislation was used in section 4 aims to verify if the residues were in conformity.

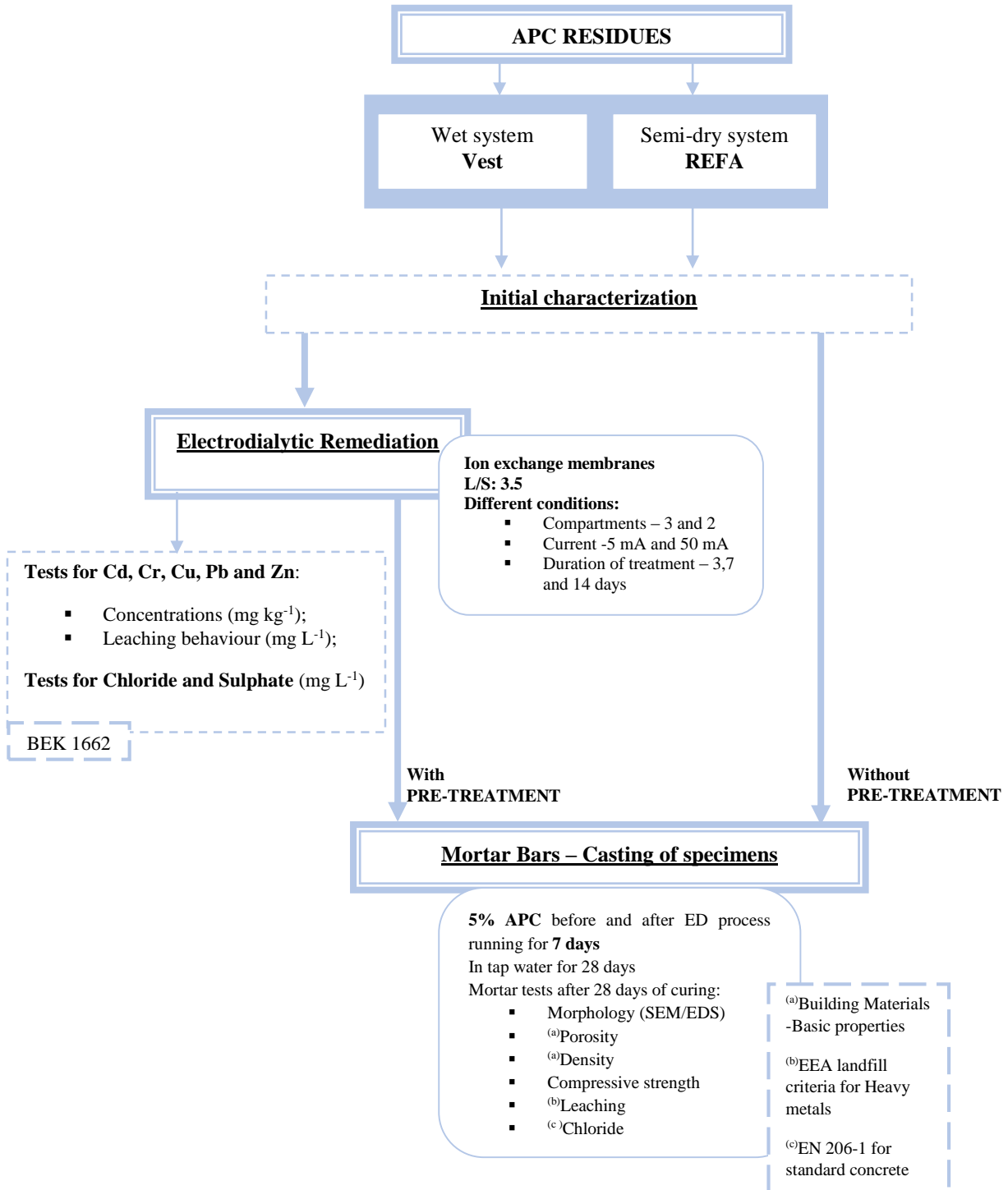


Figure 3.1. Scheme of initial characterization, ED experiments and casting of specimens

3.1 Air pollution control residues

Two types of APC residues from MSWI, were used in this study. Both were collected from two Danish waste incineration plants: one collected after a semi-dry process from I/S REFA and a second one after a wet flue gas cleaning process from I/S Vestforbrænding (Vest). I/S REFA collects and treats all kinds of households in a total of approximately 200 000 t year⁻¹, producing approximately 3 000 t year⁻¹ of APC residues. Vestforbrænding has total capacity of 600 000 t year⁻¹, with a production of APC residues of 15 000 t year⁻¹.

3.2 Characterization methods

In all methods a series of three replicates were carried out. The APC residues characterization and extraction experiments were carried out using dried ash at 105 °C for 24 h. **Total concentration** of Cd, Cr, Cu, Pb and Zn in the APC residues were measured by Inductively Coupled Plasma with optical emission spectrometry (ICP-OES), after pre-treatment according to the Danish Standard DS 259, in which 1 g of APC residue and 20 mL (1:1) HNO₃ were heated at 200 kPa (120 °C) for 30 min. After digestion, the samples were vacuum filtered through a 0.45 µm filter and diluted till 100 mL. The units used in this thesis are mg kg⁻¹ for the concentration in dry matter.

The **pH** in the APC residues were measured with a Radiometer pH-electrode in 1 M KCl at L/S ratio of 2.5 and in deionised water at liquid to solid (L/S) ratio of 5, after 1 h of agitation at 190 rpm. The **conductivity** was measured at the same time as the pH with deionised water, in a Radiometer Analytic. **Loss on ignition** (LOI) was found after 30 min at 550 °C. **Water content** was measured as weight loss after 24 h at 105 °C (calculated as weight loss over the weight of the wet sample). **Water solubility**: 100 g APC residues were suspended in 500 mL deionised water and agitated for 1 min. After settling, the water was decanted. New 500 mL deionised water were added. This was repeated three times to ensure that the APC residues were properly washed. The suspension was then filtered through a 0.165 µm filter and the APC dried residue (105 °C) weighed. **Carbonate content** was determined using a Scheibler apparatus, where a standard curve was first performed using different CaCO₃ contents combined with HCl. The APC residues were mixed with HCl and then the CaCO₃ concentration was determined.

Leaching tests on the two APC residues were made according to CEN prEN 12457-1, with slight modifications. The L/S ratio was 2, mixing 10 g of APC residue and 20 mL deionised 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 and the heavy metal concentrations in the filtrate were

determined by ICP-OES. *Levels of chloride and sulphate* were determined by Ion Chromatography (IC) after extracting 10 g of APC residue with 50 mL of deionised water overnight.

Regarding *particle size distribution* (annex A.1) and *specific surface area*, these results were performed by Laser Diffractometer. The statistics were performed using the programme GraphPad Prism 6. In order to determine if the two APC residues were different, t-test A-NOVA was performed on the initial characteristics.

3.3 Electrolytic experiments

Twenty four ED experiments were performed with the APC residues, according to the experimental conditions presented in Table 3.1. Twelve of them were performed in an ED cell with 3C, two electrodes, two ion exchange membranes (cation and anion) and a central cell compartment. The other 12 were carried out in an ED cell with 2C, two electrodes, one cation-exchange membrane and a central cell compartment, where the contaminated media was placed (Figure 3.2).

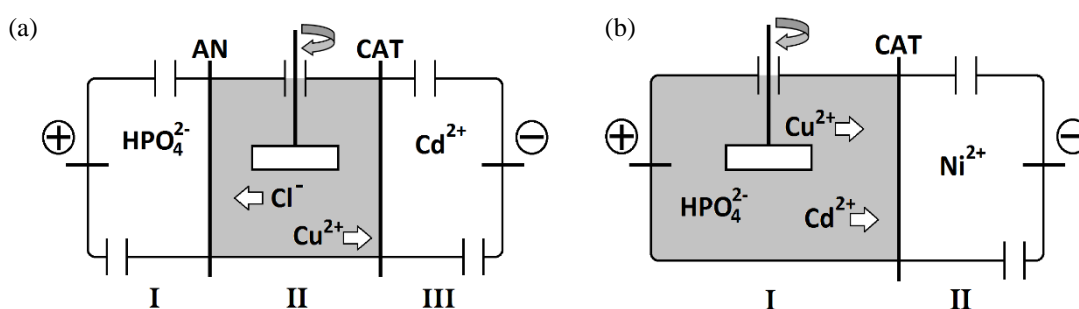


Figure 3.2. Schematic presentation the experimental ED cells. Both models developed at DTU, Denmark: (a) 3 compartment cell, (b) 2 compartment cell. (AN = anion exchange membrane, CAT = cation exchange membrane)

All experiments were performed with 350 mL of deionised water and 100 g of the APC residue, corresponding to a L/S ration of 3.5.

The ED cells were made of plastic (RIAS, Acryl XT), the internal diameter was 8 cm and the central compartment length was 10 cm. Electrode compartments were separated from the central compartment by an anion-exchange membrane AR204SZRA, MKIII, Blank and a cation-exchange membrane CR67, MKIII, Blank, both from Ionics. In the 2 compartment cell, the separation was carried out only with a cation-exchange membrane of the same brand. The surface area of the membrane corresponded to approximately 50 cm² each. The electrodes were made of platinum coated titanium wire ($\varnothing = 3$ mm) made by Grønvold & Karnov A/S. A power supply (Hewlett Packard E3612A) was used, maintaining a constant current of 5 mA and 50 mA, approximately 0.1 mA cm⁻² and 1 mA cm⁻², respectively, depending on the experiment in hand. The APC residue suspension was placed on the central

compartment, stirred 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 0-2000 L min⁻¹. Initially, the suspension reached about 3 cm below the hole where the stirrer was placed, but the height slightly differed during the experiments.

Table 3.1. Experimental conditions for the different EDR experiments

Experiments	APC residue type	Current density (mA cm ⁻²)	Duration (day)	Number of compartments
1	Vest Wet treatment	0.1	3	3
2			7	
3			14	
4			3	2
5			7	
6			14	
7		1	3	3
8			7	
9			14	
10			3	2
11			7	
12			14	
13	REFA semi-dry treatment	0.1	3	3
14			7	
15			14	
16			3	2
17			7	
18			14	
19		1	3	3
20			7	
21			14	
22			3	2
23			7	
24			14	

The anolyte and the catholyte used were 0.01 M NaNO₃ with pH adjusted to 2 with HNO₃ (1:1). In the experiments with 3C, 500 mL of anolyte and 1000 mL of catholyte were used, while in the experiments with 2C, only 500 mL of catholyte was used. The recirculation was made using “Pan World” magnetic pumps from Plastomec Magnet Pump model P05, with a performance rate of 8 L min⁻¹. Voltage and electric current was read on weekdays during the remediation period, pH of the electrolytes and the pH of the APC residue suspension were measured twice a day. pH in the electrolyte was adjusted with (1:1) HNO₃, if pH > 2. The conductivity was measured in the central compartment once a day.

At the end of the experiments the suspension in the central compartment was filtered through a 45 µm filter at normal pressure. The APC residue was digested with acid according to the procedure described in section 3.2. The membranes and stirrer were soaked in 1M HNO₃ and the electrodes in 5M HNO₃, in

order to release precipitated metals. The obtained aqueous phase of the membranes, the stirring, the electrodes and the electrolytes were all analysed for heavy metals (Cd, Cr, Cu, Pb and Zn) by ICP-OES. The pH, leaching and chloride and sulphate were also determined using the dry ash (105 °C) according section 3.2.

3.4 Mortar bars

The mortar bars were made using the raw APC residues (REFA and Vest) and those that were ED treated for 7 days. The selection of the 7 day- remediation was based on the pH of the APC residue, which should preferably be alkaline for a better aggregate with the cement. The type of cement used was an alkali cement.

The 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.

The procedure used for the mortar samples was mixed according to DS/EN 196-7: 225 mL deionised water, 450 g Ordinary Portland cement and 1350 g CEN standard sand ($\emptyset < 2$ mm), with a water/binder-ratio of 0.5 and a sand/cement ratio of 3. Five percent of cement volume was replaced with APC residue. Eleven experimental mortars were made, according to Table 3.2.

Table 3.2. Experimental conditions of mortar bars-casting of specimens

Reference	Vest		REFA	
0% of APC residue	Raw	Upgraded APC residue ED experiment: 2, 5, 8 and 11	Raw	Upgraded APC residue ED experiment: 14, 17, 20 and 23
	Substitution of cement with 5% untreated APC residue	Substitution of cement with 5% treated APC residue	Substitution of cement with 5% untreated APC residue	Substitution of cement with 5% treated APC residue

The moulding was carried out according to DS/EN 196-7. The mould consisted of three horizontal compartments so that 3 prismatic specimens of 40 x 40 mm in cross section and 160 mm in length were prepared, simultaneous 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.

Aiming 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. Porosity and density were determined at the same time, using the following equation:

$$\text{Porosity (\%)} = \frac{V_{p\grave{a}}}{V} \quad (3.1)$$

Density (kg m^{-3}):

$$\rho_d = \frac{m_{105}}{V} \quad (3.2)$$

$$\rho_f = \frac{m_{105}}{(V - V_{p\grave{a}})} \quad (3.3)$$

Where:

$$V_{p\grave{a}} = \frac{(m_{ssd} - m_{105})}{\rho_w}, \quad (3.4)$$

m_{ssd} - weight after vacuum; m_{105} - weight without vacuum; $\rho_w = 1000 \text{ kg m}^{-3}$

$$V = \frac{(m_{ssd} - m_{sw})}{\rho_w}, \quad (3.5)$$

m_{ssd} - weight after vacuum; m_{sw} - weight after vacuum under the water; $\rho_w = 1000 \text{ kg m}^{-3}$

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.

Mortar bars were then crushed and tested for heavy metal leachability and chloride content. The leaching proceeding was carried out as described in section 3.2, but for chloride determination the mortars procedure was the following: 5g 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.

4. Results and discussion

4.1 Air pollution control residues characteristics

In wet systems, like Vest, the APC residue is removed before the neutralization of acidic components. On the other hand, in semi-dry systems, like REFA, the APC residue is removed from fuel gas after the injection of slaked lime into the gas. These different systems imply different ash characteristics, which a simple visual analysis can detect (Figure 4.1). Their colour and their weight are very different, being the Vest much heavier than REFA, similar to sand. However, they both, show similarities, such as a fine to medium grain fine matrices.

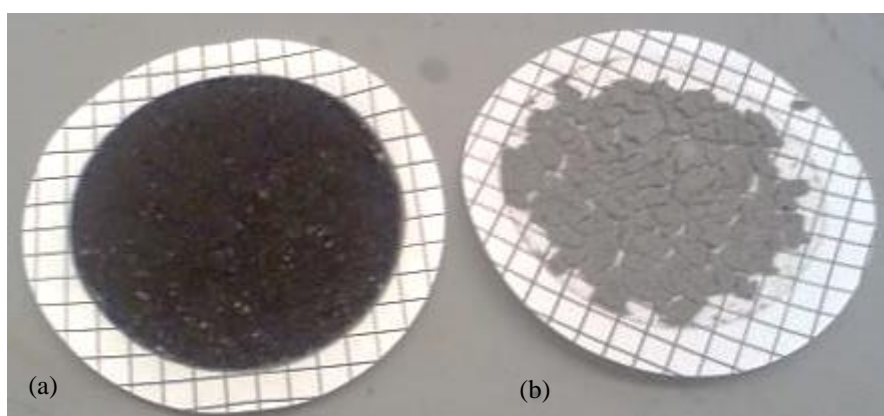


Figure 4.1. Appearance of the APC residues under study – (a) REFA and (b) Vest

Statistical analysis of the ash characteristics was carried out using GrafPad Prims 6 software. T-test was chosen because it is one-sided, since the objective was to compare each individually parameter. This test showed that the two types of APC residues are significantly different, with 99% and 95% confidence levels with some exceptions, such as water solubility and water content (Table 4.1).

Both APC residues are highly alkaline being the conductivity and carbonate content, higher for REFA than for Vest. The heavy metals present in higher concentrations were Pb (2.71 g kg^{-1} and 3.11 g kg^{-1}) and Zn (22.40 g kg^{-1} and 19.44 g kg^{-1}) for Vest and REFA respectively, which are typical for APC residues. Lima *et al.* (2010b) present similar results for their studied fly ashes: 3 g Pb kg^{-1} to 9 g Pb kg^{-1} and 5 g Zn kg^{-1} to 27 g Zn kg^{-1} .

Cadmium concentrations increase significantly with decreasing ash precipitation temperature. The capture of Cd into FA particles is mainly a physical adsorption at relative low temperatures but, at higher temperatures, FA chemisorption between Cd and aluminosilicates may take place, forming complex Cd-aluminosilicates (Lima, 2008). I/S REFA presents $88.7 \text{ mg Cd kg}^{-1}$ and Vest $97.6 \text{ mg Cd kg}^{-1}$. According

to Lima *et al.* (2008b) the flue gas stream temperature also influences the concentration of Cd in FA. Therefore, the differences between Cd concentrations of the two ashes may be related to the temperature factor as Vest ash was being subjected to a lower flue gas temperature (230 °C) compared to REFA ash (400 °C).

Table 4.1. Characteristics of APC residues from Vest and REFA (mean values \pm standard error)

Parameter	APC residue	
	Vest	REFA
pH _{H₂O} (L/S=5) ^a	12.46 \pm 0.02	12.03 \pm 0.00
pH _{KCl} (L/S=2.5) ^a	12.42 \pm 0.00	12.24 \pm 0.02
Conductivity (mS cm ⁻¹) ^a	55.33 \pm 1.11	75.24 \pm 1.82
Water content (%)	0.36 \pm 0.00	0.87 \pm 0.25
Water solubility (%)	0.76 \pm 0.06	0.66 \pm 0.06
Loss on ignition (%) ^a	0.76 \pm 0.14	4.07 \pm 0.04
Carbonate content (%) ^a	8.37 \pm 0.06	14.55 \pm 0.12
Specific surface area (cm ² g ⁻¹)	215.5 \pm 2.5	284.0 \pm 217.0
Cd (mg kg ⁻¹) ^b	97.6 \pm 0.4	88.7 \pm 2.0
Cr (mg kg ⁻¹) ^a	99.0 \pm 1.1	73.1 \pm 0.9
Cu (mg kg ⁻¹) ^a	749.1 \pm 7.0	551.2 \pm 20.7
Pb (g kg ⁻¹)	2.71 \pm 0.30	3.11 \pm 0.11
Zn (g kg ⁻¹) ^a	22.40 \pm 0.41	19.44 \pm 0.37
Leaching		
<i>pH</i>	12.4 \pm 0.0	11.8 \pm 0.0
<i>Cd</i> (mg L ⁻¹)	<i>n.d.</i>	<i>n.d.</i>
<i>Cr</i> (mg L ⁻¹)	0.02 \pm 0.00	0.03 \pm 0.00
<i>Cu</i> (mg L ⁻¹) ^a	0.01 \pm 0.00	0.27 \pm 0.02
<i>Pb</i> (mg L ⁻¹) ^a	41.9 \pm 2.3	450.0 \pm 9.6
<i>Zn</i> (mg L ⁻¹) ^a	2.41 \pm 0.23	12.70 \pm 0.39
<i>Cl</i> (g L ⁻¹) ^a	12.11 \pm 0.18	25.60 \pm 0.15
<i>SO₄²⁻</i> (g L ⁻¹) ^a	4.30 \pm 10.06	0.01 \pm 0.00

^a Significantly different ($p < 0.01$)

^b Significantly different ($p < 0.05$)

n.d. not detected

Both ashes present high level of Cr, 73.1 mg kg⁻¹ for REFA and 99 mg kg⁻¹ for Vest. However, total Cr concentration does not necessarily indicate hazardousness of Cr, being necessary to distinguish between Cr(III) and Cr(VI). Chromium(VI) from chromates, which is highly toxic compared to Cr(III). Oxidation of Cr(III) into Cr(VI) may occur when Cr₂O₃ is burned in the presence of oxygen or when Cr(OH)₃ and MnO₂ interact in moist aerobic conditions (prevented if sulphides are present) (Lima *et al.*, 2008b).

Leaching of Cr in alkaline wastes is typically in the form of Cr(III) (Quina, 2005) and in REFA and Vest the leaching is low, and not statistically significant different.

Lead presented high leaching, particularly for REFA APC residue, and this parameter does not depend on the total concentration of metal. Regarding the salts, REFA present a higher chloride and a less sulphate content, due to the type of APC system.

The low LOI obtained for Vest indicates a complete and efficient combustion during the incineration process, which means that a higher incineration temperature was achieved. Regarding carbonate content, REFA presents a high value, which was expected as in the gas cleaning process (semi-dry) lime (CaO) is one of the additives used. Once CaO is exposed to moderate amounts of water, hydration occurs forming Ca(OH)₂ that may later react with carbon dioxide forming calcium carbonate according to equation 4.1.:



The carbonate of an ash may be a relevant parameter, as CaCO₃ absorbs a range of metals in soils (Lima, 2008).

4.2 Electrolytic experiments

4.2.1 pH and conductivity

The pH and conductivity in the APC residues suspension during the EDR experiments is shown for Vest in Figures 4.2 and 4.4, and for REFA in Figures 4.3 and 4.5. The applied current of 5 mA and 50 mA could be maintained during all experiments. When 5 mA were applied, the voltage drop was between 1.3 - 2.6 V and between 1.3 - 5 V for the APC residues of Vest and REFA, respectively. The voltage drop for 50 mA was 2.5 - 7 V for Vest, and 2.8 - 7.6 V for REFA. As the current was kept constant, an increase in voltage means that there was an increase in suspension resistivity, according to Ohm's law, probably due to the decrease in the amount of ions in the ash suspension. Membrane fouling may also have contributed for it.

The pH of experiments with Vest ash suspensions decreased faster over time, this had a direct relation of more time, more acidification and more heavy metals removal. In REFA, the pH after 7 days was still alkaline (pH > 11), and after 14 days of treatment time, all of the experiments were alkaline. In some cases, the pH increased after 12 days (Figure 4.3). This was probably due to the amount of ash used and the higher buffering capacity. REFA presented a higher CaCO₃, and this characteristic, increases the

ashes buffer capacity and, due to this fact, the pH does not change easily. With Vest, the pH lowered faster in the 2C setup. On the other hand, for REFA the different setup did not change the pH behaviour.

The decrease in pH can be explained due to a combination of two reactions. During the ED treatment different hydroxides are dissolved, OH^- is removed from central compartment and water splitting may occur at the anion exchange membrane, resulting in acidification of the medium in the central cell compartment. When a neutral pH in the final ash amount is observed, it may indicate that the hydroxides have been dissolved and OH^- removed (Ottosen *et al.*, 2006). But, the acidic level cannot be explained this way. For this, H^+ ions must have been supplied to the central compartment, and the water separation at the anion exchange membrane probably played the central role.

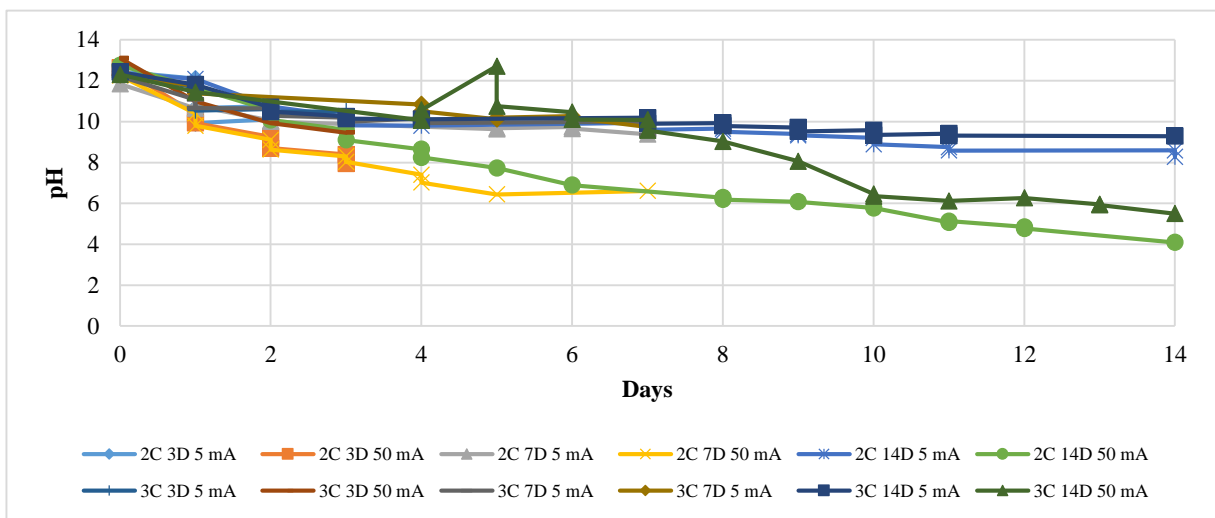


Figure 4.2. pH of the two- and the three-compartment ED cell experiments for the duration of 3, 7 and 14 days and 5 mA and 50 mA for Vest; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

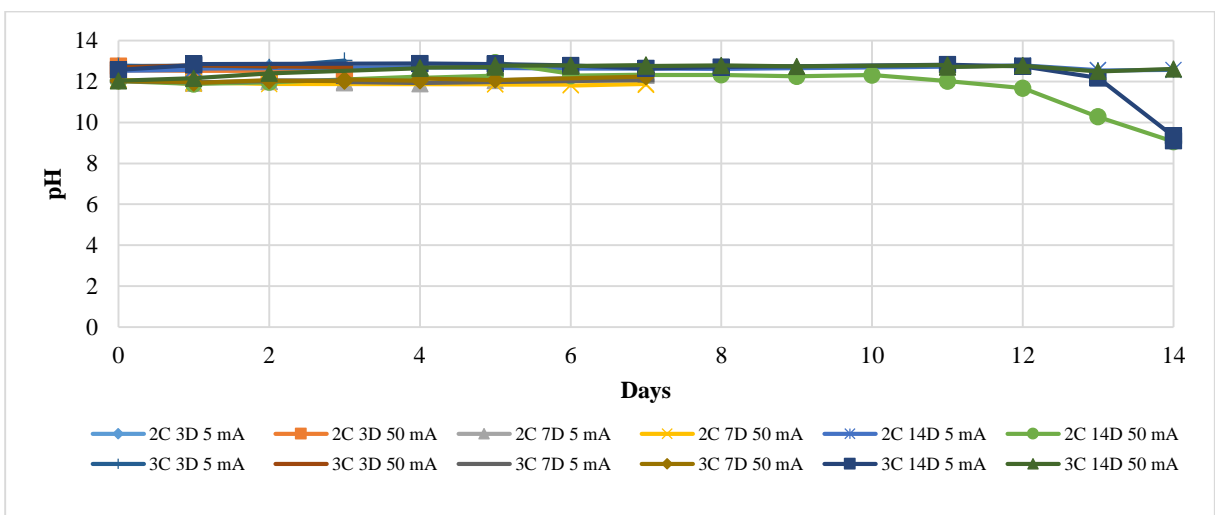


Figure 4.3. pH of the two- and the three-compartment ED cell experiments for the duration of 3, 7 and 14 days and 5 mA and 50 mA for REFA; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

The initial electrical conductivity was significantly high in all 24 experiments, especially for REFA. In all the ED experiments voltage never exceeded 7.6 V. Higher voltage was usually observed at the end of the experiments when the electrical conductivity was lower (Figure 4.4 and 4.5). The ideal remediation time should be when the electrical conductivity is low in the liquid suspension, as it means that small amounts of ions are present and able to be removed. In this study, Vest presented the lower electrical conductivity values, and despite the difficult characteristics of this residue, the voltage seems to be sufficient to remove some ions in solution. However, when REFA was used electrical conductivity increased in some of the experiments (Figure 4.5). This suggests that the applied current density was not sufficient for removing all ions in the experiments with this L/S ratio (3.5). Furthermore, the low voltage shows that there were no problems due to membrane fouling.

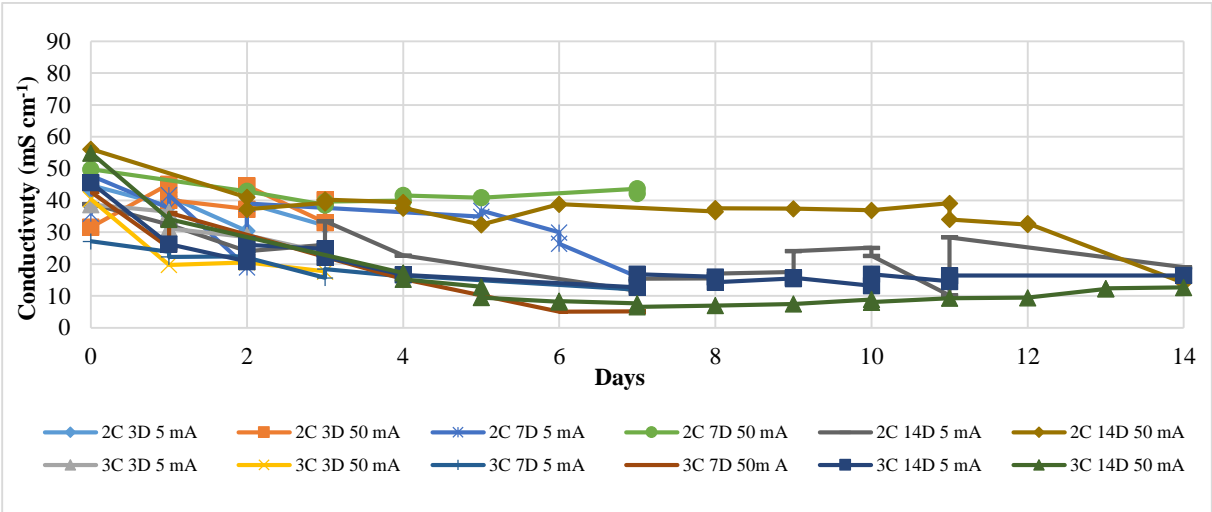


Figure 4.4. Conductivity of the two- and the three-compartment ED cell experiments for the duration of 3, 7 and 14 days and 5 mA and 50 mA for Vest; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

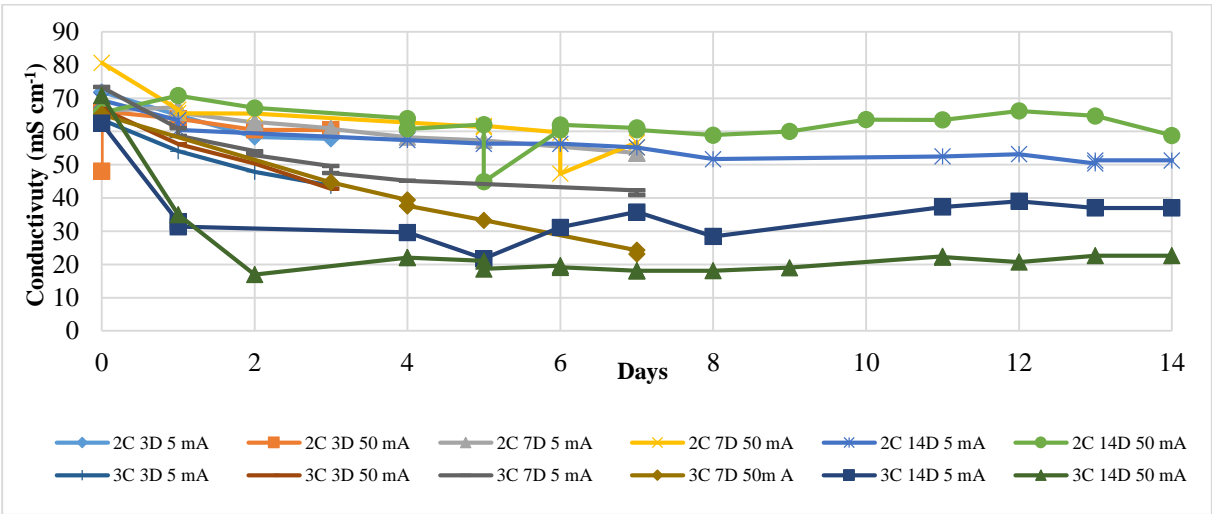


Figure 4.5. Conductivity of the two- and the three-compartment ED cell experiments for the duration of 3, 7 and 14 days and 5 mA and 50 mA for REFA; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

The mass balances for the elements showed high variability for all experiments (Table 4.2). An inhomogeneous distribution of metals in the ash and as a result imperfect mass balances are expected when working with this type of samples. Finally, although careful handling of all samples precipitation of insoluble compounds may occur for instance in set-up tubing. The mass balance rate should be between 90-110% in the best situation or, on a broader scale between 85-120%. However as Table 4.2 data, it was not always the case. Recoveries below the rate can be due to some solution leakage from central cell compartment during the experiments. These losses may occur due to the rapid passage of ions or excess ash in the ED cell. During the experiments, volume decrease in the electrolytes occurred and this may be due to a faster velocity of the electrolyte entering the anode/cathode compartment comparing to the output velocity. This passage presses the membrane and the electrolyte can pass into the central compartment, causing an increase of the central solution volume, therefore the solution may exit through the agitator hole.

An incomplete extraction of the heavy metals in the initial ash may have resulted in mass balances ratios above 120%. The extraction was carried out using the DS 259 standard in which nitric acid is used. For a complete heavy metal extraction acid digestion could have been performed using much powerful mixtures such as: hydrofluoric acid or *aqua regia*.

Table 4.2. Recovery rates of Cd, Cr, Cu, Pb and Zn and final pH at the end of the ED experiments for Vest and REFA APC residues; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Experiment	pH in the APC residues		Recovery (%)									
			Cd		Cr		Cu		Pb		Zn	
	Vest	REFA	Vest	REFA	Vest	REFA	Vest	REFA	Vest	REFA	Vest	REFA
2C 3D 5 mA	11.0	12.8	90	93	91	86	94	91	99	67	81	115
2C 3D 50 mA	10.3	12.8	154	86	95	65	123	69	148	89	115	116
2C 7D 5 mA	10.8	12.9	90	118	94	113	103	113	110	92	91	88
2C 7D 50 mA	8.9	12.8	131	131	131	127	137	123	116	125	91	99
2C 14D 5 mA	10.6	12.8	95	82	105	77	103	79	111	85	99	100
2C 14D 50 mA	6.4	10.9	101	104	120	98	90	106	78	102	45	147
3C 3D 5 mA	11.1	12.9	99	43	100	40	117	42	129	54	117	54
3C 3D 50 mA	10.6	12.9	100	58	113	53	112	56	68	59	138	76
3C 7D 5 mA	10.7	12.9	75	116	76	113	82	109	91	88	89	87
3C 7D 50 mA	11.2	13.0	119	120	112	110	105	113	38	103	80	87
3C 14D 5 mA	10.6	10.1	95	61	95	57	95	61	118	70	97	83
3C 14D 50 mA	8.2	11.7	120	75	113	69	122	75	66	87	105	103

Due to the imperfect mass balances, and in order to keep all the results, the removal percentages were calculated by dividing the amount of heavy metals that remained in the ash after the ED process, by the

sum of the amounts of heavy metals detected in all cell compartments at the end of the experiments. Thus, obtained the percentages that are still in the ash.

4.2.2 Removal and mobilization of heavy metals

The best heavy metals removal for the APC residue with wet and semi-dry cleaning system are presents in Figure 4.6.

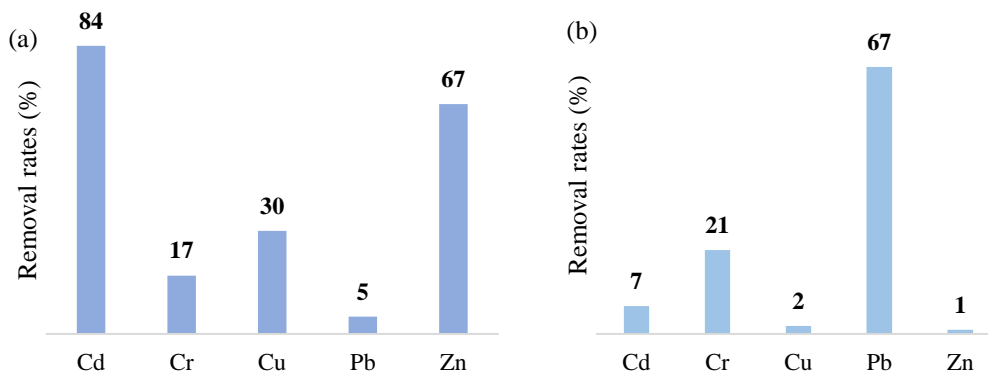


Figure 4.6. Best removal rates (%) for Cd, Cr, Cu, Pb and Zn during the ED experiments: (a) Vest and (b) REFA

For 24 ED experiments, removal percentages are in annex (T.1 and T.2), with Cu presenting the worst values. Lima *et al.* (2010b) proved that ash type, duration and dissolution were the most significant variables on heavy metal migration during the ED experiments. Increasing remediation time leads to higher removal efficiencies, while increasing the dissolution of the ash during EDR implies in lower removal efficiencies. Figures 4.7 – 4.11 present the final distribution of Cd, Cr, Cu, Pb and Zn in the two types of ash including not only the electrolytes, but also heavy metals found at the membranes, electrodes and in the middle solution, as well as the residual amounts left in the ash. The anode compartment only makes sense in experiments with 3C.

Figure 4.7 illustrates the distribution of Cd in the cell at the end of the 24 ED experiments. The best results occurred when a significant fraction of Cd was removed towards the cathode side, probably as Cd^{2+} . According to Lima *et al.* (2008b), better separation of Cd should be achieved when the soluble chlorides are removed prior to the ED treatment. When pH decreases in ash suspensions, reduction of chloride content occurs due to electromigration, and Cd will be more easily removed towards the cathode. In some ED experiments, although most of the metal was removed to the cathode side, there is still an important amount that remained in the ash suspension. This indicates that the removal process was still not finished, probably or due to the presence of uncharged complexes ($CdCl_2^0$), which do not electromigrate under the influence of an electric field (Lima *et al.*, 2008b). The mobilization for Vest

was higher than in REFA. In REFA, after the ED treatment, a majority of the Cd was still found in the ash and only a small amount was removed to the electrolytes.

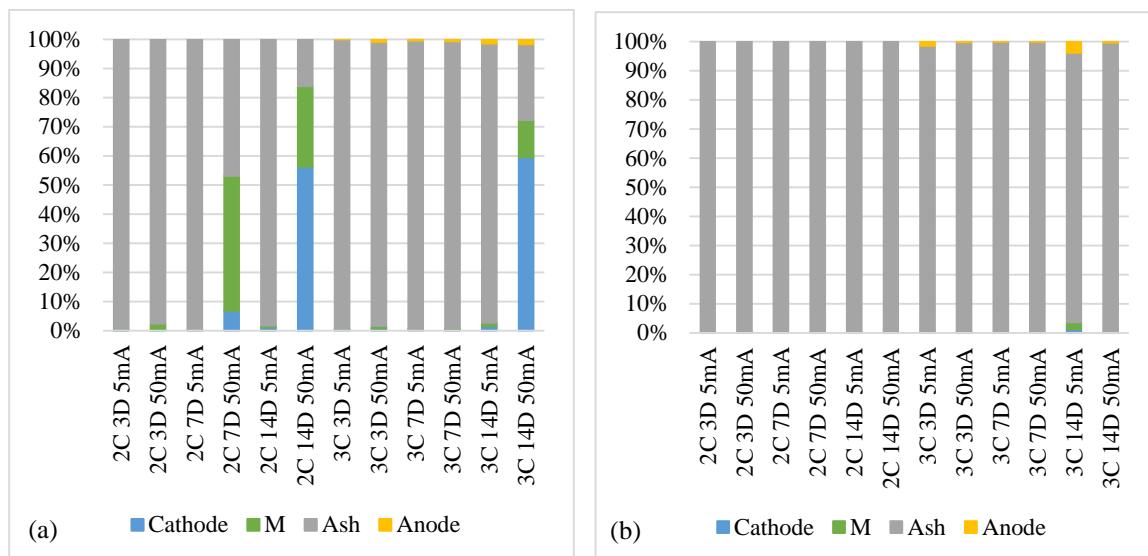


Figure 4.7. Cadmium distribution after the 24 ED experiments: (a) Vest and (b) REFA. (Cathode – electrode cathode, electrolyte(-) and cation-exchange-membrane; Anode – electrolyte(+) and anion-exchange membrane; M – middle compartment; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Most of the Cr was found in the suspension liquid or remained in the ashes, even in the experiments with the best removal percentages (Figure 4.8). This observation may be attributed to the two oxidation states of Cr in an acidic aqueous medium, Cr(III) and Cr(VI). Ionic complexes that are negatively charged are the most abundant form with Cr(III) found, for example, on oxalates ($\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$) or positively charged as Cr(VI).

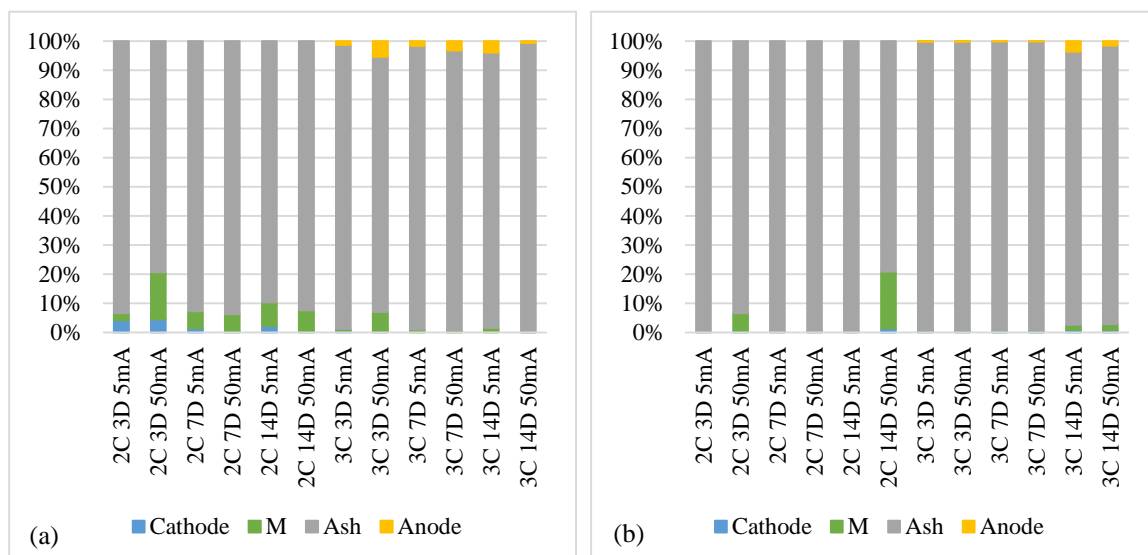


Figure 4.8. Chromium distribution after the 24 ED experiments: (a) Vest and (b) REFA. (Cathode – electrode cathode, electrolyte(-) and cation-exchange-membrane; Anode – electrolyte(+) and anion-exchange membrane; M – middle compartment; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Figure 4.9 shows Cu removal percentages obtaining for the 24 ED experiments. They were low in both ashes. These probably occurred because of the very large amount of Cu in the raw ash. Still a low removal is mostly found in the cathode side, probably as Cu^{2+} . For Cu the ED experiments need some adjustments, e.g. longer experiments, as over time the medium becomes acidified. Above pH 6, hydrated ion Cu^{2+} is progressively hydrolysed, which allows a larger and stronger adsorption to ash constituents (Ribeiro, 1992). For pH above 7, much of the Cu in the ash solution is complexed with the organic matter (Ribeiro, 1992). Although the matrix is ash, the LOI was high particularly for REFA.

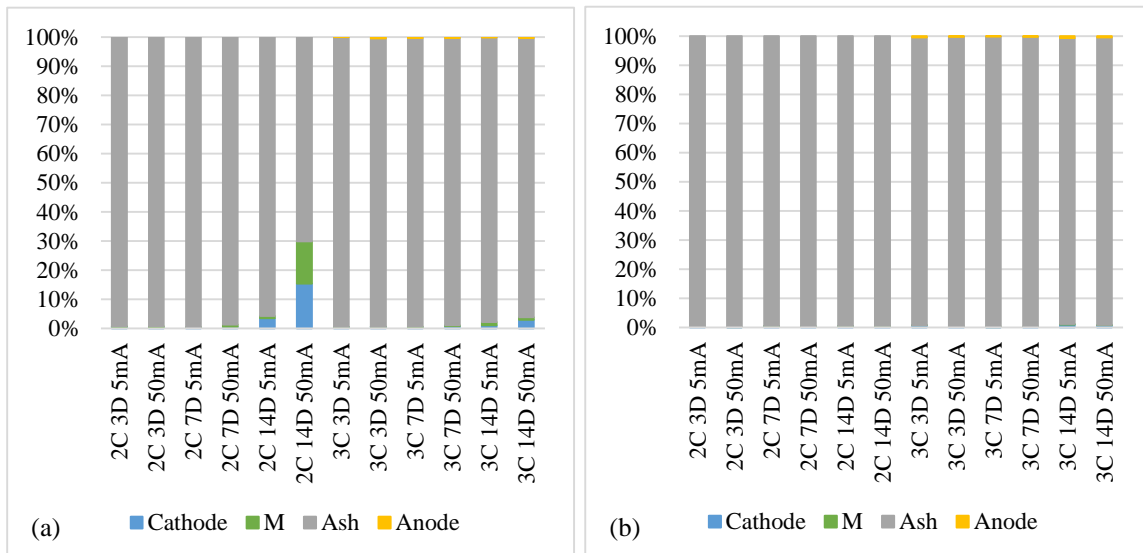


Figure 4.9. Cooper distribution after the 24 ED experiments: (a) Vest and (b) REFA. (Cathode – electrode cathode, electrolyte(-) and cation-exchange-membrane; Anode – electrolyte(+) and anion-exchange membrane; M – middle compartment; (xC – x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

The mobilization of Pb was particularly successful in the ash from REFA, contrary to Vest ash. This may be due to the different characteristics that are dependent on the gas cleaning system (as previously referred). In wet systems the amount of sulphates in the final residue is higher, since they are taken before neutralizing acidic components. According to Ferreira *et al.* (2008), due to the presence of SO_4^{2-} , PbSO_4 complexes, which are relatively insoluble can be formed and, this makes Pb solubilisation more difficult in Vest residue. Figure 4.10 shows that Pb is mobilized for both sides, cathode and anode. Again, according to Ferreira *et al.* (2008), Pb may be present in the form of $\text{Pb}(\text{CO}_3)_2^{2-}$ migrating to the anode side, and as Pb^{2+} being mobilized towards cathode. About the setup, in REFA the use of 2C seems to be less successful, although for the 14 days experiments and high current strength, the mobilization occurs.

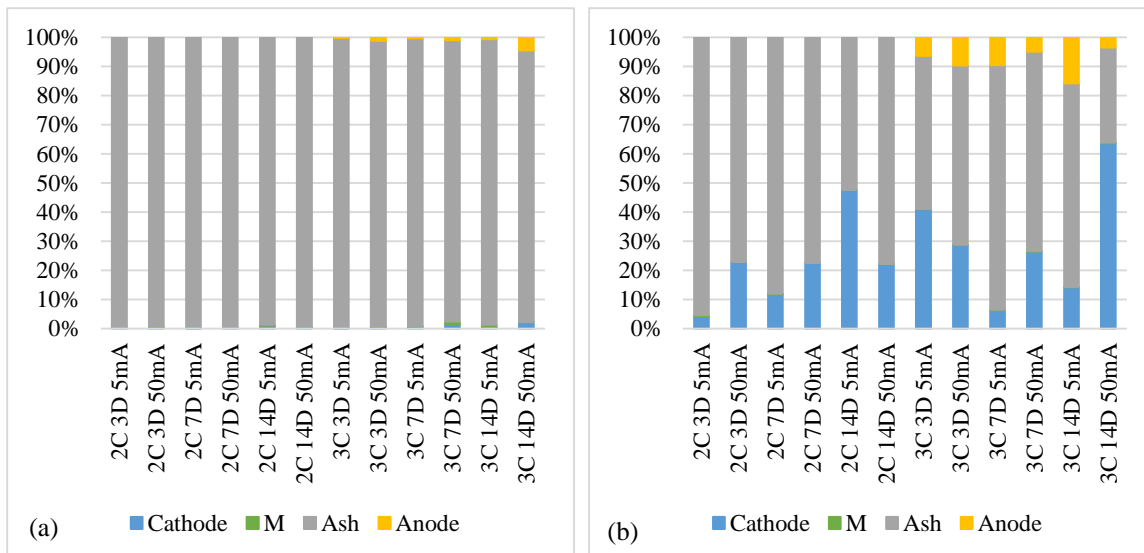


Figure 4.10. Lead distribution after the 24 ED experiments: (a) Vest and (b) REFA. (Cathode – electrode cathode, electrolyte(-) and cation-exchange-membrane; Anode – electrolyte(+) and anion-exchange membrane; M – middle compartment; (xC – x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

For REFA ash the best Zn removal rate was not significant (1%), which be due to pH. Ferreira (2005) studied that the pH influences the mobilization of some heavy metals being this parameter very important, particularly for Zn. The pH in all of the ED experiments with REFA (Figure 4.2) remained above pH 7, and in basic pH Zn is immobile as $Zn_5(OH)_6(CO_3)_2$. In some experiments with Vest, pH was below 7 and almost the whole amount of Zn that was removed was found in cathode side, probably as Zn^{2+} (Figure 4.11). For the experiment with 2C (7 and 14 days of duration) and 3C (7 days of duration), with high current (Annex T.1), a good mobilization was achieved.

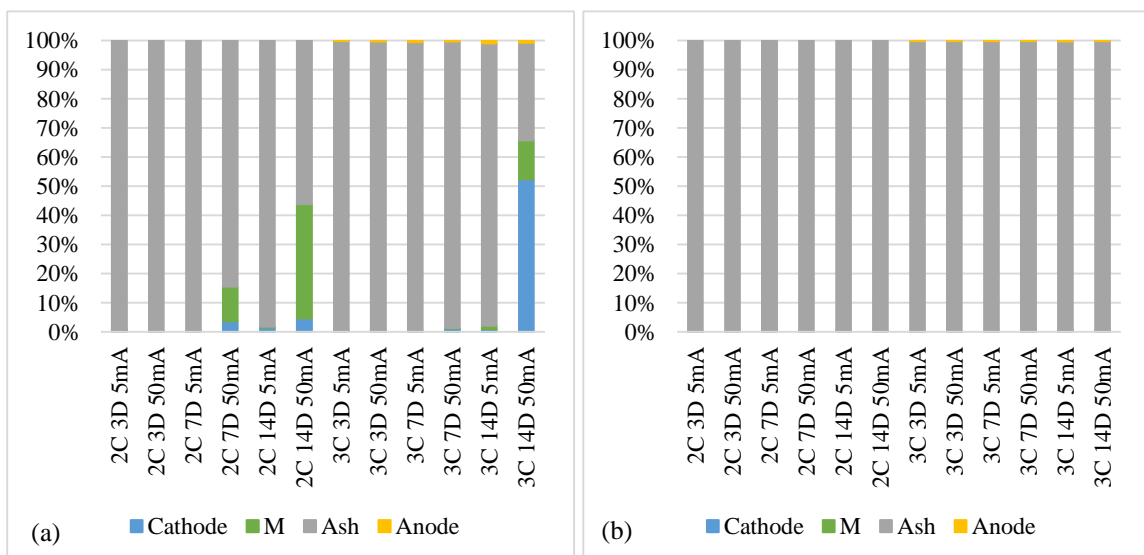


Figure 4.11. Zinc distribution after the 24 ED experiments: (a) Vest and (b) REFA. (Cathode – electrode cathode, electrolyte(-) and cation-exchange-membrane; Anode – electrolyte(+) and anion-exchange membrane; M – middle compartment; (xC – x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

4.2.3 Leaching behaviour

More important than the total amount of heavy metals left in the ash, is the amount that is in an easily leachable fraction, since it poses the highest environmental risk. If the leaching is low, it can be a great advantage and the beginning for thinking about a potential reuse. The reduced leaching also means that the mobile parts of the metals were removed during the electro-remediation, even though the total metal concentrations increased due to ash dissolution.

The leaching behaviour allowed to identify main problems in these types of residue - the high amounts of heavy metals (mainly Pb and Zn), which can be released into the environment, as well as high soluble fraction (mainly associated with Cl^- or SO_4^{2-}). In fact, the main negative environmental impact of APC residues results from leaching processes which produce solutions with toxic characteristics for living beings.

The pH is directly related to the amount of leached metals. At a more acidic pH, it is expected a higher mobility of metals, and consequently more leaching. Figures 4.12 and 4.13 are related to pH and leachable amount for Vest and REFA ash, respectively, subjected to ED process. The figures also compare the quantities of each metal leached with the limitations imposed by BEK 1662/ 2010 - use of waste products in construction industry – which include the classes C1 and C3. C1 has a free use and C3 has a restricted use. The ideal scenario would be to have all metals in category C1. Experiments with * indicate zero values for metal leaching. The results showed significantly reduced leaching of heavy metals from upgraded APC residue from Vest, even with higher total heavy metal content. Looking at Cd, the experiments with several durations, and consequently with different acidification solution, increase the leaching behaviour of this metal. The leached Cr concentration was however increased in upgraded ash of all experiments compared to the raw ash, and this should be investigated, since it is difficult and important to stabilize Cr in mortars. In this study, it was not investigated if Cr was present as Cr(IV) or Cr(III), but it is important to include in future studies. Section 4.2.2 showed that Cu was very stable in the ash suspension, with a high amount, but without mobilization, whereas leached Cu showed that all of the values were below C3 after treatment. Lead presents a very soluble amount fraction, and for the upgraded ashes from Vest it was particularly successful compared to the other studies: 3.8 mg Pb L^{-1} (Kirkelund *et al.*, 2010). Regarding Pb, values of zero were it obtained for leaching, and only 2 upgraded ashes below C1 but almost all the ED experiments were below C3. Zinc presents increased leaching after experiments with 14 days and high current (50 mA).

Summarizing, the worst leaching results were obtained for 2 and 3 cell compartments for 14 days of ED process, as well as 7 days of ED treatment with a 2C. The best removal rates, obtained with lower pH, present higher values for leaching. Chromium, is the only heavy metal which after EDR, increased all their leaching values, compared to the raw residue.

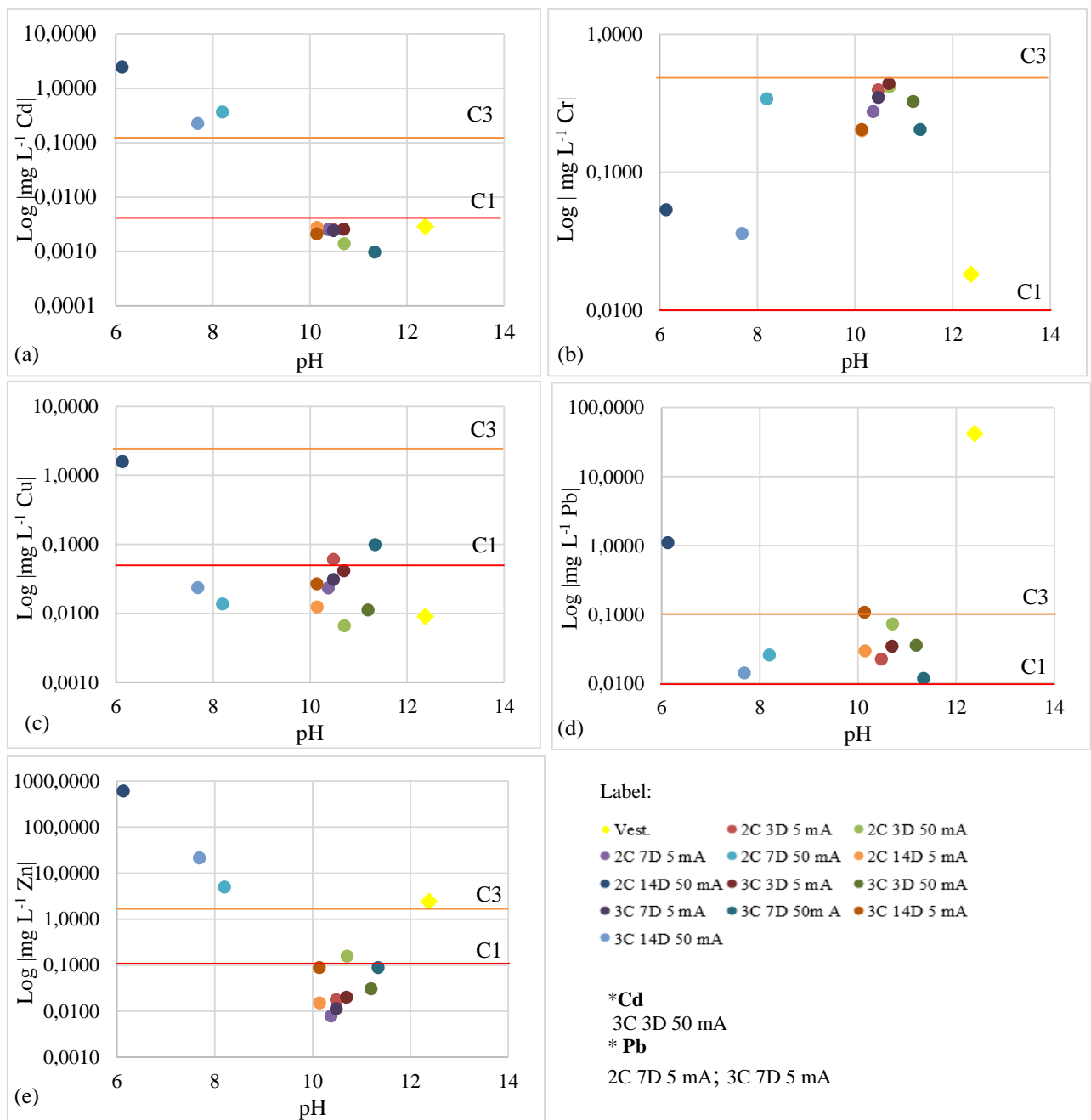


Figure 4.12. Leaching concentrations (mg L⁻¹) of heavy metals from Vest in the raw APC residues and after ED process: (a) Cd; (b) Cr; (c) Cu; (d) Pb and (e) Zn (The y axis do not have the same scale); (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Upgraded ashes from REFA presented a reduced Cd leaching. All the values were below C1, with the exception of experiment 2C 3D 5 mA. As occurred in the Vest experiments, the leached Cr increased with ED process, but nevertheless, it continues with most of values below C3. The values above this standard were observed for the 14 days of ED duration time and high current in both setups (2C and 3C). For Cu, all of the leaching values were in C3 and C1, obtained no value above standards and there was a decrease when comparing to the raw residue (Figure 4.13 c). For Pb and Zn the leaching results

presented high mobility. Lead presented a successful removal in ash from REFA, and it probably made the metal very leachable.

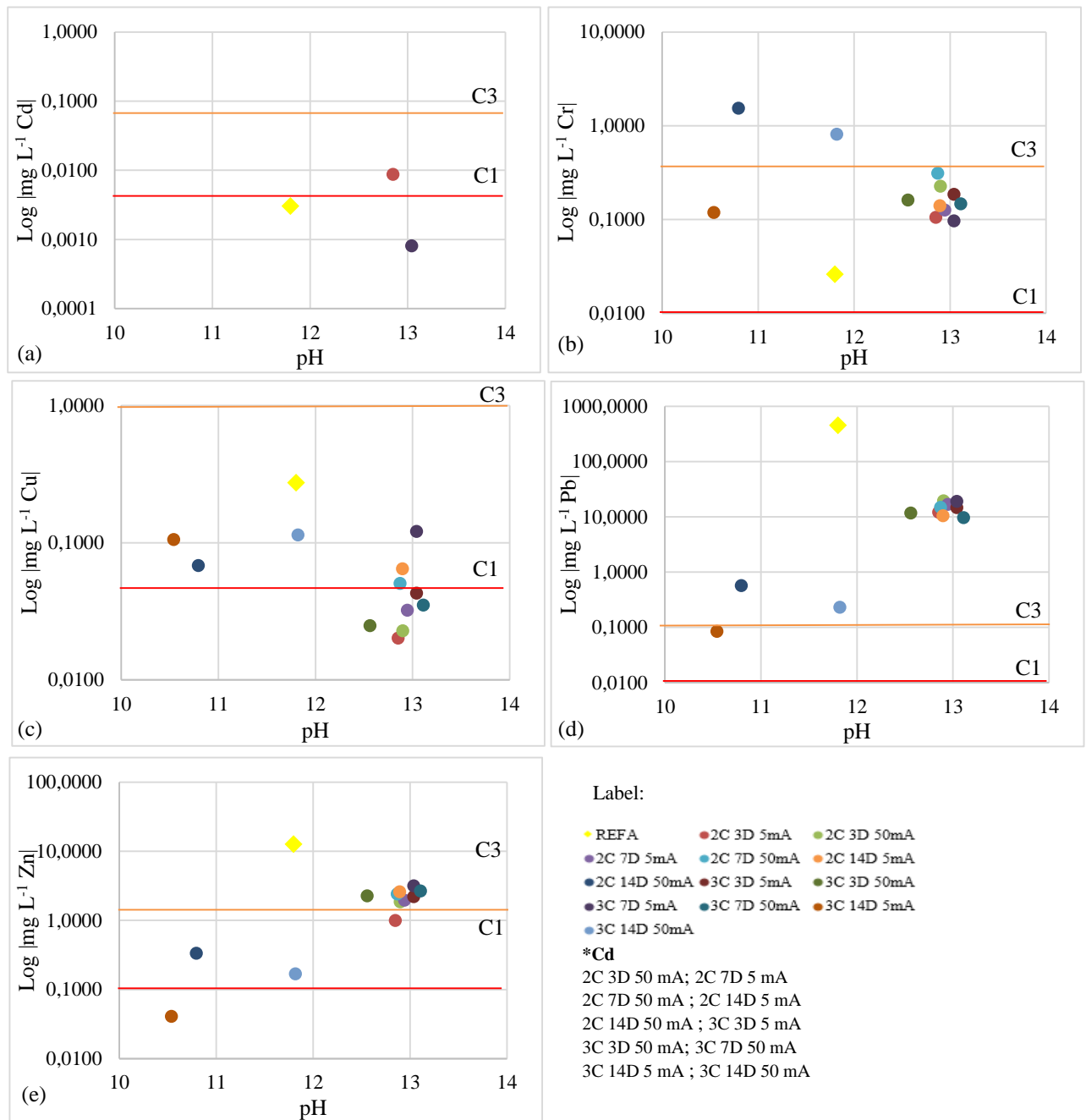


Figure 4.13. Leaching concentrations (mg L^{-1}) of heavy metals from REFA in the raw APC residues and after ED process: (a) Cd; (b) Cr; (c) Cu; (d) Pb and (e) Zn (The yy axis do not have the same scale); (xC – x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

4.1.1 Removal of salts (Cl^- and SO_4^{2-})

In raw residues REFA presented more chloride than Vest ash. Figure 4.14 shows that with the ED process for Vest ash the Cl^- tend to lower to values below C1, and in all experiments below C3, which opens a great perspective for future reuse. In the case of REFA, the chloride quantity decreased, but still above C1 in all of the ED experiments.

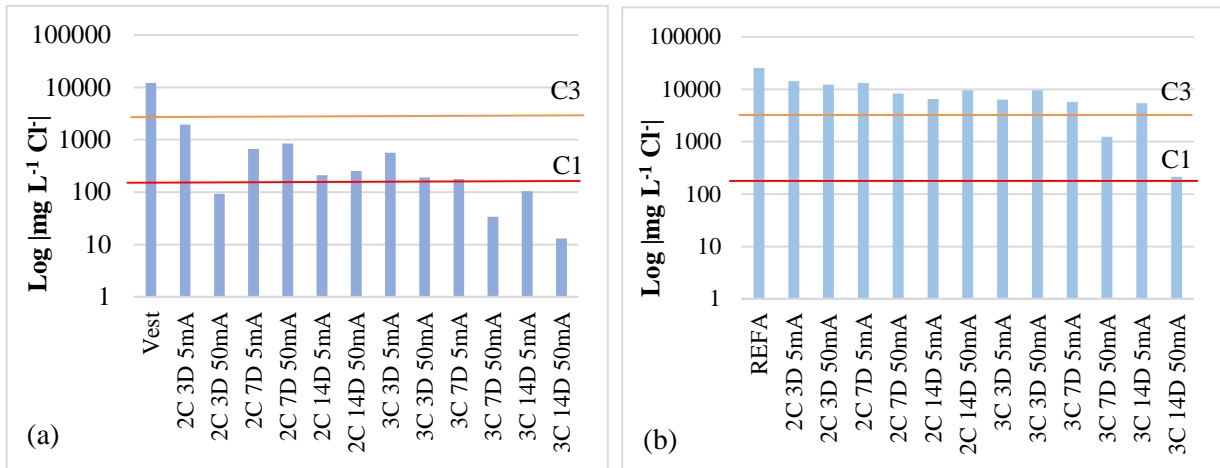


Figure 4.14. Chloride concentration (mg L^{-1}) in the raw APC residues and after 24 ED experiments: (a) Vest and (b) REFA; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Regarding sulphates in the raw APC residue of Vest, it presented a very high content because of the wet process that originates it. Analysing Figure 4.15, the ED treatments, led to an increase amount of sulphates, which became more leachable than in raw ash from REFA. This may occur because, in the beginning, the sulphates are complexed, free or in a mineral form. After ED process the metals were removed, the sulphate ion became in a soluble form.

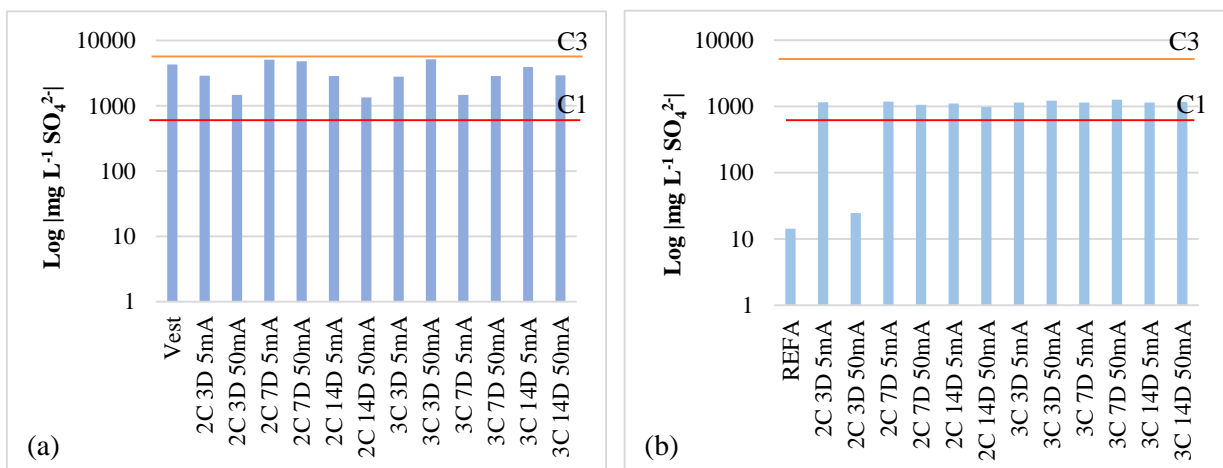


Figure 4.15. Sulphate concentration (mg L^{-1}) in the raw APC residues and after 24 ED experiments: (a) Vest and (b) REFA; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

4.2 Mortar bars

4.2.1 SEM/EDS

The morphology of the raw APC residues and upgraded (7 days of duration ED treatment) APC residues from Vest and REFA, which were used in mortar bars preparation, is presented at the SEM/EDS images of Figure 4.16. 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 4.16 shows that the APC residues particles are mostly of a small shape, of two different type: particles of type (X) are formed in the combustion chamber having a spherical shape, composed of aluminosilicate matrices (glass particles), although deposited on their surface as they are entrained by the gases and particles of type (Y) appear highly polycrystalline from the processes of condensation as the gases cool down. According to Quina (2005) 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) observed that by leaching the microporosity of the particles increased, due to the removing salts. They also noted that small particles could remain adsorbed on the surface of the largest particles. Furthermore, Le Forestier & Libourel (1998) 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) 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 Figure 4.16 changes are clear from the form of raw residue to residue upgraded. The largest changes in shape occurred for experiences with 2C cell design (Figure 4.16 c, d, e and f).

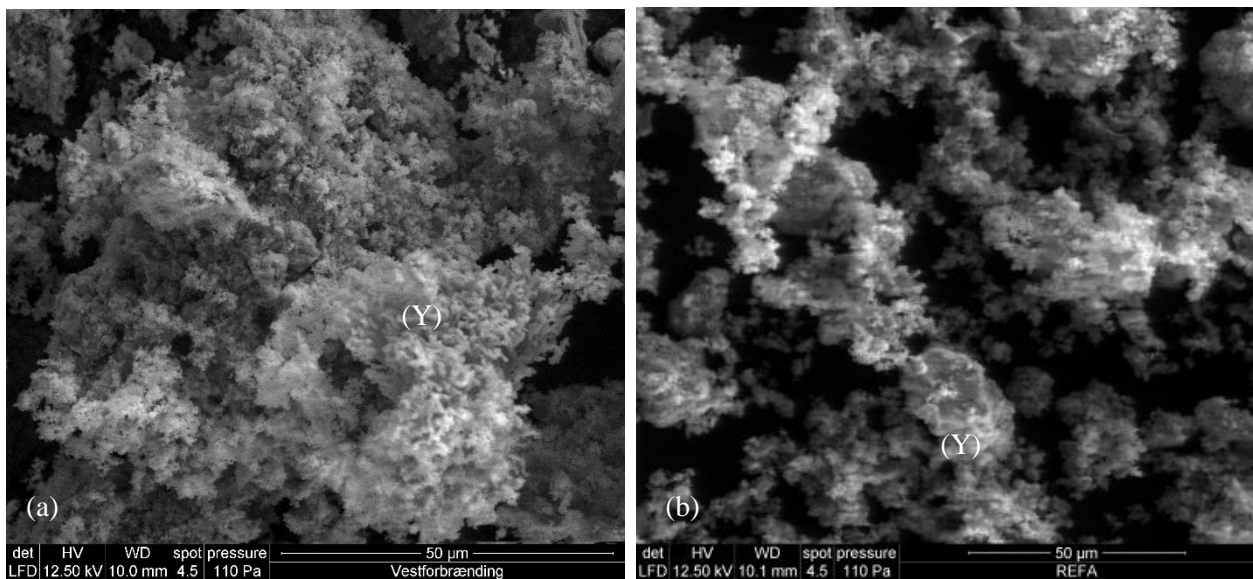


Figure 4.16. Images of SEM before ED treatment: (a) raw Vest and (b) raw REFA; After ED treatment (7 days of duration time): Vest - (c) 2C 5 mA, (e) 2C 50 mA, (g) 3C 5 mA, (i) 3C 50 mA and REFA - (d) 2C 5 mA, (f) 2C 50 mA, (h) 3C 5 mA, (j) 3C 50 mA; magnification: 1000x; (X) - glass particles, (Y) - polycrystalline particles; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

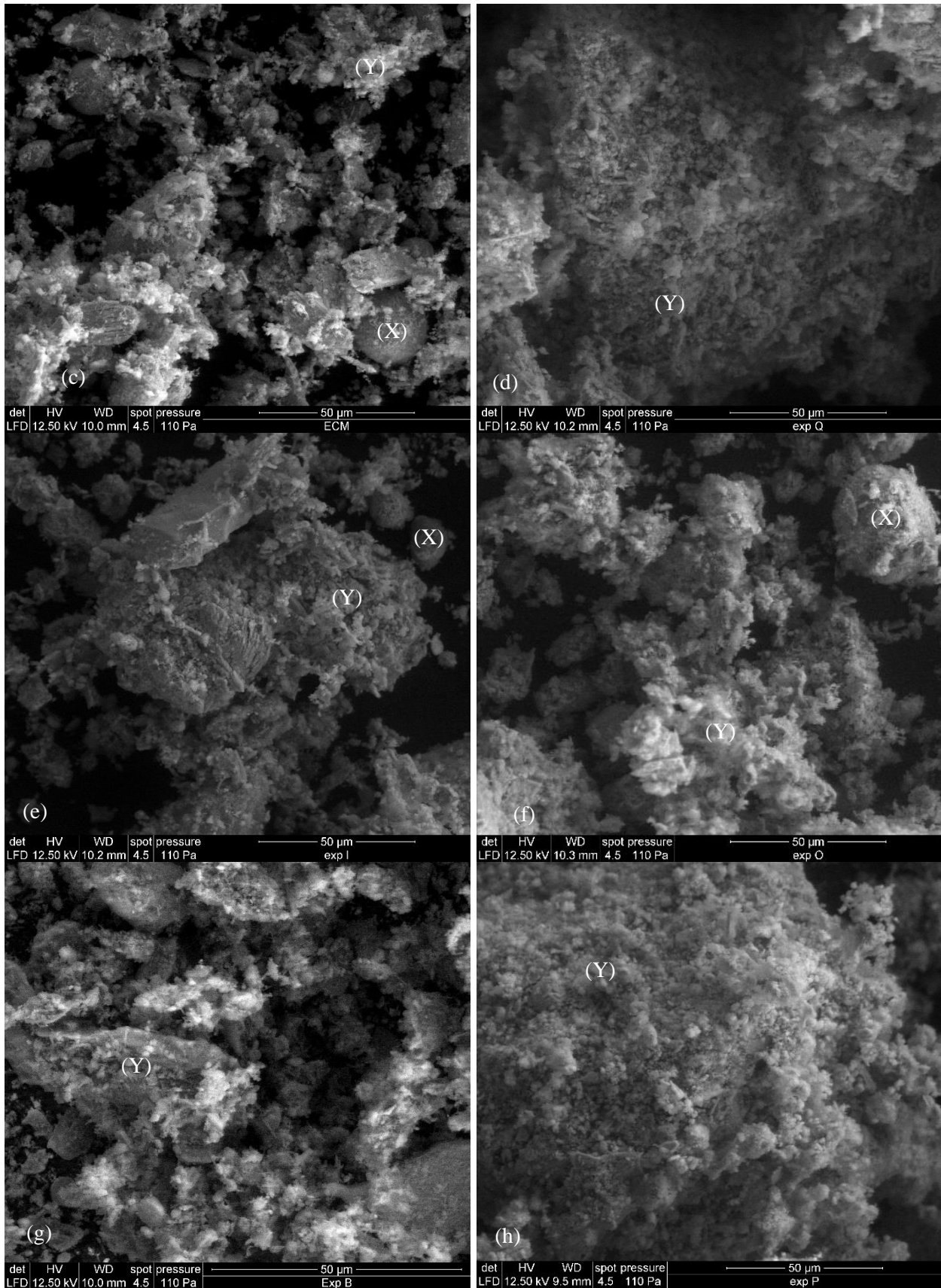


Figure 4.16. (cont. 1) Images of SEM before ED treatment, (a) raw Vest and (b) raw REFA; After ED treatment (7 days of duration time): Vest - (c) 2C 5 mA, (e) 2C 50 mA, (g) 3C 5 mA, (i) 3C 50 mA and REFA - (d) 2C 5 mA, (f) 2C 50 mA, (h) 3C 5 mA, (j) 3C 50 mA; magnification: 1000x; (X) - glass particles, (Y) - polycrystalline particles; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

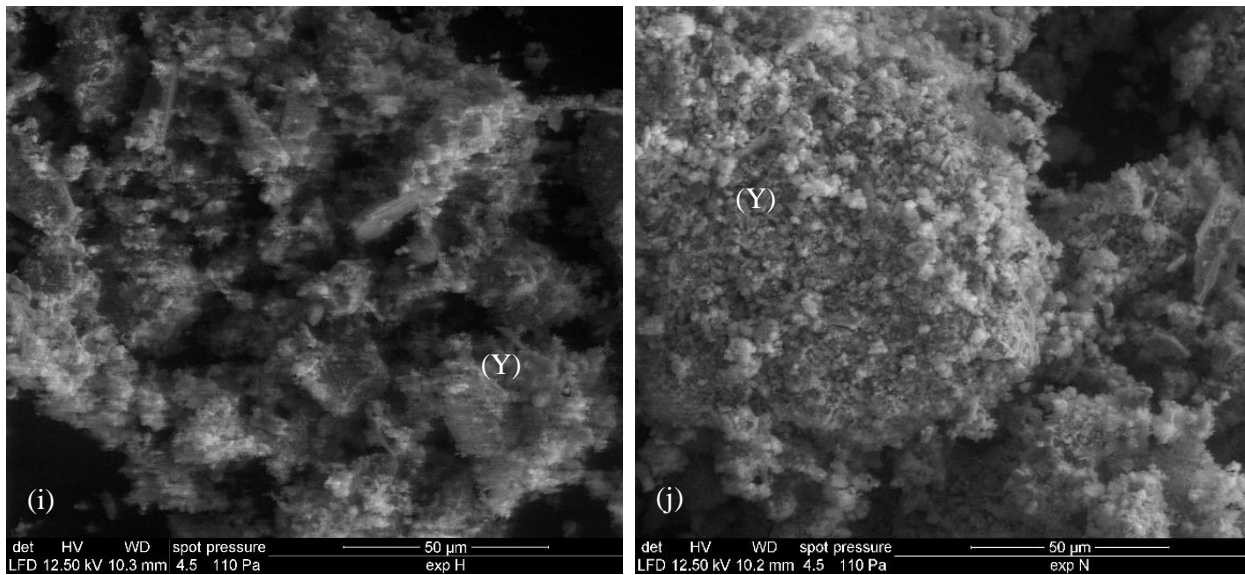


Figure 4.16. (cont. 2) Images of SEM before ED treatment: (a) raw Vest and (b) raw REFA; After ED treatment (7 days of duration time): Vest - (c) 2C 5 mA, (e) 2C 50 mA, (g) 3C 5 mA, (i) 3C 50 mA and REFA - (d) 2C 5 mA, (f) 2C 50 mA, (h) 3C 5 mA, (j) 3C 50 mA; magnification: 1000x; (X) - glass particles, (Y) - polycrystalline particles; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

4.2.2 Porosity and density and compressive tests

Table 4.3 presents the porosity and density values obtained for the tests on mortar bars after 28 days of curing time. According to Gottfredsen & Nielsen (2008) the reference values given for the cement is 20%. Comparing with 20%, porosity decreases with the addition of ashes. Comparing with reference mortar, with 0% of APC residues the porosity increase. According to tests done by Frutuoso (2013) 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 due to 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. Table 4.3 shows that the experiments more similar to the reference were the experiences with 2C to Vest and one 3C 50 mA for REFA.

Table 4.3. Porosity and density of specimens: reference; substitution 5% of raw and upgraded APC residues from Vest and REFA as cement; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

		Specimens									
Reference		Raw Vest	Vest 2C 5mA	Vest 2C 50mA	Vest 3C 5mA	Vest 3C 50mA	Raw REFA	REFA 2C 5mA	REFA 2C 50mA	REFA 3C 5mA	REFA 3C 50mA
Porosity (20%)	16	18	17	17	18	18	18	18	18	18	17
ρ_d (2100 kg m ⁻³)	2146	2085	2113	2118	2119	2109	2115	2133	2110	2102	2129
ρ_f (2650 kg m ⁻³)	2558	2544	2541	2579	2547	2557	2553	2592	2571	2574	2587

Compressive strength is relevant to define the mortar (Figure 4.17), determining its strength capacity. In literature, compressive strength measured after 28 days shows resistance: ≥ 32.5 , 42.5 or 52.5 MPa (Quina, 2005). According to Frutuoso (2013) the higher value, less deformable the mortar will be. The compressive strength is related to the porosity of the material, which increases with the decreasing of the latter. The compressive strength generally increases with longer curing times. The ED experiments Vest APC residue with 50 mA and 2C has a higher mechanical strength than the reference, regarding that the reference shows a lower porosity value. This may be related to the origin and form of the aggregate, since this type of aggregate has a great heterogeneity in its composition and particles size. The same happens with the raw REFA APC residue, which can be explained due to the coarser aggregates that contributes to an increased mechanical strength of mortars. According to Figure 4.17 the two higher compression values, are found in Vest APC residue with 2C and 50 mA, and the raw REFA. According to Cenni *et al.* (2001) high Cl^- content accelerates hardening, at the same time that free Cl^- induces in steel corrosion. That was probably what happened, mainly for REFA, because at the beginning this APC residue presented a very high Cl^- content. In MSWI APC residue is regarded, sulphate content an important factor to lower compressive strengths when added in mortars due to crack formation (Lima *et al.*, 2012). On experiments with ash from REFA, it was possible that this happened because after ED treatment the amount of sulphates significantly increased.

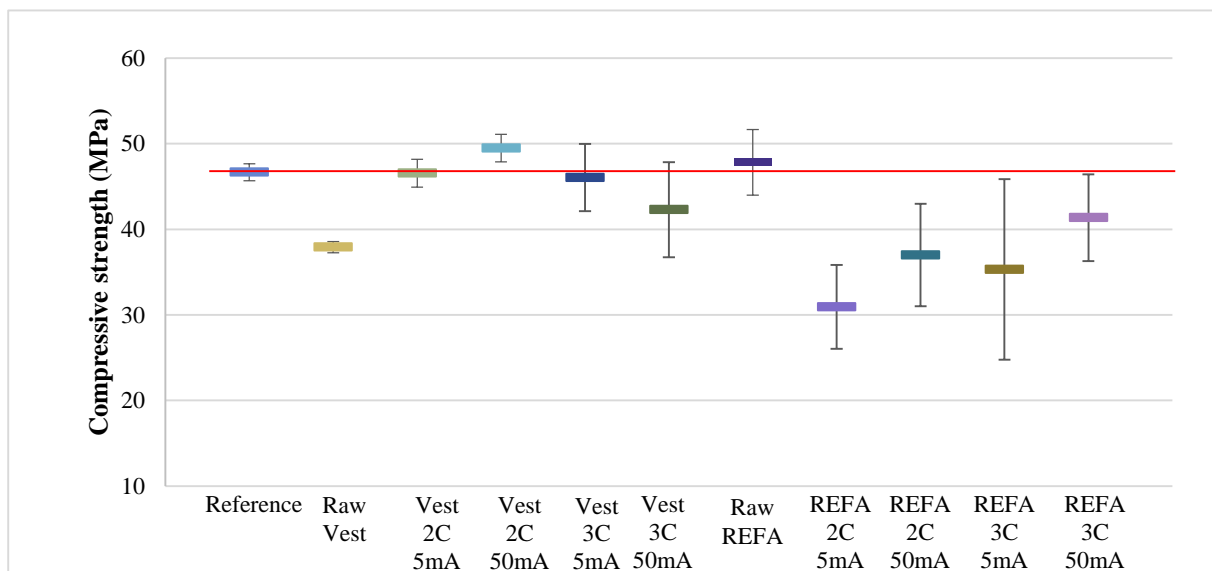


Figure 4.17. Compressive strength of specimens after 28 days curing for mortar samples: reference; substitution 5% of raw and upgraded APC residues from Vest and REFA as cement (mean values \pm standard error); (xC – x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

4.2.3 Leaching behaviour

Concrete's high pH is believed to immobilize heavy metals. However, due to FA high specific surface, some of the heavy metals are placed there and prone to leach (Pedersen, 2002b). According to Wiles (1996) heavy metals such as Pb, Cu and Cd are susceptible of leaching from MSW fly ashes. There is no legal regulation limiting the leachability of heavy metals from regular concrete in Denmark. Then, like Lima *et al.* (2012) proposed, in this study it will be used the European Environment Agency (EEA) criteria for landfill deposition of waste and leachability values of the mortars after prEN 12457-1. This gives an overview of the increase on metal leachability from the blended mortar. Table 4.4 presents the values of leached heavy metals for the reference, raw APC residues and the upgraded APC residues. Not only for the reference value as for other specimens, leached Cd was zero, which is quite different from literature values (0.07 mg L^{-1}) Lima *et al.* (2012). According to Shih *et al.* (2005), Cr and Cu are almost totally trapped/incorporated into clinker, not presenting a threat to leach. However, heavy metals speciation may play an important role on their leachability. The reference values are in some cases higher than those of both raw residues. Vestforbrænding appears to be particularly successful in upgrade of its APC residue, and the new setup (2C) combined with low current, show the best results (Table 4.4). Yu *et al.* (2005) found that leaching of heavy metals depends on the type of solidified ash, but does not depend on the initial concentrations. Table 4.4 shows that in the case of adding 5% of ash from Vest, Cr did not increase leaching, in experiments 2C with 5 and 50 mA and residue without ED treatment. Yu *et al.* (2005), also concluded that Cr(VI) soluble species are effectively immobilized by the cement base material and can be found adsorbed or precipitated with silicates or calcium compounds, as $\text{Ca}_2\text{CrO}_5 \cdot 3\text{H}_2\text{O}$ or in C-S-H gel, where SiO_4^{4-} is substituted by CrO_4^{2-} .

It should be stressed that in this study, only a small percentage of APC residue was included in the mortars and consequently low concentrations of heavy metals were measured in the leachates. So, there is an immobilization of contaminants, and these results are very promising. Although there are some cases in which there is an increased leaching of metals after EDR, only one value exceeded the established EEA standard landfill criteria for metals leachability. For upgraded residue from REFA, the amounts of leached metals increases, with some exceptions. May be for REFA ash, the incorporation of raw residue to be the most appropriate choice, the amounts of leached some heavy metals increases in relation to residue without ED treatment.

Table 4.4. EEA landfill criteria for heavy metals leachability; Experimental data obtained by prEN 12457-1 on mortar: reference; substitution 5% of raw APC residues and upgraded APC residues from Vest and REFA as cement; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Specimens with 5% of APC residues												
EEA landfill criteria (mg L ⁻¹)			Vest					REFA				
			7 days of ED treatment					7 days of ED treatment				
Class 1			Raw	2C 5mA	2C 50mA	3C 5mA	3C 50mA	Raw	2C 5mA	2C 50mA	3C 5mA	3C 50mA
Cd	≤ 0.1	0	0	0	0	0	0	0	0	0	0	0
Cr	≤ 0.5	0.04	0.03	0.03	0.03	0.09	0.07	0.05	0.09	0.08	0.07	0.06
Cu	≤ 2	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.01
Pb	≤ 0.5	0.08	0.05	0.04	0.05	0.15	0.02	0.03	0.01	0.04	0.02	0.07
Zn	≤ 4	0.03	0.02	0.01	0.01	0.06	0.02	0.05	0.07	0.10	0.09	0.05
pH	5.5 - 12	12.4	12.4	12.4	11.6	12.4	11.1	12.4	12.4	12.3	12.4	12.7

4.2.4 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 (Frutuoso, 2013). Corrosion process happened because soluble salts present a weak interaction with cement matrices. The biggest difficulty of S/S process is related with high amount of soluble salts content. Decreasing this amount may pass to washing the APC residue before incorporation in cement (Quina, 2005). Table 4.5, showed the results of chloride contents in the reference and in the specimens previously described.

Table 4.5. EN 206-1 European standard for concrete; Amount of chloride in mortar: reference; substitution 5% of raw APC residues and upgraded APC residues from Vest and REFA as cement; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

Amount of Cl ⁻ in specimens											
Reference	Raw Vest	Vest 2C 5mA	Vest 2C 50mA	Vest 3C 5mA	Vest 3C 50mA	Raw REFA	REFA 2C 5mA	REFA 2C 50mA	REFA 3C 5mA	REFA 3C 50mA	
mg kg⁻¹	1.9	4.2	2.3	2.2	2.1	2.4	6.5	7.1	2.9	2.5	2.1
EN 206-1 (0.2%)	0.2 %	0.4 %	0.2 %	0.2 %	0.2 %	0.2 %	0.7 %	0.7 %	0.3 %	0.3 %	0.2 %

The results are in conformity to 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 increases after the including of 5% ash in cement, but the values for upgraded Vest ash showed a similarity with reference. For upgraded ash from REFA the values were higher, with an exception in 3C 50 mA experiment (Table 4.5). *Valorsul* a Portuguese incinerator presents a semi-dry treatment for cleaning flue gas, like REFA, so some of conclusions can be applied to this plant, with some concerns, since the characteristics of the APC residues are influenced by several factors, including the country where they are from.

5. Conclusions

This study aimed to understand if the ED process is an appropriate pre-treatment for further reuse of APC residues in mortar bars. This subject is a challenging one, because this type of waste usually presents of high amounts of heavy metals and salts. Thus, two APC residues were studied: one resulting from the treatment of a wet cleaning fuel gas from the incinerator plant Vest; and another from a semi-dry gas cleaning from incinerator plant REFA, both in Denmark. In Portugal, *Valorsul* incinerator which serves Lisboa, presents a semi-dry treatment for flue gas, so some of conclusions of this study can be extended to this plant. As mentioned, the ash characteristics, are influenced by several factors related to each plant, such as the composition of the waste that is burned. Therefore, further studies should be made in order to reach more conclusions

With the fundamental aim of analysing the environmental impact regarding a second use of the APC residues, a battery of 24 ED experiments with Vest and REFA APC residues was carried out and a series of variables (current, duration of treatment, and cell compartments) were defined. The successful removal of heavy metals and reduction of their leaching behaviour from these residues is important for their further possible application, e.g. in building materials. Reducing the amount of heavy metals and noticing their mobility, may lead to a safer use, as understanding their behaviour when mixed with cement can lead to a reduced impact in the environment and consequently to humans.

A statistical method (t-test) was used to analyse the initial characteristics of two APC residues, reaching the conclusions that these ashes were statistically significant different for 99% or 95% of confidence levels, in almost all parameters. Flue gas cleaning treatments do influence the ashes characteristics and their behaviour when submitted to ED treatment. Therefore, this is a main conclusion and each waste must be individually treated its characteristics, being each case a different one.

In ED process, pH seems to be the most important factor in the heavy metals removal rates success. Other factors such as treatment duration and electric current intensity also influence the mobility of metals in the ash. For the longest tested duration (14 days) the ED treatment showed highest removal rates for these types of ash. The chlorides and sulphates also influence, once heavy metals tend to complex with these species. The number of ED cell compartments present have different results, 2C was efficient in the ash from Vest, and unlike the ash from REFA 3C shows a higher metal removal rate.

Cadmium, Zn and Pb presented the highest remediation rates, even if at the end of the ED treatment, their values were above C3. Thus, the ED process may not be the solution for a successful remediation of APC residues, when the criterion is only based on the total concentrations. However, for a second use of the material, is leaching one of the criteria that has more relevance and the ED treatment was successful in many cases.

Thus, for Vest APC residue, leaching was promising since. The application of low DC presented values below C1 and gets two values of zero for Cd and Pb. 10% of the ED experiments showed an increase on heavy metals leaching, 43% of at C1 values and 47 % at C3 values, according to BEK 1662 standards. However, for REFA APC residue leaching presented remaining heavy metals levels above C3, with the exception of Cd that obtained values of zero in almost all ED experiments. It even occurred that leaching was increased after some ED treatment. Conformity assessment allowed to identify the most problematic species from the residue: Pb, Zn and Cl⁻.

Finally, a specific reuse was studied for the two APC residues: mortar manufacture. The suitability for this reuse was defined by four parameters: porosity and density, compressive strength, heavy metals leachability and chloride content. It was concluded that the material obtained from S/S treatments incorporating 5% of APC residue from Vest met the requirements for the studied heavy metals. The use of upgraded waste as building materials while protecting the environment regarding compounds released by leaching was than a success.

Leaching tests proved that adding 5% of APC residues to cement based material affects the leachability of heavy metals, and sometimes in a positive way. Experiments with the raw residue and residue upgraded with 2C ED cell presented the best results. Regarding REFA APC residue, the use of ED as a pre-treatment did not seem appropriate, since the amounts of leached heavy metals increases in relation to residue without pre-treatment. In both cases Cd removal soluble fraction presented an efficiency of 100%. The compressive strength showed that in some cases the strength is increased with the addition of APC residue.

Furthermore, adding this type of APC residue might present a threat for steel corrosion in reinforced concrete structures due to the highly soluble Cl⁻ content. The soluble salts have a weak interaction with cement matrices. In the case of Vest ash in most of performed tests Cl⁻ remained compared to the reference, but the same did not happen with REFA ash.

The problem of Cl⁻ in REFA ash, can only be overcome if its content is reduced. Yet insulation measures for the building material will always be required. In fact, one of the biggest difficulties in treating this residue relates to its high content of soluble salts, which does limits its application of further products. Decreasing the amount of Cl⁻ may pass by a washing process before the incorporation of this APC residues in cement.

The stabilization of APC residue is difficult, once its characteristics may float according to the waste that is burned as well as burning conditions. A consequence, it is hard to work out a standard for MWSI APC residue for concrete. Vest ash appears to be an appropriate choice for this with a pre-treatment with ED process. For REFA ash, further treatment adjustments are required and more studies is envisaged for reuse must be carried out before this.

Our society is based on consumption. Although some authors already talk about de-growth, there is still a great deal of waste to be handled. In this context, it is relevant to study methods for its reduction and recovery aiming preservation and ecosystems protection. This study aimed to contribute for the treatment and reuse of APC residues.

6. Future developments

At the end of this study, some issues were unsolved, and so proposals arise for further developments in respect to the ED treatment and the S/S process for APC residues upgraded residues. Some suggestions are following given to complement the investigation:

Electrodialytic Remediation Process

- Chemical speciation of heavy metals in the system would contribute to understand their behaviour;
- Perform a washing process before ED process, in order to reduce the problem of soluble salts, identified as the most problematic aspect in replacing ash on mortar bars;
- Use an acidifying agent as it would possibly increase acidification process, and thus increase the removal efficiencies for heavy metals and salts from APC residues;
- Change the L/S ratios- especially for REFA ash: the space of the cell seemed to be insufficient for stirring the solution in the central cell compartment. Increasing the L/S ratio would help to increase metals mobility. Another alternative would be to do an experiment with ED cells on a larger scale which being tested now at Technical University of Denmark.

S/S treatment

- Extend the investigation for incorporation of the washed residue, possibly to the REFA APC residue, as the washing may remove the high amount of chlorides. Thus, a viable further reuse as aggregate in building materials could be tested;
- Analyse the potential increase of sulphates in the aggregates due to the incorporation of upgraded APC residues and the eventual increase in gaseous emissions regarding SO_x;
- Further study the effect of aging processes, evolution heat and effect on the elasticity of the material, after replacement of cement with varying percentages of upgraded ash.

General developments

- Evaluate not only heavy metals, but also organic micropollutants in APC residues. The issue of dioxins and furans as well as PCBs and PAHs;
- Consider the recovery of studied pollutants (heavy metals), particular by focus in which are present in higher amounts (Pb and Zn), conduct studies aiming at heat treatment of APC residues (vitrification, sintering or fission, for instance);
- Using statistical studies and mathematical models for the optimization of methods. Actually, with the high numbers of experimental results that were performed in this study, it is justified to use a deeper level of statistical and mathematical modelling.

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Annexes

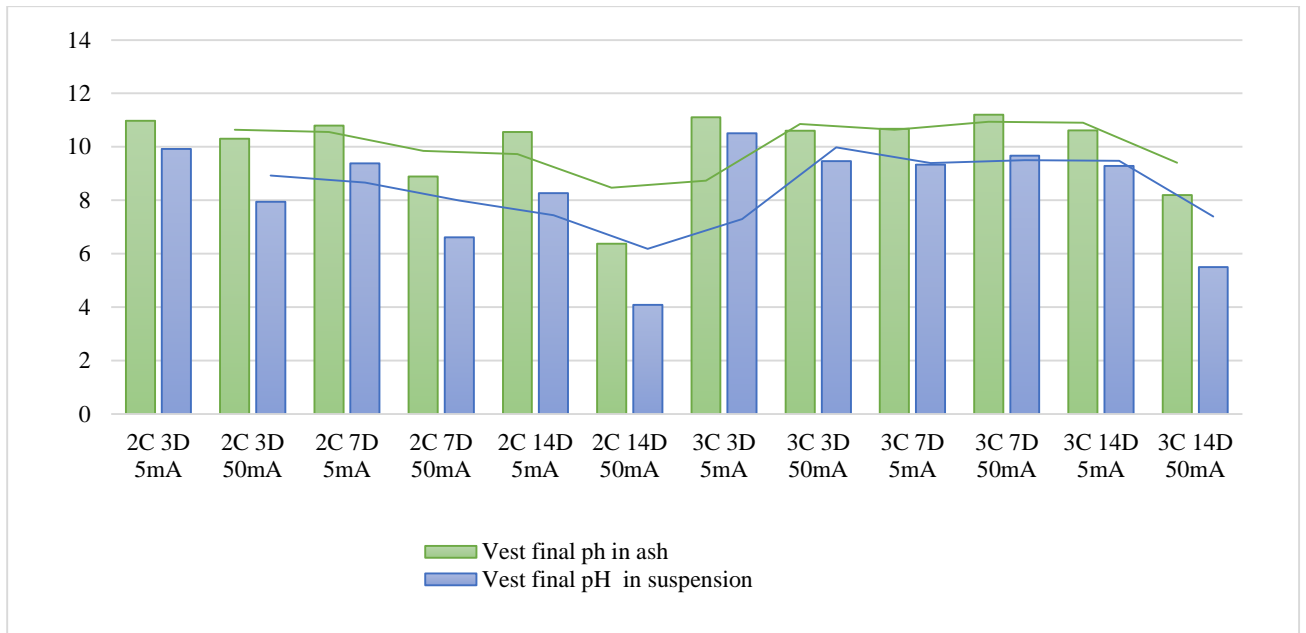
A.1. Results performance by Laser Diffractometer - Particle size distribution for raw APC residues from Vest and REFA

T.1. Table of removal rates in 12 ED experiments from Vest APC residues; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

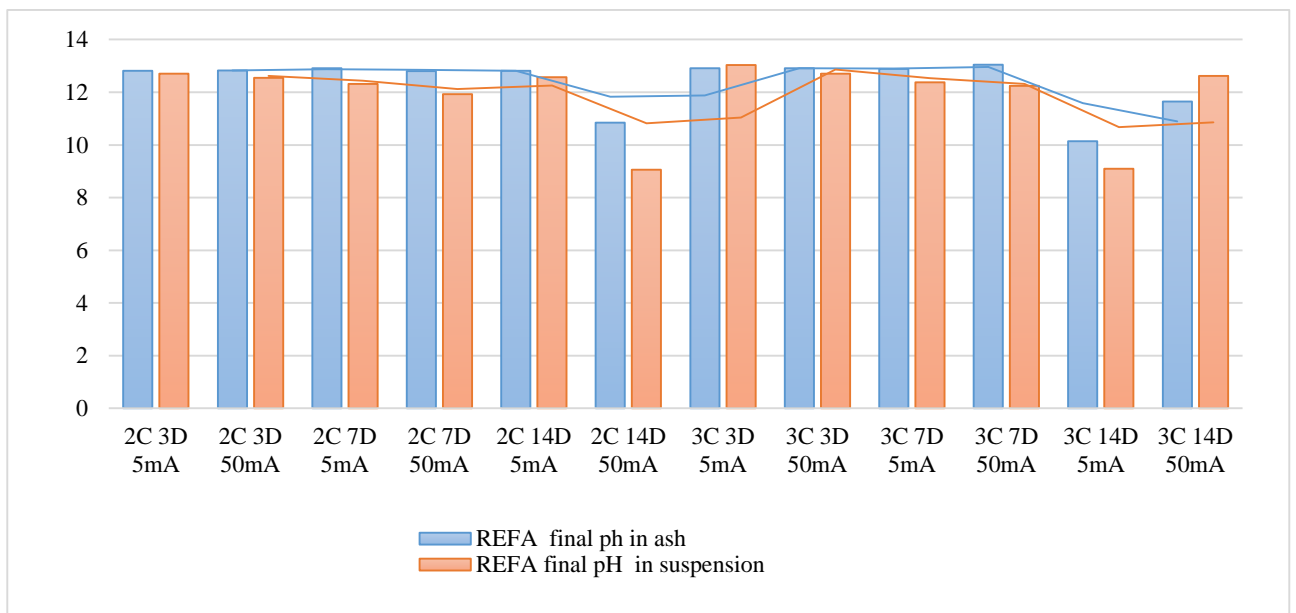
	Vest % ED Remediation				
	Cd	Cr	Cu	Pb	Zn
2C 3D 5mA	0.5	2.8	1.7	0.9	0.8
2C 3D 50mA	2.5	17.1	0.9	2.8	0.3
2C 7D 5mA	0.3	6.3	0.4	5.4	0.3
2C 7D 50mA	53.2	7.3	1.2	1.4	15.6
2C 14D 5mA	1.8	11.9	4.6	4.9	1.9
2C 14D 50mA	83.9	10.9	29.9	1.3	43.9
3C 3D 5mA	0.3	3.2	0.6	0.3	0.4
3C 3D 50mA	2.6	12.5	1.0	2.1	0.7
3C 7D 5mA	1.1	4.3	1.0	1.2	0.9
3C 7D 50mA	1.4	4.2	1.6	3.4	1.7
3C 14D 5mA	4.2	6.0	2.5	2.3	3.2
3C 14D 50mA	73.9	1.2	4.2	3.2	66.5

T.2. Table of removal rates in 12 ED experiments from REFA APC residues; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

	REFA % ED Remediation				
	Cd	Cr	Cu	Pb	Zn
2C 3D 5mA	0.2	0.3	0.4	6.4	0.2
2C 3D 50mA	0.4	0.6	0.3	26.6	0.2
2C 7D 5mA	0.3	0.4	0.6	14.5	0.4
2C 7D 50mA	0.2	5.2	0.8	24.3	0.5
2C 14D 5mA	0.4	0.5	0.8	50.9	0.5
2C 14D 50mA	0.9	21.0	0.6	23.1	0.3
3C 3D 5mA	0.3	1.2	1.2	47.5	0.5
3C 3D 50mA	0.5	0.8	0.6	38.8	0.3
3C 7D 5mA	0.2	0.4	0.5	16.2	0.4
3C 7D 50mA	0.2	0.9	0.6	31.6	0.4
3C 14D 5mA	7.4	6.2	1.9	30.4	0.9
3C 14D 50mA	0.4	4.4	1.3	67.4	0.6



F.1. The difference between pH in dry ash and pH in suspension in end of 12 ED experiments with APC residue from Vest; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)



F.2. The difference between pH in dry ash and pH in suspension in end of 12 ED experiments with APC residue from REFA; (xC –x number of compartments, C compartments; xD – x remediation time, D days; x mA- x intensity of DC)

