Ana Rita Sarmento Gonçalves

Licenciada em Ciências de Engenharia do Ambiente

Analysis of chromium behaviour and speciation during the electrodialytic process

Dissertação para obtenção do Grau de Mestre em
Engenharia do Ambiente, perfil de Engenharia Sanitária

Orientador: Professora Doutora Alexandra de Jesus Branco Ribeiro, CENSE, DCEA, FCT-UNL

Co-orientador: Professora Doutora Gunvor Marie Kirkelund, DTU Byg, Technical University of Denmark

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ANALYSIS OF CHROMIUM BEHAVIOUR AND SPECIATION DURING THE ELECTRODIALYTIC PROCESS

“Olha para as tuas mãos, imagina tudo aquilo que elas serão capazes de construir. O mundo espera pelo invisível que, hoje, só tu és capaz de ver. Existe música por nascer no interior do silêncio. O possível é o futuro do impossível.”

José Luís Peixoto

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Sumário

O interesse no crómio (Cr) provém do uso alargado deste metal pesado em processos industriais que provoca a sua emissão para o ambiente na forma de resíduos líquidos, sólidos e gasosos. O efeito do Cr no ambiente e nos organismos vivos depende primariamente da sua forma química, dado que o Cr(III) é um micronutriente essencial ao ser humano, outros animais e plantas, e o Cr(VI) é altamente tóxico e um carcinogénico humano conhecido.

Este estudo teve como objectivo avaliar se o processo electrodialítico (ED) é um tratamento apropriado para remover Cr, através de uma análise crítica à especiação deste metal, antes e após as experiências ED, de modo a perceber as possíveis interconversões entre Cr(III)-Cr(VI) que ocorrem durante o tratamento.

O processo ED foi a técnica de tratamento aplicada a dois tipos de matrizes que contêm Cr: solo contaminado com arseniato de cobre e crómio (CCA) e cinza volante proveniente da incineração de resíduos sólidos urbanos. De forma a estudar a remoção do Cr, foram usadas três configurações ED: uma nova configuração, a célula composta (2/3C ou 3/2C), com três compartimentos, corrente eléctrica alternada entre dois ânodos e diferentes condições experimentais iniciais, uma configuração com três compartimentos (célula 3C) e outra configuração com dois compartimentos (célula 2C). As taxas de remoção de Cr obtidas neste estudo foram de 10-36% no caso do solo, e 1-13% no caso da cinza volante. As taxas de remoção de Cr mais elevadas foram alcançadas nas experiências de 26 dias: 36% no caso do solo, 13% no caso da cinza volante. Relativamente às experiências de 13 dias, as taxas de remoção de Cr mais elevadas foram atingidas com a célula composta 2/3C: 24% no caso do solo, 5% no caso da cinza volante.

Foi realizada a análise do Cr(VI) antes e após as experiências ED para avaliar eventuais alterações na especiação do Cr que ocorreram durante o tratamento. Esta análise foi elaborada através de dois métodos: USEPA Método 3060A, para a extração do Cr(VI); e Hach Company Método 8023, para a deteção do Cr(VI). Apesar das diferenças na concentração do Cr total, os dois materiais apresentaram uma especiação similar, sendo o Cr(III) a espécie principal e o Cr(VI) menor do que 3% do Cr total, antes e depois do tratamento. Relativamente à cinza volante, a concentração de Cr(VI) encontrava-se inicialmente abaixo do limite de deteção do método e permaneceu desse modo após o tratamento. Relativamente ao solo, a concentração de Cr(VI) diminuiu após o tratamento.

A oxidação de Cr(III) a Cr(VI) não ocorreu durante o processo ED, uma vez que a concentração de Cr(VI) nas matrizes não aumentou após o tratamento. Consequentemente, os resultados deste estudo indicam que o processo ED é uma técnica apropriada para remediar matrizes que contenham Cr, dado que contribui para a remoção do Cr sem causar interconversões entre Cr(III)-Cr(VI).

Palavras-chave: cinza volante; solo; processo electrodialítico; especiação do Cr

Abstract

The interest in chromium (Cr) arises from the widespread use of this heavy metal in various industrial processes that cause its release as liquid, solid and gaseous waste into the environment. The impact of Cr on the environment and living organisms primarily depends on its chemical form, since Cr(III) is an essential micronutrient for humans, other animals and plants, and Cr(VI) is highly toxic and a known human carcinogen.

This study aimed to evaluate if the electrodialytic process (ED) is an appropriate treatment for Cr removal, through a critical overview of Cr speciation, before and after the ED experiments, to assess possible Cr(III)-Cr(VI) interconversions during the treatment.

ED was the treatment technique applied to two types of matrices containing Cr: chromate copper arsenate (CCA) contaminated soil and municipal solid waste incineration (MSWI) fly ash. In order to study Cr remediation, three EDR set-ups were used: a new set-up, the combined cell (2/3C or 3/2C), with three compartments, alternating current between two anodes and different initial experimental conditions, one set-up with three compartments (3C cell) and the other set-up with two compartments (2C cell). The Cr removal rates obtained in this study were between 10-36% for the soil, and 1-13% for the fly ash. The highest Cr removal rates were achieved in the 26 days experiments: 36% for the soil, 13% for the fly ash. Regarding the 13 days experiments, the highest Cr removal rates were attained with the 2/3C set-up: 24% for the soil, 5% for the fly ash.

The analysis of Cr(VI) was performed before and after ED experiments to evaluate eventual changes in Cr speciation during the treatment. This analysis was conducted by two methods: USEPA Method 3060A, for the extraction of Cr(VI); and Hach Company Method 8023, for the detection of Cr(VI). Despite the differences in Cr total concentration, both matrices presented a similar speciation, with Cr(III) being the main species found and Cr(VI) less than 3% of Cr total, before and after the treatment. For fly ash, Cr(VI) was initially below the detection limit of the method and remained that way after the treatment. For soil, Cr(VI) decreased after the treatment.

Oxidation of Cr(III) to Cr(VI) did not occur during the ED process since there was no increase in Cr(VI) in the matrices after the treatment. Hence, the results of this study indicate that ED is an appropriate technique to remediate matrices containing Cr because it contributes to Cr removal, without causing Cr(III)-Cr(VI) interconversions.

Keywords: fly ash; soil; electrodialytic process; Cr speciation

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Abbreviations and acronyms

2C – Cell with two compartments

3C – Cell with three compartments

2/3C – Combined cell with three compartments and alternating current (starts in anode B)

3/2C – Combined cell with three compartments and alternating current (starts in anode A)

13D – Thirteen days

26D – Twenty-six days

AAS – Atomic absorption spectroscopy

AN – Anion exchange membrane

APC – Air pollution control

ATSDR – Agency for Toxic Substances and Disease Registry

CAT – Cation exchange membrane

CC – Combined cell

CCA – Chromate copper arsenate

Cr(III) – Trivalent chromium

Cr(VI) – Hexavalent chromium

DC – Direct current

EC – European Commission

ED – Electrodialytic

EDR – Electrodialytic remediation

EK – Electrokinetic

EKR – Electrokinetic remediation

FA – Fly ash

IAWG – International Ash Working Group

IC – Ion chromatography

ICP-OES – Inductively coupled plasma with optical emission spectroscopy

L/S – Liquid to solid ratio

LOI – Loss on ignition

MSWI – Municipal solid waste incineration

S – Soil

SEM/EDX – Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy

USEPA – United States Environmental Protection Agency

XRD – X-ray diffraction

1. Introduction

Chromium (Cr) is released as a contaminant to the environment, as a result of human activities through production of wastewater in metal smelting, electroplating, tanning, metallurgy, polishing, painting, pigment manufacture, chrome plating, leather tanning, dyestuff industries, and waste by-products in wood preservation and power generation facilities, such as municipal solid waste incinerators (Chirenje et al., 2004; Astrup et al., 2005; Zakaria et al., 2009). The two most important chemical forms of Cr are trivalent Cr (Cr(III)) and hexavalent Cr (Cr(VI)) and they determine its toxicity. Cr(III) is an essential micronutrient for humans, other animals and plants, whereas Cr(VI) is classified as a human carcinogen (ATSDR, 2012). Since Cr is not degradable, knowing its speciation in contaminated matrices from human activities is important to understand the environmental impact that can result from their contamination.

In Europe, several industrial activities have been contributing to this contamination. In wood preservation, before chromate copper arsenate (CCA) preservative was completely prohibited, it had been widely used and its improper disposal and leakage resulted in contaminated sites with Cr, Cu and As. Nowadays, most of these sites still need to be remediated.

Cr release also occurs in municipal solid waste incineration (MSWI), which is a widely used treatment technology in waste management strategy that aims to recover energy, at the same time that hygenizes and minimizes the volume of solid waste. As a result, MSWI produces residues that are characterized as hazardous waste, such as fly ash and air pollution control (APC) residues, due to their high alkalinity, heavy metal content and their potential leaching, as well as other contaminants content, namely soluble salts and toxic organic compounds, and their safe disposal presents a major environmental challenge.

To remediate Cr contaminated sites or to reduce Cr toxicity in a residue to possibly use it as a secondary resource, advanced treatment is needed. In this study, the treatment used was the electrodialytic process (ED). ED is a technique in which contaminants are removed from contaminated matrices by applying an electric field, which forces their movement into concentration chambers through ion exchange membranes. ED was applied to two types of matrices containing Cr: CCA contaminated soil and MSWI fly ash. Three ED set-ups were used: a combined cell (2/3C or 3/2C) with three compartments, alternating current between the two anodes and different initial experimental conditions, a cell with three compartments and a third cell with two compartments.

Aim and research

The overall aim of this study was to evaluate if the ED process is an appropriate treatment for Cr removal. To accomplish this aim, a series of laboratory experiments using different ED set-ups were conducted and the following questions were studied:

i. Do the different set-ups influence Cr removal?
ii. Does the ED process influence Cr speciation?

iii. Is the leaching of Cr in the MSWI fly ash affected by the ED process?

iv. Can relations between Cr and other elements (Al, Ca, Fe, K, Na and Mn) be found in the matrices studied?

2. Chromium

2.1 Element

Chromium (Cr) is a metallic element present in soil, water, rocks, fauna and flora, and volcanic and dust gases. Although Cr is the 22nd most abundant element in the Earth's crust, with an average concentration of 100 ppm, it is never found in nature as a free metal. (Emsley, 2011; Encyclopædia Britannica Online, 2015a). The commercial source of Cr is chromite, a mineral oxide of chromium and iron ($FeCr_2O_4$). The main producing areas of chromite are South Africa, Russia, Albania, the Philippines, Zimbabwe, Turkey, Brazil, India and Finland (Encyclopædia Britannica Online, 2015b). Besides its natural occurrence, Cr is also released to the environment as a result of human activities through production of waste streams in metal smelting, electroplating, tanning, metallurgy, polishing, painting, pigment manufacture, chrome plating, leather tanning, dyestuff industries, wood preservation and power generation facilities such as municipal solid waste incinerators (Bluskov et al., 2005; Dianyi Yu, 2008) .

Cr is a transition metal, in group 6 of the periodic table. It exists in several oxidation states from -2 to +6 valence. Its toxicity, mobility and bioavailability depend on its chemical form. The most important and stable states are Cr(0) (elemental chromium), Cr(III) (trivalent chromium) and Cr(VI) (hexavalent chromium).

Cr(0) does not occur naturally, it is produced by industrial processes and is mainly found in alloys, such as stainless steel, and in chrome plated objects (Gómez & Callao, 2006).

Cr(III) is the most stable oxidation state and occurs naturally in chromite ores (Zayed & Terry, 2003). Cr(III) is an essential micronutrient for the proper functioning of living organisms, that helps to maintain the normal metabolism of glucose, cholesterol and fat in human bodies (Anderson, 1989; Kimbrough et al., 1999). Cr(III) in the form of oxides, hydroxides, and sulphates is less toxic and relatively insoluble in water. Its lower mobility is due to its bond to organic matter in soil and aquatic environments (Weng et al., 1994). As Cr(III) is unable to permeate through cell membranes, it is not readily bioavailable and therefore is considered to be less toxic than other Cr compounds (Kumaresan & Riyazuddin, 1999).

Cr(VI) is the second most stable oxidation state of Cr. Rarely occurring in nature, most of Cr(VI) compounds are manufactured as products or by-products. Cr(VI) compounds are irritant due to their high solubility and diffusivity through cell membranes. This explains why Cr(VI) is 500 to 1000 times more toxic to a living cell than Cr(III) (Costa, 2003; Petrilli & De Flora, 1977).

The chemistry of Cr in the environment depends on pH, Cr concentration, hydrolysis, redox reactions, complexation and/or adsorption. Figure 2.1 presents a diagram of the occurrence of dominant Cr species in diluted aqueous solutions, in the absence of any complexing agents other than H_2O or OH (T=25 °C), as a function of pH and redox potential, under each species is thermodynamically stable. Cr(III) dominant species in diluted aqueous solutions are the following: in acidic solutions, pH between

0 and 4, Cr(III) exists as hexa-aqua $Cr(H_2O)_6^{3+}$ complex (abbreviated as Cr^{3+}); in less acidic solutions, pH between 4 and 6, $Cr(H_2O)_6^{3+}$ undergoes hydrolysis to produce $Cr(H_2O)_5(OH)^{2+}$ (abbreviated as $Cr(OH)^{2+}$) and $Cr(H_2O)_4(OH)_2^{+}$ (abbreviated as $Cr(OH)_2^{+}$) species; in the neutral to alkaline pH region, between 6 and 11.5, Cr is mainly precipitated as a sparingly soluble $Cr(OH)_3$(s); in alkaline solutions, at pH higher than 11.5, the precipitate re-dissolves, resulting in formation of tetrahydroxo $Cr(OH)_4^{-}$ complex (Ščančar & Milačič, 2014). For Cr(VI), the range of dominant species is the following: in acidic solutions, pH lower than 0.7, Cr(VI) exists as H_2CrO_4 (chromic acid); between pH 0.7 and 6.5, Cr(VI) exists as $HCrO_4^{-}$ (hydrogen chromate) and $Cr_2O_7^{2-}$ (dichromate); in alkaline solutions, above pH 6.5, only CrO_4^{2-}(chromate) exists (Unceta et al., 2010).

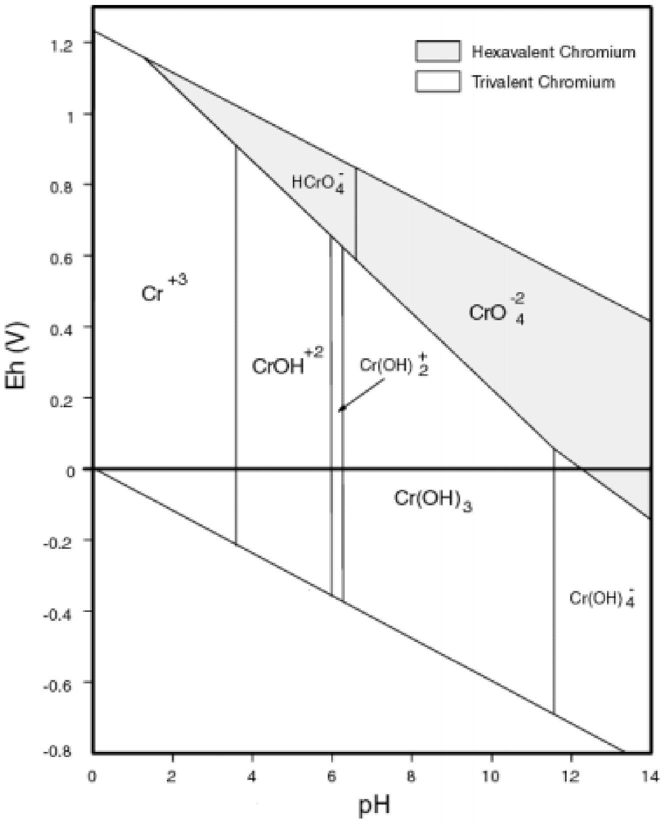

Figure 2.1: Pourbaix's Eh-pH diagram for Cr species dominating in diluted aqueous solutions in the absence of any complexing agents other than H_2O or OH, T=25 °C (USEPA, 2000)

2.2 Environmental and human risks

In nature, Cr exists in food, air, water and soil, mostly as Cr(III). It is only as a result of human activities that substantial amounts of Cr(VI) become present. Health effects of Cr compounds can vary with the route of exposure. For the general population, ingestion is the primary route of exposure to Cr and dermal is a minor route of exposure. For the occupational population, inhalation is the predominant route of exposure to Cr (ATSDR, 2012).

Cr is released into the atmosphere via industrial, commercial, and residential combustion of natural gas, oil, coal and waste and from emissions from metal industries. Approximately 1/3 of atmospheric releases are believed to be in the form of Cr(VI). Cr is primarily removed from the atmosphere by fallout and precipitation, with a residence time inferior to 10 days (ATSDR, 2012).

The main sources of Cr contamination in soil and groundwater are electroplating, textile manufacturing, leather tanning, pigment manufacturing, wood preservation and Cr waste disposal (USEPA, 2000). The most significant groundwater and soil contamination problem associated with the use of CCA is Cr(VI), which is acutely toxic, mutagenic, and carcinogenic in the environment. It is also very soluble, mobile, and moves at a rate essentially the same as the groundwater (Palmer & Puls, 1994).

In general, Cr is not bioaccumulated or biomagnificated. Contrary to Cr(VI), Cr(III) is an essential nutrient for humans, in amounts of 50-200 µg/day, and necessary for the metabolism of insulin. It is also essential for other animals, whereas it is not known whether it is an essential nutrient for plants, but all plants contain the element (EC, 2002). Cr(VI) is much more toxic than Cr(III), for acute and chronic exposure, and its compounds are regulated through the “Classification, Labelling and Packing” Regulation (Regulation EC 1272/2008). Table 2.1 presents some of Cr(VI) compounds classified in this regulation, as well as their industrial uses. In Table 2.2, the potential human and animal health effects from exposure to Cr compounds are summarized.

Table 2.1: Identification and industrial uses of some of the Cr(VI) compounds regulated by Regulation EC 1272/2008 (adapted from Council of the European Union, 2008; Geddie, 2013)

Identification	Chemical formula	CAS No	Uses
Chromium trioxide	CrO_3	1333-82-0	Chromium plating, aluminium anodizing and chemical intermediate for CCA wood preservatives. Ceramic glazes, coloured glass, metal cleaning, inks and paints.
Calcium chromate	$CaCrO_4$	13765-19-0	Metal primers, corrosion inhibitors, high temperature batteries.
Lead chromate	$PbCrO_4$	7758-97-6	Decorating china, pigment in industrial paints, rubber and plastics, pigment in oil paints and watercolours, and printing fabrics.
Sodium dichromate	$Na_2Cr_2O_7$	7789-12-0	Inks, oxidizing agent in manufacture of dyes and other synthetic organic chemicals, electric batteries, manufacture of chromic acid, other chromates and chrome pigments, corrosion inhibiting paints, colorant for glass and component of CCA wood preservatives.
Strontium chromate	$SrCrO_4$	7789-06-2	Corrosion inhibiting pigment, plating additive.
Zinc chromate	$Zn\ CrO_4$	–	Priming paints for metals, varnishes and pigments in aerospace paints.

Table 2.2: Potential human and animal health effects from exposure to Cr compounds (adapted from ATSDR, 2012)

System	Health effects
Respiratory	Most common health problem in workers exposed to Cr. The health effects include irritation of the lining of the nose, runny nose, and breathing problems (asthma, cough, shortness of breath, wheezing) following inhalation exposure. The concentrations of Cr in air that can cause these effects may be different for different types of Cr compounds, with effects occurring at much lower concentrations for Cr(VI) compared to Cr(III). However, the concentrations causing respiratory problems in workers are at least 60 times higher than levels normally found in the environment.
Gastrointestinal	The main health effects seen in animals are irritation, ulceration, and stomach and small intestine lesions following oral exposure to Cr(VI).
Hematological	Results of acute, intermediate, and chronic duration studies in animals identify the hematological system as one of the most sensitive effects of oral exposure to Cr(VI). Cases of hematological effects like microcytic and hypochromic anemia have been reported in humans after the ingestion of lethal or sub lethal doses of Cr(VI) compounds.
Reproductive	The following reproductive effects of Cr(VI) in humans have been reported: significant increase in the number of morphologically abnormal sperm, significant decreases on sperm count and motility, and greater incidences of complications during pregnancy and childbirth.
Dermal	Cr(VI) compounds can produce effects on the skin and mucous membranes. Cr allergic dermatitis is typically elicited by dermal contact in sensitized individuals.
Cancer	USDHHS(1), IARC(2), and USEPA have classified Cr(VI) as a human carcinogen. IARC has classified Cr(III) as not classifiable as to its carcinogenicity to humans. In workers exposed to Cr, inhalation of Cr(VI) has shown to cause lung cancer. Mixed results have been found in studies of populations living in areas with high levels of Cr(VI) in the drinking water. In laboratory animals, Cr(VI) compounds have shown to cause tumours to the stomach, intestinal tract, and lung.

(1) USDHHS - United States Department of Health and Human Services; (2) IARC - International Agency for Research on Cancer

2.3 Chromium in CCA contaminated soil

Chromate copper arsenate (CCA) is a wood preservative that has widely been used for wood treatment, considerably expanding the lifespan of the treated wood exposed to environmental conditions, fungi, insects and marine organisms. The first CCA formulation was developed in 1933 by Kamesam, at the Forest Research Institute in India (Coggins, 1991). It is an inorganic water-based preservative that contains Cr(VI), Cu(II) and As(V). In the CCA solution, As(V) acts as an insecticide, Cu(II) functions as a fungicide and Cr(VI) binds the arsenic and copper to the wood (Song et al., 2006). The highly acidic solution (pH 1.5-2.5) is introduced into the pore space of the wood by pressure (Jang et al., 2002).

In 2002, the estimated production of CCA treated wood was around 20 million m^3 with a consumption of 300 000 t of preservative chemicals (Humphrey, 2002). In the early 2000s, the European Commission (EC) drew up draft proposals to limit the use of CCA, based on the dangers posed to human health and the environmental impacts when CCA treated wood is burnt or disposed of. In 2006, the EC published a directive (2006/139/EC (EC, 2006)) that introduced restrictions to the use of CCA preservatives and CCA treated wood in residential and domestic construction (Smith et al., 2008).

Soil contamination in wood preservation sites is either due to spills of preservation liquid during handling, leaking pipes or drippings of freshly impregnated wood (Bhattacharya et al., 2002). Because of the high concentrations of metals in the CCA solution, relatively small leaks or spills may result in high concentrations of metals in the soil that are potentially harmful to human health and the environment (Jang et al., 2002). As arsenic, chromium and copper cannot be degraded, if these soils are not remediated, some species of these the contaminants will leach from the soil and may contaminate groundwater.

Bioavailability of Cr in contaminated soils is highly dependent on the soil properties, such as pH, redox conditions and the quantity of organic matter. As presented in Figure 2.2, Cr mobility in soils is generally controlled by oxidation, reduction, adsorption, desorption and precipitation, besides other surface complexation processes (Ottosen et al., 2015).

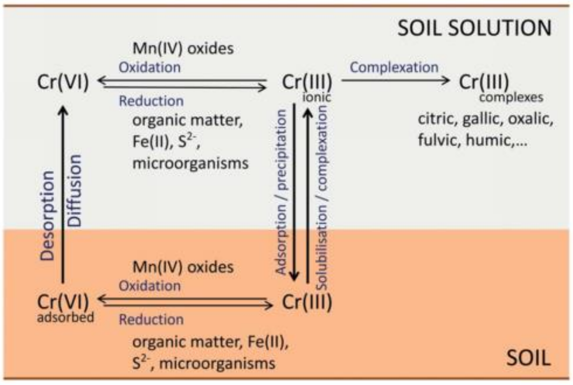

Figure 2.2: A simplified scheme of cycling and transformation of Cr species in soil/soil solution (Ščančar & Milačič, 2014)

Table 2.3 presents the dominant species of Cr found in a CCA contaminated soil and their behaviour in soil and groundwater. In the CCA solution, Cr is present as Cr(VI). As observed in Table 2.1, Cr(VI) is present in the form of chromate (CrO_4^{2-}) and is adsorbed by positively charged surfaces in the soil like iron and aluminium oxides and reduced to Cr(III) by organic matter. Chromate has a high leaching potential, but its mobility is highly dependent on the content of organic matter in the soil. This means that the occurrence of chromate is often connected to sandy soils, because the organic matter content of loamy soils will react with chromate to chromite, which forms insoluble Cr(III) oxides at pH above 6 (Nielsen, 2013). Previous studies of CCA contaminated soils have shown that Cr is the CCA contaminant with the lowest mobility in the soil, therefore being associated with the top soil and organic fractions, presumably as Cr(III) (Lund & Fobian, 1991; Andersen et al., 1996).

Table 2.3: Chemical properties of Cr as a CCA contaminant and its behaviour in soil and groundwater systems (adapted from Nielsen, 2013)

Metal	**Redox state**	**Dominant speciation and formulation**	**Behaviour in soil**	**Mobility in groundwater**
Cr	Cr(VI)	CrO_4^{2-} (pH>6.5)	Partly retained by iron oxides, reduced by organic matter	High, if no organic matter is present
	Cr(III)	$Cr(OH)_2^+$ (4<pH<6) $Cr(OH)_3$ (s) (6<pH<11.5)	Forms solid phase	Low solubility

Although the use of arsenic based wood preservatives, such as CCA, in wood preservation was completely suspended in Denmark in the late 1990s, more than one hundred CCA contaminated soil sites exist and the majority still need to be remediated (Nielsen et al., 2011). Although the natural concentration of Cr in terrestrial soils is within the range of 1-100 mg/kg (Nystrøm, 2001), in CCA contaminated soils the concentration of Cr may reach 300-600 mg/kg (Kowalski et al., 2015). In Table 2.4, the criteria for Cr contaminated soil and its different pollution classes applicable in Denmark are presented.

Table 2.4: Classification of polluted soils regarding Cr concentration (adapted from Frederiksberg kommune, 2001)

	Polluted soil			
Substance	**Class 1** Unpolluted	**Class 2** Slightly polluted	**Class 3** Polluted (disposed of)	**Class 4** Very polluted (disposed of or treated)
Cr(VI) (mg/kg)	0 - 20	20 - 35	35 - 50	>50
Cr total (mg/kg)	0 - 500	500 - 750	750	>750

2.4 Chromium in MSWI fly ash

Municipal solid waste incineration (MSWI) is used worldwide as a treatment technology in a waste management strategy. This technology reduces the volume of waste by approximately 90% and allows energy recovery in the form of heat and electricity (Abbas et al., 2001). However, this technology generates residues that are characterized as hazardous waste, such as fly ash and APC residues, and their safe disposal presents a major environmental challenge. In many countries, the disposal is done in specially designed landfills, after a stabilization process (Dias-Ferreira, 2005). In Denmark, around 100 000 t of fly ash and APC residues are produced annually but no specific statutory order regulates the management of these MSWI residues and the current policy is not to allow their temporary storage or landfilling in Denmark, treated or not treated. Therefore the current solution in Denmark is to export fly ash and APC residues to either Norway or Germany. In Norway, these residues are used for neutralization of acid waste and, in Germany, for backfilling salt mines (Astrup, 2008).

The hazard nature of fly ash and APC residues arises from their high alkalinity (pH 10–12), high concentration of several heavy metals and their potential leaching, high concentration of soluble salts as well as trace quantities of toxic organic compounds (e.g. dioxins, furans) (Pedersen et al., 2003; Dias-Ferreira, 2005; Jensen et al., 2015). Fly ash is a MSWI residue defined by the International Ash Working Group (IAWG) (1997) as ‘‘the particulate matter carried over from the combustion chamber and removed from the flue gas stream prior to addition of any type of sorbent material’’. The amount of fly ash normally constitutes 10–30 kg/t of incinerated waste, depending on the properties of the waste, the combustion technology and the particulate collection system (Hjelmar et al., 2010). The speciation of heavy metals in fly ash is highly influenced by the metal’s behaviour and fate during the combustion process. More volatile metals may vaporise during combustion and condense on the surface of fly ash particles when the flue gas cools down downstream of the boiler, enriching the fly ash in volatile elements. On the other side, the bottom ash retains the non-volatile elements (Pedersen, 2003).

The major sources of Cr in MSWI are residues of glue, matches, machine oils, metal scrap and building matrices (Abbas et al., 2001). Cr is a non-volatile element in the combustion zone due to the fact that most of its compounds have boiling points exceeding 1500 °C. Thus, being highly retained in the bottom ash (Hjelmar et al., 2010). Only a small amount of Cr that enters the MSWI facility is found in the fly ash. IAWG (1997) analysed fly ash data from several MSWI facilities in Europe and North America, and the total content of Cr in fly ash and bottom ash are presented in Table 2.5.

Table 2.5: Concentration of Cr in fly ash and bottom ash from several MSWI facilities in Europe and North America (adapted from IAWG, 1997)

Element	Bottom ash		Fly ash	
	Range	Average	Range	Average
Cr (mg/kg)	23 - 3200	1610	140 - 1100	620

The process of leaching depends on several physical and chemical factors and can be defined as the dissolution of a soluble constituent from a solid phase into a solvent. It occurs as a consequence of the chemical reactions taking place at the scale of the individual waste particles as well as of the contaminant transport processes via the fluid moving through the solid particles. It has been demonstrated that the leaching properties of contaminants in MSWI residues are controlled by their speciation, which depends on the pH, redox potential and the presence of organic and inorganic complexing agents (Sabbas et al., 2003).

Interest in the leaching behaviour of Cr has been growing over the last years, mainly due to the European Directive (2003/33/EC) that established criteria and procedures for the acceptance of waste at landfills. In order to comply with the legislation, it is necessary to study the leaching potential of Cr and to develop techniques to control it. In MSWI residues, Cr is hypothesized to be present mainly as Cr(VI), due to the oxidation of Cr(III) to Cr(VI), that takes place during the combustion of the waste and its alkaline pH (Astrup et al., 2005). However, a study on the impact of solid fuel combustion technology on valence speciation of Cr in fly ash has shown that, for MSWI fly ash and the other fly ashes examined, the dominant form of Cr present is Cr(III) (Świetlik et al., 2014). These results are presented in Figure 2.3. Nonetheless, the presence of Cr in waste leachates is mostly due to the leaching of the highly water soluble Cr(VI), because Cr(III) has very low solubility (Cornelis et al., 2008).

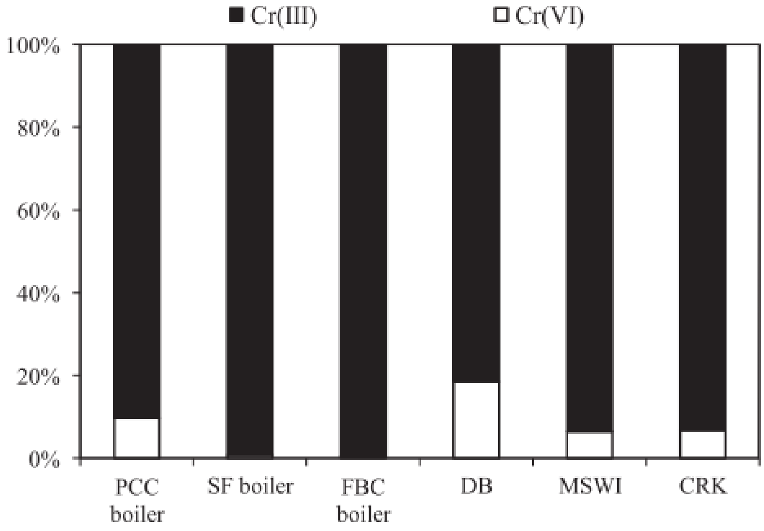

Figure 2.3: Cr valence speciation in fly ashes generated in real solid fuel furnaces based on various combustion technologies (Świetlik et al., 2014)

2.5 Influence of other elements on chromium speciation

Cr speciation in the environment and in by-products or residues from industrial processes is influenced by other elements. Al, Fe, Ca, K, Mn and Na have been studied to understand how their compounds affect Cr speciation.

In soil, Cr(III) is in close association with Fe(III) due to their similar geochemical behaviour, which plays an important role both in soil mineral formation and sorption processes (Sipos et al., 2014). Cr(III) is also associated with Al(III) due to their ionic potentials, which are close enough to allow the substitution of one another to occur in many mineral and organic structures (Bartlett & James, 1988). In soil, Mn is the only oxidizing agent that favours the oxidation of Cr(III) to Cr(VI). The oxidation of Cr(III) depends mostly on the initial concentration of Cr(III), the amount of high valence state Mn and the soil pH (Bartlett & James, 1979; Chinthamreddy & Reddy, 1999). Cr(VI), in the form of chromate (CrO_4^{2-}), is adsorbed by positively charged surfaces in the soil like iron and aluminium oxide. Although organic matter is the primary reducing agent of Cr(VI) in soil, it can also be reduced to Cr(III) by Fe(II), from dissolution of the Fe(II) components of hematite and biotite in acidic media (Eary & Rai, 1991).

Several authors have examined the thermodynamic characteristics of the interaction between Cr species and different metal oxides, such as Al, Fe, Ca, K and Na on fly ashes from various combustion technologies (Astrup et al., 2005; Chen et al., 2012; Lehmusto et al., 2012; Chen et al., 2013; Verbinnen et al., 2013; Świetlik et al., 2014). One of the findings was that Cr(VI) formation is positively correlated with the reduction potential of the elements. Thus, the element with the highest reduction potential exhibits the largest capability in electron transfer, by activating bulk oxygen which in turn promotes the formation of Cr(VI) (Chen et al., 2013). Another major finding was that the interaction between Al-O_2-Cr(VI) should be carefully considered when interpreting Cr leaching data. This is due to the fact that, most likely, Al(0) reactivity in the ashes is a critical factor affecting Cr leaching from incineration residues (Astrup et al., 2005).

3. Electrodialytic process – A remediation technique

The electrokinetic phenomenon was discovered in 1809 by Reuss, who observed that water could be transported within a porous matrix by applying an electric DC field (Reuss, 1809; Hansen et al. 2015). The ED process is an enhancement of the electrokinetic process (EK), combining the electrokinetic movement of ions with the principle of electrodialysis (Gomes, 2014). The difference between the techniques results from the type of membranes used in each case. In EK, passive membranes are used to separate the contaminated matrix from the electrolytes, only acting as physical barriers. On the contrary, ED uses ion exchange membranes that act both as physical and chemical barriers (Nystrøm, 2001).

The ED process applied to solid waste matrices began to be developed in 1992 at the Technical University of Denmark where it was patented in 1995 (PCT/DK95/00209) (Ottosen et al., 2005). The technique was originally developed to remove heavy metals from polluted soils (Ottosen, 1995; Hansen, 1995) and has proven to be an efficient one for soil remediation (Ottosen et al. 1997; Ottosen et al. 2005; Ribeiro et al. 2007; Jensen et al. 2007; Buchireddy et al. 2009; Sun et al. 2012; Ottosen et al. 2013; Ottosen et al. 2015). However, ED has also been applied for the removal of heavy metals from other solid waste matrices, such as harbour sediments (Kirkelund et al., 2009), CCA treated wood waste (Ribeiro et al., 2000; Christensen, 2004), mine tailings (Hansen et al., 2008), biomass ash (Hansen et al., 2005), sewage sludge ash (Pazos et al., 2010), MSWI ash (Pedersen, 2002a; Dias-Ferreira et al., 2005) and MSWI air pollution control residues (Magro, 2014).

3.1 General principle

The main principle of ED is that ions, including heavy metal ions, move in an electric field. The application of a low level direct current between two electrodes generates an electric field that when applied to a medium containing charged particles (e.g. a water saturated soil matrix), will transport the charged species in the medium towards one of the electrodes, according to their charge. The current works as a cleaning agent, as the negative ions (anions) move towards the positively charged electrode (anode) and positive ions (cations) move towards the negatively charged electrode (cathode) (Christensen, 2004). Three main transport mechanisms are responsible for this movement: electromigration, electroosmosis and electrophoresis (Figure 3.1).

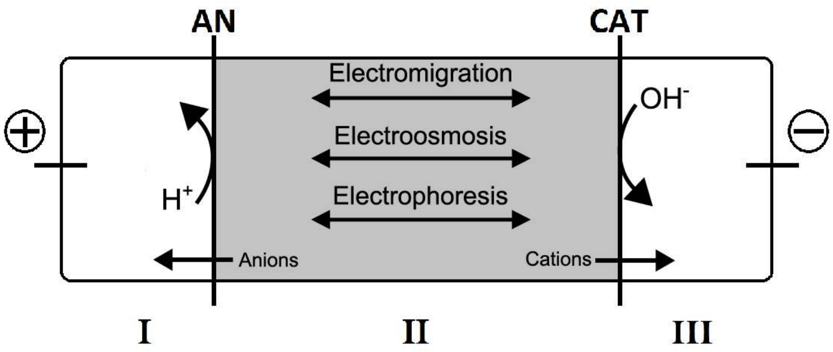

Figure 3.1: Schematic representation of the ED principle and transport mechanisms in a 3 compartment cell. AN-anion exchange membrane; CAT-cation exchange membrane (adapted from Magro, 2014)

3.2 Transport mechanisms

Electromigration

Electromigration is the most important mechanism for transporting charged species out of the contaminated matrix and consists on the transport of ions and ion complexes to the electrode of opposite charge under an applied electric field. Therefore, the anions and cations present in the medium will be transported towards the anode and cathode, respectively. Electric current always tends to flow through a matrix where the electric resistance is the lowest. In soil, this occurs in the diffuse double layer, where the ions are accumulated and non-specifically adsorbed (Ottosen, 1995).

The electromigration transport is described by Equation 3.1 (Acar & Alshawabkeh, 1993), where J_j^m is the migrational flux, u_j^* is the effective ionic mobility, c_j is the molar concentration of specie j and ∇E is the gradient of the electrical potential:

$$J_j^m = - u_j^* c_j \nabla E \qquad \textbf{(3.1)}$$

Electroosmosis

Electroosmosis describes the flow of an ionic solution under the influence of an applied electric field relative to a charged surface. When the electric field is applied, the ions in the matrix are transported to the electrode of opposite charge and carry their water of hydration, consequently exerting a viscous drag on the fluid around them (Mitchell & Soga, 1993; Ribeiro, 1998). Electroosmosis is the major mechanism of removal of uncharged and/or weakly dissociated organic contaminants (Ribeiro, 1998).

The electroosmotic flux is described by Equation 3.2 (Acar & Alshawabkeh, 1993), where J_j^e is the electroosmotic mass flux, k_e is the electroosmotic permeability, c_j is the molar concentration of specie j, c_w is the molar concentration of water (≈ 1) and ∇E is the gradient of the electrical potential:

$$J_j^e = - k_e (c_j / c_w) \nabla E \qquad \textbf{(3.2)}$$

In EDR, the electroosmotic transport is reduced significantly by the use of ion exchange membranes, making ED suitable for selective transport of small, charged species (Jensen, 2005).

Electrophoresis

Electrophoresis is the movement of charged particles or colloids under the influence of an electric field. The charged particles are attracted electrostatically to one of the electrodes and repelled from the other (Ribeiro, 1998). The contaminants that are bound to mobile particulate matter can be transported in this manner (Virkutyt et al., 2002). This mechanism is rarely encountered in EDR (Jensen, 2005).

Diffusion

Diffusion is the movement of species under a chemical concentration gradient. In general, in the usual conditions of electrokinetic treatments, this is a secondary transport and only in some areas of the medium, where gradients are especially high, this can be important as, e.g. the areas where acid and basic fronts, or metal cations and hydroxyl ions, are to meet (Ribeiro & Rodríguez-Maroto, 2006). The diffusive flux is described by Fick's first law in Equation 3.3 (Acar & Alshawabkeh, 1993), where J_j^d is the diffusive mass flux, D_j^* is the effective diffusion coefficient and $\nabla(c_j)$ is the gradient of the molar concentration of specie j:

$$J_j^d = - D_j^* \nabla(c_j) \tag{3.3}$$

3.3 Ion exchange membranes

The use of ion exchange membranes as separators, between processing solutions surrounding the electrodes and the matrix, adds electrodialysis to the process (Couto et al., 2013).

Ion exchange membranes are made of polymers with fixed charged groups. Due to the electric current, these membranes function as an interface that allows the transport of counter-ions (ions with opposite charge as the surface of the membrane) and prohibits the transport of co-ions (ions with the same charge as the surface of the membrane) (Hansen et al., 1997; Nystrøm, 2001). Figure 3.2 shows a sketch of an ion exchange membrane. In EDR, two types of membranes are used: the cation exchange membrane and the anion exchange membrane.

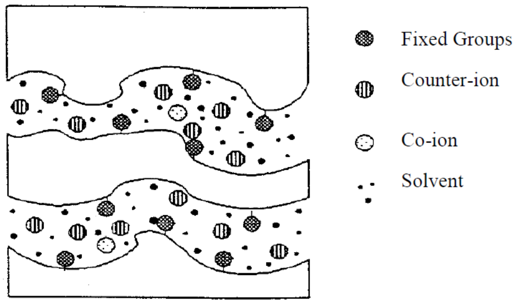

Figure 3.2: Sketch of an ion exchange membrane (Hansen, 1995)

The replacement of the passive membranes by ion exchange membranes presents several advantages that increase the efficiency of the removal process (Ottosen, 1995; Ribeiro, 1998):

- Due to electrodialysis, the extracted ions from the matrix compartment and the new ions formed at the electrodes are prevented from passing again into the matrix compartment. Therefore, electric current is only carried by the ions originally in the matrix compartment (with the exception of the H^+ ions produced in the anolyte which are able to cross the anion exchange membrane into the matrix compartment), overcoming the problem of waste of current that was also used to move ions between the electrodes compartments.
- The fact that the cation exchange membrane only allows cations to pass through leads to a higher efficiency on the transport of heavy metals from the medium to the cathode.
- The control of the pH gradients created in the contaminated medium is facilitated and it is possible to control the electrolytes solution at a certain pH. Hence, keeping the catholyte solution in acidic conditions, with the addition of acid every day, will maintain the transport of cations from the medium to the cathode.

3.4 Electrode reactions

In ED, inert electrodes (carbon, platinum or titanium electrodes) are used to prevent interferences in the electrodes reactions (Nystrøm, 2001). The applied electric current leads to electrolysis of water in the electrode compartments and vaporization of gases. The water electrolysis generates an acidic medium at the anode and an alkaline medium at the cathode and is described by the following equations:

$$\text{Anode: } 2\ H_2O \rightarrow O_2\ (\uparrow) + 2\ H^+ + 4e^- \qquad \textbf{(3.4)}$$

$$\text{Cathode: } 2\ H_2O + 2e^- \rightarrow H_2\ (\uparrow) + 2\ OH^- \qquad \textbf{(3.5)}$$

At the anode, the reaction results in the production of H^+ ions whereas, at the cathode, results in the production of OH^- ions. In ED, the use of a cation exchange membrane between the matrix and the cathode compartment avoids the propagation of the OH^- and other anions from the cathode compartment into the matrix, as it acts as a perfect rectifier. But the use of an anion exchange membrane between the anode compartment and the matrix does not avoid the propagation of the H^+ ions from the anode compartment into the matrix. However, this occurrence does not represent a limitation but instead it helps the mobilization and movement of heavy metals in the matrix due to their desorption/dissolution (Ribeiro, 1998; Ottosen et al., 2000; Jensen, 2005).

When the metal concentration in the cathode compartment increases, precipitation of the metal at the cathode surface can occur:

$$\text{Cathode: } Me^{n*} + ne^- \rightarrow Me \qquad \textbf{(3.6)}$$

$$\text{Cathode: } Me(OH)_n + ne^- \rightarrow Me + nOH^- \qquad \textbf{(3.7)}$$

If chlorides are present in the solution, chlorine gas can be produced at the anode (Equation 3.8) and special care should be taken.

$$\text{Anode: } 2\,Cl^- \rightarrow Cl_2\,(\uparrow) + 2e^- \tag{3.8}$$

3.5 Electrodialytic remediation of chromium in CCA contaminated soil

The removal of heavy metals from soil is one of the most studied processes in electrodkinetic remediation (EKR) (Virkutyte et al., 2002) and in electrodialytic remediation (EDR) (Ottosen, 1995; Ribeiro, 1998). Several EKR and EDR experiments have been performed with various soil types polluted by different heavy metals. The soil type and the combination of heavy metals influence the acidic front development and the heavy metal desorption/dissolution, affecting the remediation results. The pH and redox conditions in the soil are also important factors affecting heavy metal retention (Ottosen et al., 2009). In electrochemical remediation of soil, the order of removal of different heavy metals has been reported as follows: Ni ≈ Zn > Cu > Cr in a soil polluted from a chlor-alkali factory (Suèr et al., 2003); Zn > Cu ≈ Pb and Cu > Cr (Ottosen et al., 1997) or Cd > Zn > Cu > Pb > Ni >> Cr or Cu > As > Cr (Jensen, 2005) in different industrial polluted soils. In order to further increase heavy metal removal efficiency in EDR, pH control, addition of enhancement solutions (Nystrøm, 2001; Velizarova et al., 2004), use of pulse current (Sun, 2013), stirring the medium in the central compartment (Jensen et al., 2006) and the use of new ED cell set-ups, have been tested.

Tables 3.1 and 3.2 present results for ED experiments made on soils from wood preservation sites contaminated with CCA. Table 3.1 summarizes different Cr removal rates obtained by several authors using conventional unenhanced treatment. Table 3.2 summarizes different Cr removal rates obtained by several authors applying enhanced treatment.

In Table 3.1, Cr removal, for the conventional treatment, was within the range of 2%-28%, confirming that Cr is one of the most difficult heavy metals to remove from soil. In Table 3.2, it is shown that the use of enhanced treatment improves the Cr removal for some experiments (3%-51%) but the majority of them still present low removals rates for Cr.

In soil, Cr exists mainly as Cr(III) or Cr(VI), depending on the prevailing redox potential. Cr(VI) adsorption increases with decreasing pH, whereas on the contrary, Cr(III) desorption increases with decreasing pH. Since the speciation of Cr in the initial soil was not characterized in these experiments, it is not possible to conclude from the results if the main reason for the low Cr removal is due to the adsorption of Cr(VI) at low pH or because the final pH was not low enough to desorb Cr(III).

Table 3.1: Previous studies on ED treatment of soils from wood preservation sites contaminated with CCA using conventional unenhanced treatment

ED cell type	Number of ED compartments	Current density (mA/cm^2)	Duration (days)	pH initial / pH final	Cr removal rate (%)	References
Stationary	3	0.2	18	7.2 / -	7	(Ribeiro, 1998)
Stationary	3	0.2	35	7.2 / -	7	(Ribeiro, 1998)
Stationary	3	0.2	65	7.2 / -	6	(Ribeiro, 1998)
Stationary	3	0.2	85	7.2 / -	10	(Ribeiro, 1998)
Stationary	3	0.2	125	7.2 / -	15	(Ribeiro, 1998)
Stirred	3	0.05	7	7.3 / 4.4	4	(Ottosen et al., 2009)
Stirred	3	0.05	14	7.3 / 4.5	14	(Ottosen et al., 2009)
Stirred	3	0.05	22	7.3 / 4.0	28	(Ottosen et al., 2009)
Stirred	3	0.1	7	7.3 / 4.1	2	(Ottosen et al., 2013)
Stirred	3	0.2	14	6.4 / 3.0	16	(Ottosen et al., 2013)

Table 3.2: Previous studies on ED treatment of soils from wood preservation sites contaminated with CCA using enhanced treatment

Enhancement	ED cell type	Number of ED compartments	Current density (mA/cm^2)	Duration (days)	pH initial /pH final	Cr removal rate (%)	References
0.25 M ammonium citrate	Stationary	4	0.2	21	7.8 / 9.0	3	(Dias-Ferreira et al., 2015)
0.50 M ammonium citrate	Stationary	4	0.2	21	7.8 / 9.0	3	(Dias-Ferreira et al., 2015)
1 M ammonium citrate	Stationary	4	0.2	21	7.8 / 9.0	6	(Dias-Ferreira et al., 2015)
1 M ammonium citrate	Stationary	4	1	21	7.0 / 8.0	7	(Dias-Ferreira et al., 2015)
1 M ammonium citrate	Stationary	4	1	42	7.0 / 8.0	14	(Dias-Ferreira et al., 2015)
1 M ammonium citrate	Stationary	4	1.5	42	7.0 / 8.0	10	(Dias-Ferreira et al., 2015)
1 M ammonium citrate	Stationary	4	1	117	7.0 / 8.0	35	(Dias-Ferreira et al., 2015)
1 g I_2 in 350 mL	Stirred	3	0.05	7	6.6 / 3.1	8	(Ottosen et al., 2009)
<a1 g I_2 in 350 mL	Stirred	3	0.05	14	6.6 / 2.9	11	(Ottosen et al., 2009)
pH adjusted with HNO_3 to 1 in soil suspension	Stirred	3	0.1	7	6.6 / 3.1	46	(Ottosen et al., 2009)
pH adjusted with HNO_3 to 1 in soil suspension	Stirred	3	0.1	14	6.6 / 3.0	51	(Ottosen et al., 2009)

3.6 Electrodialytic remediation of chromium in MSWI fly ash

The first ED experiments made to evaluate the removal of heavy metals from MSWI fly ash were performed by Pedersen (2002b) with a stationary cell. Difficulties on the functioning of the initial experiments such as precipitation in the electrolytes, self-hardening of the fly ash inside the cell, poor control of the pH and long remediation, led to an adjustment of the ED cell design. Pedersen (2002b) introduced a stirring rod in the central compartment to agitate the medium. Several experiments have been made with the stirred cell and the adjustment has proven to have improved the ED efficiency, by increasing the removal of heavy metals and decreasing the remediation time. In order to further increase the removal efficiency of heavy metals from MSWI fly ash, experiments with the addition of enhancement solutions have been made. Recently, a new ED cell set-up with 2C developed at the Technical University of Denmark was filed for patenting (WO2015/032903). This set-up has been tested to assess its efficiency on the removal of heavy metals from MSWI fly ash and APC residue (Magro, 2014).

Tables 3.3 and 3.4 present results for ED experiments carried out with MSWI fly ash collected before exposure to flue gas cleaning additives. They summarize different Cr removal rates obtained by several authors using conventional unenhanced and enhanced treatments, respectively Tables 3.3 and 3.4.

In Table 3.3, Cr removal, for the conventional treatment, was within the range of 1%-5%, confirming that Cr is one of the most difficult heavy metals to remove from MSWI fly ash. In Table 3.4, is shown that the use of enhanced treatment improves the Cr removal for some experiments (2%-44%) but the majority of them still present low removals rates for Cr.

Table 3.3: Previous studies on ED treatment of MSWI fly ash collected before exposure to flue gas cleaning additives using conventional unenhanced treatment

ED cell type	Number of ED compartments	Current density (mA/cm^2)	Duration (days)	pH initial / pH final	Cr removal rate (%)	References
Stirred	5	0.8	14	12.2 / 6.5	5$^{(a)}$	(Pedersen, 2002a)
Stirred	2	0.1	14	12.4 / 8.5$^{(a)}$	3.8	(Magro, 2014)
Stirred	2	1	14	12.4 / 4.0$^{(a)}$	3.8	(Magro, 2014)
Stirred	3	0.1	14	12.4 / 9.5$^{(a)}$	4.5	(Magro, 2014)
Stirred	3	1	14	12.4 / 5.5$^{(a)}$	1.1	(Magro, 2014)

$^{(a)}$ values read from graphics

Table 3.4: Previous studies on the electrodialytic treatment of MSWI fly ash collected before exposure to flue gas cleaning additives using enhanced treatment

Enhancement	ED cell type	Number of ED compartments	Current density (mA/cm^2)	Duration (days)	pH initial /pH final	Cr removal rate (%)	References
0.5 M ammonium citrate in 2.5% NH_3	Stationary	5	0.8	70	10.8 / 6.9	2	(Pedersen et al. 2001)
0.5 M ammonium citrate in 2.5% NH_3	Stationary	5	0.8	70	12.2 / 8.1	3	(Pedersen et al., 2001)
0.25 M ammonium citrate in 2.5% NH_3	Stirred	5	0.8	14	12.2 / 8.9	20	(Pedersen, 2002a)
0.25 M ammonium citrate in 1.25% NH_3	Stirred	5	0.8	5	12.2 / 9.5	$0^{(a)}$	(Pedersen et al., 2005)
0.25 M ammonium citrate in 1.25% NH_3	Stirred	5	0.8	14	12.2 / 8.9	$20^{(a)}$	(Pedersen et al., 2005)
0.25 M ammonium citrate in 1.25% NH_3	Stirred	5	0.8	35	12.2 / 8.2	$21^{(a)}$	(Pedersen et al., 2005)
0.25 M ammonium citrate in 1.25% NH_3	Stirred	5	0.8	70	12.2 / 6.9	$44^{(a)}$	(Pedersen et al., 2005)
0.25 M Na-citrate	Stirred	5	0.8	14	12.2 / 10	$15^{(a)}$	(Pedersen, 2002a)
2.5% NH_3	Stirred	5	0.8	14	12.2 / 9.6	7	(Pedersen, 2002a)

$^{(a)}$ values read from graphics

4. Matrices and methods

4.1 Soil

The soil used in this study was collected from the Collstrop site in Hillerød, Denmark, that covers 55000 m^2 and was abandoned after 40 years of wood preservation activities (Nielsen et al., 2011). In Denmark, Collstrop was one of the major companies in wood preservation and operated in 13 different sites.

The soil is a loamy sand deposited during the last glaciation (Ottosen et al., 1997) and is contaminated with Cr, Cu and As, as a consequence of the use of the Boucherie method with CCA preservatives for wood preservation on site. With the Boucherie method, preservatives dripped from the poles where they were applied and were often spilled directly on the soil (Ottosen et al., 2003). At the Collstrop site, where the Boucherie method was extensively used, the vegetation is still highly affected by the CCA that was spilled on the soil (Figure 4.1). The soil sample was collected from the top layer of the soil, after the superficial layer was removed, therefore guaranteeing the removal of most organic matter, on April of 2014 and it was stored in a bucket with a close-fitting lid, until use. The sample location is marked in Figure 4.1.

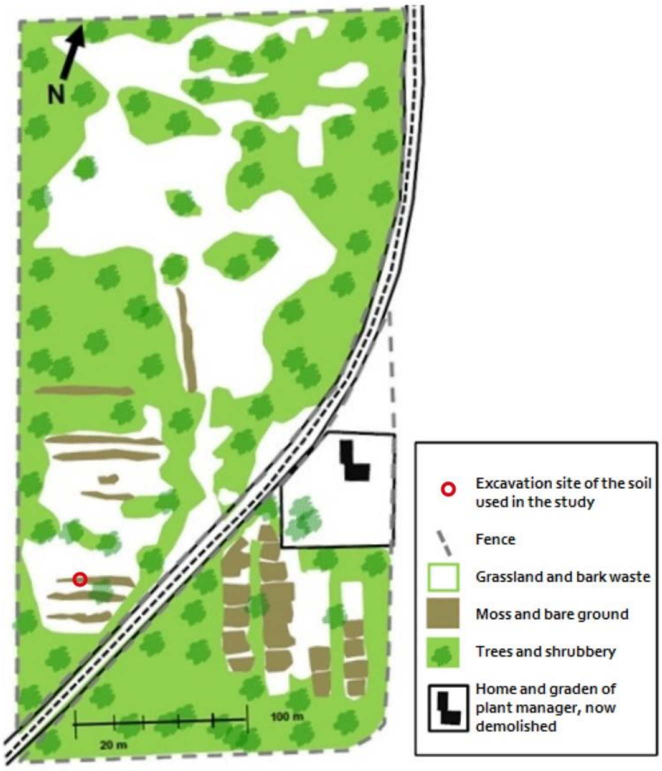

Figure 4.1: Sketch of the vegetation present on the Collstrop site in Hillerød, Denmark, with the indication of the soil sample location (adapted from Nielsen, 2013)

4.2 Fly ash

The MSWI fly ash was collected at I/S Vestforbræding, a municipal solid waste incinerator located in Glostrup, Denmark. I/S Vestforbræding has a total incineration capacity of 600 000 t/year and produces annually 15 000 t of APC residues in which fly ash are included (Astrup, n.d.). The fly ash sample was collected from a wet flue gas cleaning system before the neutralization of the acidic components by the wet scrubber process and it was sieved through a 1 mm sieve before it was stored in a bucket with a close-fitting lid, until use.

4.3 Characterization methods

The characterization and extraction experiments of the matrices were carried out using dried ash and soil at 50 ºC for 24 h and 105 ºC for 24 h, respectively. Triplicates were made for all the analysis except for the sequential extraction procedure and for the pH desorption procedure, where only two replicates were made. The leaching tests made on the fly ash were conducted before and after the EDR experiments. Cr(VI) analysis and sequential extraction procedure were conducted before and after the EDR experiments for both matrices in study.

Total concentration of Al, Ca, Cr, Fe, K, Mn and Na in the matrices were measured by Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES), after pre-treatment according to DS 259, in which 1 g of matrix and 20 mL (1:1) HNO_3 was heated at 200 kPa (120 ºC) for 30 min. After digestion, the samples were vacuum filtered through a 0.45 µm filter and diluted until 100 mL. The units used in this study are mg/kg in dry matter.

The **pH** in the matrices was 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 2.5, after 1 h of agitation at 190 rpm.

The **conductivity** was measured at the same time as the pH with deionised water with a Radiometer Analytic electrode.

Loss on ignition (LOI) was calculated as weight loss after heating the matrix at 550 ºC for 30 min.

Water content was measured as weight loss after 24 h at 105 ºC (calculated as weight loss over the weight of the wet sample).

For the **water solubility** of the fly ash, 100 g of the fly ash 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 matrix was properly washed. The suspension was then filtered thought a 0.165 µm filter and the matrix, dried at 105 ºC, was weighed.

Carbonate content was determined using a Scheibler apparatus, where a standard curve was first performed using different $CaCO_3$ contents combined with HCl. The matrices were mixed with HCl and then the $CaCO_3$ concentration was determined.

Leaching tests on the fly ash were made according to DS/EN 12457-3, with slight modifications. The L/S ratio was 2, mixing 10 g of matrix and 20 mL deionised water. The suspension was shaken for 24 h on a horizontal shaker. The pH of the fly ash suspension was measured before vacuum filtration through a 0.45 μm nucleo filter and the heavy metal concentrations in the filtrate were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

Water soluble chloride of the fly ash was determined by Ion Chromatography (IC) after extracting 10 g of matrix with 50 mL of deionised water overnight.

For the **Cr(VI) analysis**, the extraction method used was an alkaline digestion (USEPA Method 3060A (USEPA, 1996)) with slight modifications. USEPA Method 3060A was made in triplicate on 1.25 g of dried matrix before and after the EDR experiments. 25 mL of digestion reagent, 200 mg of $MgCl_2$ and 0.25 mL of 1 M phosphate buffer were added to the matrix; the vial was covered with a watch glass and agitated for 5 min with no heating. The vial was then heated up to 90-95 ºC and agitated for 1h. The vial was cooled to room temperature and the digestion was filtered through a 0.45 μm nucleo filter. The pH of the filtrate was adjusted with 5.0 M nitric acid drop at the time, with constant stirring, until the pH of 7.5 was achieved. The adjusted filtrate was then filtered again through 0.45 μm nucleo filter to remove any flocculent precipitate resulting from the reaction of Mg with the 5.0M nitric acid. The filtrate was transferred to a 50 mL volumetric flask and diluted for further analysis.

USEPA Method 3060A states that that most common and reliable methods for the analysis of Cr(VI) solubilized in the alkaline digestate are the diphenylcarbazide (DPC) based methods. These methods are based on the reaction of Cr(VI) with DPC, that results on a purple-red Cr-diphenylcarbazone complex which is detected by UV-VIS spectrophotometry at 540 nm. For detection, Hach Company Method 8023 was used. This method uses the single dry powder formulation ChromaVer® 3 Chromium Reagent that contains an acidic buffer combined with 1.5-diphenylcarbohydrazide which reacts to give a purple colour when Cr(VI) is present (Hach Company, n.d.). A sample of 10 mL was collected from the 50 mL volumetric flask and a ChromaVer® 3 Chromium Reagent Powder Pillow was added to it and was dissolved through 8 min of agitation. After that the sample was measured by UV-VIS spectrophotometry (Spectroquant Nova 60 equipment from Merck) at 540 nm. The detection limit of this method is between 2.0 mg Cr(VI)/kg and 24.4 mg Cr(VI)/kg.

A **sequential extraction** was carried out in duplicate, on 0.5 g of matrix before and after selected EDR experiments, following the three step procedure described by the EC Standards, Measurements and Testing Programme (SMT) (Quevauviller et al., 1997), with the addition of a step 4:

- Step 1 (exchangeable) - Extraction with 20 mL of 0.11 M CH_3COOH pH 3 for 16 h.
- Step 2 (reducible) - Extraction with 20 mL of 0.1 M NH_2OH-HCl pH 2 for 16 h.
- Step 3 (oxidizable) - Extraction with 5 mL of 8.8 M H_2O_2 for 1 h; then heating to 85 ºC for 1 h, with lid fitted; followed by evaporation of the liquid phase at 85 ºC until it had reduced to <1 mL by removal of the lid. The addition of 5 mL of 8.8 M H_2O_2 was repeated, followed by heating to

85 ºC for 1 h and removal of the lid for evaporation until almost dry. After cooling, 25 mL of 1 M NH_4OOCCH_3 pH 2 was added and the extraction was carried out for 16 h.

- Step 4 (residual) - Digestion with HNO_3 according to DS 259 (2003), to determinate the residual Cr phase in the matrix.

Between each step of the sequential extraction procedure, the sample was centrifuged at 3000 rpm for 15 min and the supernatant was decanted and collected for subsequent analysis by Atomic Absorption Spectroscopy (AAS).

Before the addition of a new reagent, the sample was washed with 10 mL of distilled water and kept on the horizontal shaker for 15 min. Then the sample was centrifuged at 3000 rpm for 15 min and the supernatant decanted and carefully discarded.

All extractions were performed at room temperature and a horizontal shaker at 190 rpm was used to keep the residue in continuous suspension during the extractions.

The **pH desorption** procedure was made in duplicate, by mixing 1 g of fly ash and 5 g of soil, respectively, with 25 mL of reagent. The reagents for the fly ash were: distilled water and HNO_3 0.01 M, 0.05 M, 0.1 M, 0.2 M, 0.3 M, 0.5 M. The reagents for the soil were: distilled water and HNO_3 0.01 M, 0.02 M, 0.03 M, 0.05 M, 0.1 M. The suspensions were shaken for 7 days on a horizontal shaker and the pH was measured after the suspensions settled for 15 min. Then the suspensions were vacuum filtrated through a 0.45 μm nucleo filter and 20 mL of sample were collected for subsequent analysis by Atomic Absorption Spectroscopy (AAS).

4.4 ED experiments

Three ED set-ups were used in this study: one set-up with two compartments (2C cell), one set-up with three compartments (3C cell) and a new set-up, a combined cell (2/3C or 3/2C), with three compartments, alternating current between two anodes and different initial experimental conditions.

4.4.1 Two compartment cell (2C)

This is a recent set-up (Figure 4.2) that has two compartments, two electrodes (anode and cathode) and one cation exchange membrane. The anode is directly inserted in the matrix compartment (compartment I) and allows a faster acidification of the suspension and consequently a faster dissolution of the elements present. Although, this set-up only removes cations, as the anions are extracted from the matrix and remain in suspension in compartment I.

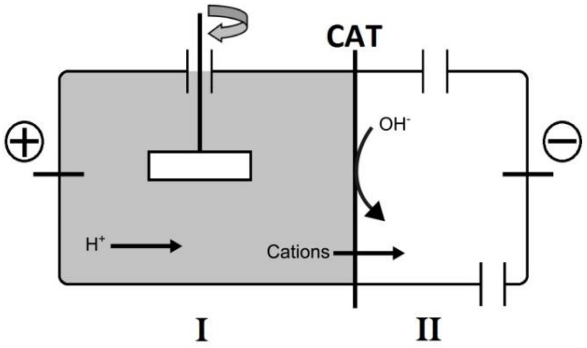

Figure 4.2: The experimental set-up of the 2 compartment cell developed at DTU, Denmark.

4.4.2 Three compartment cell (3C)

This set-up (Figure 4.3) is the conventional cell, which has three compartments, two electrodes (anode and cathode) and two ion exchange membranes (anion and cation). In this set-up, the anions are removed to the compartment I and the cations to the compartment III. The dissolution of the elements present in the matrix is slower than in the 2C cell because it depends on the acidification of the suspension through water splitting at the anion exchange membrane and migration of H+ to the suspension compartment (compartment II).

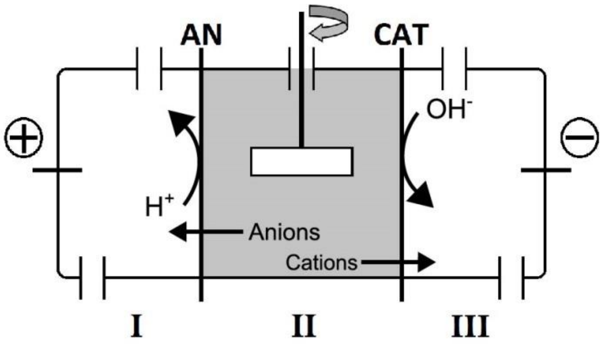

Figure 4.3: The experimental set-up of the 3 compartment cell developed at DTU, Denmark.

4.4.3 Combined cell (2/3C or 3/2C)

The combined cell (Figure 4.4) is a new set-up that combines the advantages of the 2C and 3C set-ups. It consists on a three compartment cell with three electrodes: one anode in compartment I, another anode in the matrix compartment (compartment II) and one cathode in compartment III.

The anodes of this set-up function in an ON-OFF mode, with an alternation of the current supply between them through a switch device. The cathode is always ON. When the anode in compartment I (anode A) is ON, the other anode is OFF and the set-up functions as a 3C cell. When the anode in compartment II (anode B) is ON, the other anode is OFF and the set-up functions as a 2C cell.

The terminology 2/3C refers to this set-up with an initial experimental beginning at anode B for two days, and the terminology 3/2C refers to this set-up with an initial experimental beginning at anode A for two days. After these first two days, the switch device is connected to both anodes to allow them to function in an ON-OFF mode.

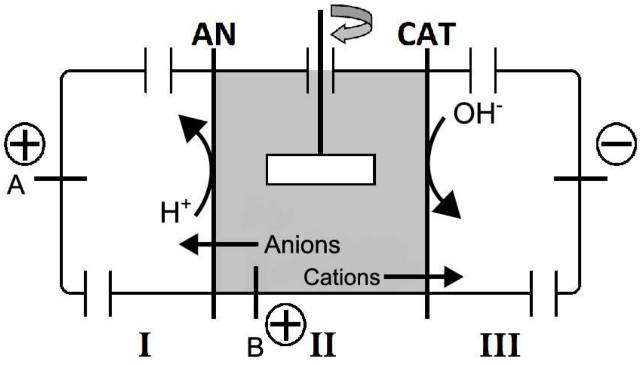

Figure 4.4: The new experimental set-up (2/3C or 3/2C) of the ED cell with the addition of the switch device, developed at DTU, Denmark, with two anodes (anode A, in compartment I, and anode B, in compartment II) and one cathode.

Ten ED experiments were conducted according to the experimental conditions presented in Table 4.1. All the experiments were made with a suspension of 350 mL of deionised water and 100 g of the matrix, corresponding to an L/S ratio of 3.5. Two of the experiments were conducted with the 2C cell, other two were conducted with the 3C cell and another six were conducted with the combined cell (two with the 3/2C, and four with the 2/3C).

Four ED experiments carried out with the combined cells 2/3C and 3/2C had a duration of 13 days and the alternating current frequency was every day. The duration of the other ED two experiments carried out with the combined cell 2/3C was 26 days and the alternating current frequency was every day.

Table 4.1: Experimental conditions for ED experiments (FA/S-X-YD; where FA- fly ash; S- soil; X- set-up (2C, 3C or CC (2/3C or 3/2C)); and YD-duration in days).

Experiment	Matrix	Cell set-up	Alternating current frequency	Current density (mA/cm^2)	Duration (days)
FA-3C-13D	Fly ash	3C	-	1	13
FA-3/2C-13D	Fly ash	3/2C	Every minute	1	13
FA-2C-13D	Fly ash	2C	-	1	13
FA-2/3C-13D	Fly ash	2/3C	Every minute	1	13
FA-2/3C-26D	Fly ash	2/3C	Every day	1	26
S-3C-13D	Soil	3C	-	0.2	13
S-3/2C-13D	Soil	3/2C	Every minute	0.2	13
S-2C-13D	Soil	2C	-	0.2	13
S-2/3C-13D	Soil	2/3C	Every minute	0.2	13
S-2/3C-26D	Soil	2/3C	Every day	0.2	26

The ED cells were made of Plexigas with an internal diameter of 8 cm and length of the matrix compartment of 10 cm. The ion exchange membranes used were obtained from Ionics (anion exchange membrane AR204 SZRA B02249C and cation exchange membrane CR67 HUY N12116B). The electrodes were platinum coated titanium. A power supply (Hewlett Packard E3612A) was used to maintain a constant current of 10 mA or 50 mA, 0.2 mA/cm^2 or 1 mA/cm^2, respectively. The suspension in the matrix compartment was stirred by a flexible plastic fab attached to a glass stick and connected to an overhead stirrer (RW 11 "Lab egg" stirrer from IKA). The electrolytes (anolyte and catholyte) used were 0.01 M $NaNO_3$ with pH adjusted to 2 with 1:1 HNO_3 and had a volume of 500 mL each. The electrolyte’s recirculation was made using “Pan World” magnetic pumps.
Voltage, current and electrical conductivity were read daily, whereas pH of the catholyte and pH of the suspension were measured twice a day. If the pH in the catholyte was over 2 it was adjusted with 1:1 HNO_3.

After the ED experiments, the suspension was filtered through a 45 µm paper filter before heavy metal measurements. The dried matrix was digested according to DS 259 and heavy metals determined. The stirrer was soaked in 1 M HNO_3 and the electrodes were soaked in 5 M HNO_3 to measure the amount of heavy metals that were adsorbed to them.

In the disassembling of the cell after the ED experiments, a new procedure was used for the analysis of the membranes: for the cleaning, the matrix attached to the membranes was removed with a spoon into the 45 µm paper filter used for the suspension and the membranes were rinsed with the suspension and dried with paper; for the weighting, the glycerine part of the membrane was cut out, the membrane was divided in 9 pieces (Figure 4.5a) and then the pieces were regrouped in 5 groups per membranes (Figure 4.5b) and weighted; for the drying, the 5 groups were kept in the oven at 105ºC over night; for the digestion, the 5 groups per membrane were individually digested according to DS 259 with modifications on the weight of the sample (~0.5 g).

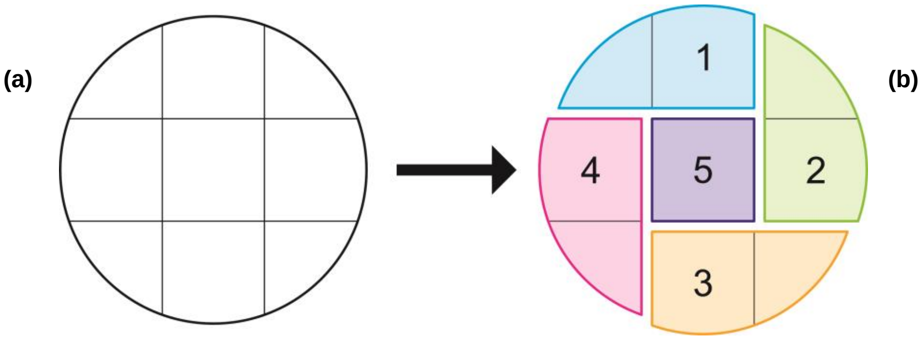

Figure 4.5: Schematic representation of the new procedure for analysing the membranes: (a) the membrane is divided in 9 pieces; (b) the 9 pieces of the membrane are regrouped into 5 groups

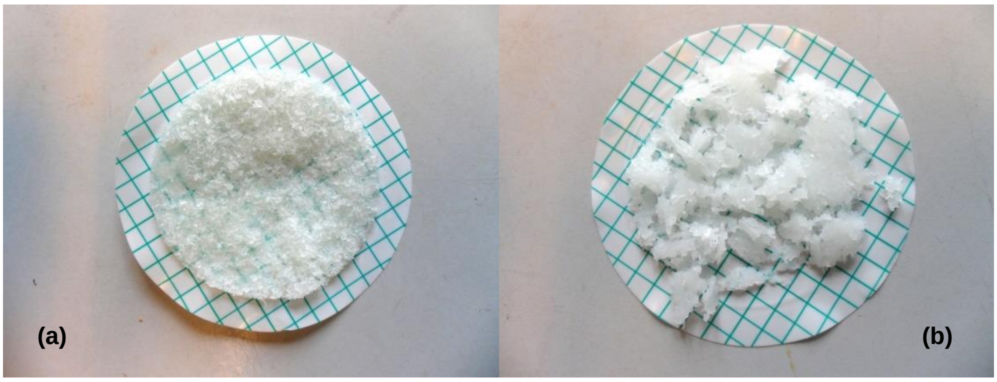

Figure 4.6: Appearance of the membranes after digestion: (a) anion exchange membrane, (b) cation exchange membrane

The obtained aqueous phase of the membranes, the stirrer, the electrodes, the electrolytes and the filtered liquid from the middle compartment were all analysed for heavy metals by ICP-OES. The leaching tests, for the fly ash, the Cr(VI) analysis and the sequential extraction procedure were conducted for both matrices with the dried matrices (105 ºC) obtained after EDR treatment, according to the procedures described in section 4.3.

5. Results and discussion

5.1 Characterization of the matrices

In order to statistically determine if the two matrices studied are different, a t-test (type=3: two-sample unequal variance (heteroscedastic)) was performed on the initial characteristics. The t-test was chosen because it is one-sided, since the objective was to compare each individually parameter. This test showed that the two matrices are significantly different for all the parameters, with 95% confidence levels, except for the loss on ignition parameter (Table 5.1).

Table 5.1: Initial characteristics of soil and fly ash (mean values ± standard error)

Parameter	**Matrix**		**Statistical difference**
	Soil	**Fly ash**	
pH_{H2O} (L/S=2.5)	6.3 ± 0.0	12.4 ± 0.0	[a]
pH_{KCl} (L/S=2.5)	6.4 ± 0.0	12.5 ± 0.0	[a]
Conductivity (mS/cm)	0.18 ± 0.01	47.6 ± 2.4	[a]
Water content (%)	10.8 ± 0.6	0.32 ± 0.10	[a]
Water solubility (%)	–	20.0 ± 0.3	–
Loss on ignition (%)	0.20 ± 0.04	0.19 ± 0.01	[b]
Carbonate content (%)	0.47 ± 0.10	11.2 ± 0.4	[a]
Chloride (mg/L)	–	6,200 ± 48	–
Al (mg/kg)	1,800 ± 70	24,900 ± 1,100	[a]
Ca (mg/kg)	1,000 ± 100	136,400 ± 7,600	[a]
Cr (mg/kg)	214 ± 14	80.5 ± 10.9	[a]
Cr (VI) (mg/kg)	4.65 ± 0.69	< 2.00(1)	[a]
Fe (mg/kg)	3,000 ± 60	6,500 ± 30	[a]
K (mg/kg)	375 ± 18	46,700 ± 3,400	[a]
Mn (mg/kg)	130 ± 10	550 ± 9	[a]
Na (mg/kg)	227 ± 2	31,800 ± 1,900	[a]
Leaching			
pH	–	12.3	–
Cr (mg/L)	–	0.01 0.00	–

(1) This value is below the lower detection limit of the method

[a] Significantly different ($p < 0.05$)

[b] Not significantly different

pH

The speciation of heavy metals in any matrix is highly pH dependent. The matrices present a very different initial pH, which is close to neutral for the soil, and alkaline for the fly ash.

Conductivity

Conductivity measures the matrices' ability to conduct electric current. The soil has low conductivity, which means that the soil has high resistivity and opposes to the passage of the current. On the contrary, the fly ash, which has high conductivity, allows an easy passage of the current.

Water content

As expected, fly ash has very low water content when compared to the soil, because it is a product of incineration.

Water solubility

This parameter was only measured for the fly ash and represents the maximum amount of fly ash that dissolves in water, which is related to the high amount of salts and minerals present in the fly ash.

Loss on ignition

Loss on ignition analysis was used to determine the organic matter content of the matrices. For both matrices, the organic matter content is low.

Carbonate content

This parameter indicates the buffering capacity of the matrices. The soil has a low buffering capacity, but the fly ash has a significant buffering capacity, which will affect the decrease in pH during EDR experiments.

Chloride

This parameter was only measured for the fly ash. The chloride content in fly ash limits its application as basis for construction matrices, because water-soluble chlorides such as potassium chloride (KCl), sodium chloride (NaCl), and calcium chloride hydrate ($CaCl_2 \cdot 2H_2O$) in fly ash are easily washed away (Chen et al., 2012).

Cr and other elements content

Due to the nature of the matrices, their content in Cr and the in elements (Al, Ca, Fe, K, Mn and Na) that were studied is significantly different. Regarding the total Cr and Cr(VI), the soil presents higher values than the fly ash, due to the contamination with CCA preservatives. The Cr(VI) content for the fly ash is below the detection limit of the method used for analysis. For the other studied elements, the fly ash presents significantly higher values than the soil, due to the heterogeneous composition of the municipal solid waste that was incinerated.

Cr leaching

This parameter was only measured for the fly ash, to asses to possibility of reusing the fly ash for construction matrices. Fly ash is considered hazardous waste due to its heavy metal content and mobility, and wash out of the heavy metals and soluble salts when in contact with water, resulting in the contamination of the surrounding environment.

pH desorption

With the purpose of understanding Cr and the other elements behaviour in different pH conditions, pH desorption curves were carried out for both matrices (Figure 5.1).

According to Reddy & Chinthamreddy (2003), Cr(III) compounds are soluble under highly acidic conditions, whereas Cr(VI) solubility increases at neutral/alkaline conditions. In Figure 5.1a, Cr desorption in soil started at pH<4, indicating Cr(III) solubility since Cr(VI) is not desorbed under acidic conditions.

According to Flyvbjerg & Hjelmar (1997), oxides solubility occur in the range 2<pH<6, carbonates between 6<pH<9 and hydroxides between 10<pH<13, for fly ash. In Figure 5.1b, Cr desorption started at pH<4 which, according to Flyvbjerg & Hjelmar (1997), means that Cr was probably in the form of Cr(III) oxides. A low percentage of Cr was also desorbed at pH>10, which may be due to the presence of Cr(VI) in the fly ash. Furthermore, aqueous concentrations of Cr(VI) under acidic to slightly alkaline conditions are primarily controlled by adsorption/desorption reactions (Apte et al., 2006). The presence of mineral compounds influence Cr(VI) adsorption, especially aluminium or iron oxides at pH<7 (Pohlandt-Schwandt, 1999). Lima et al. (2008) studied different types of fly ash and find out that MSWI fly ash contained Fe_2O_3 as a crystalline mineral and that it was probably adsorbing Cr(VI) at low pH values. Therefore, at pH<7 Cr(VI) is expected to be mainly adsorbed to the iron oxides and only Cr(III) desorbed.

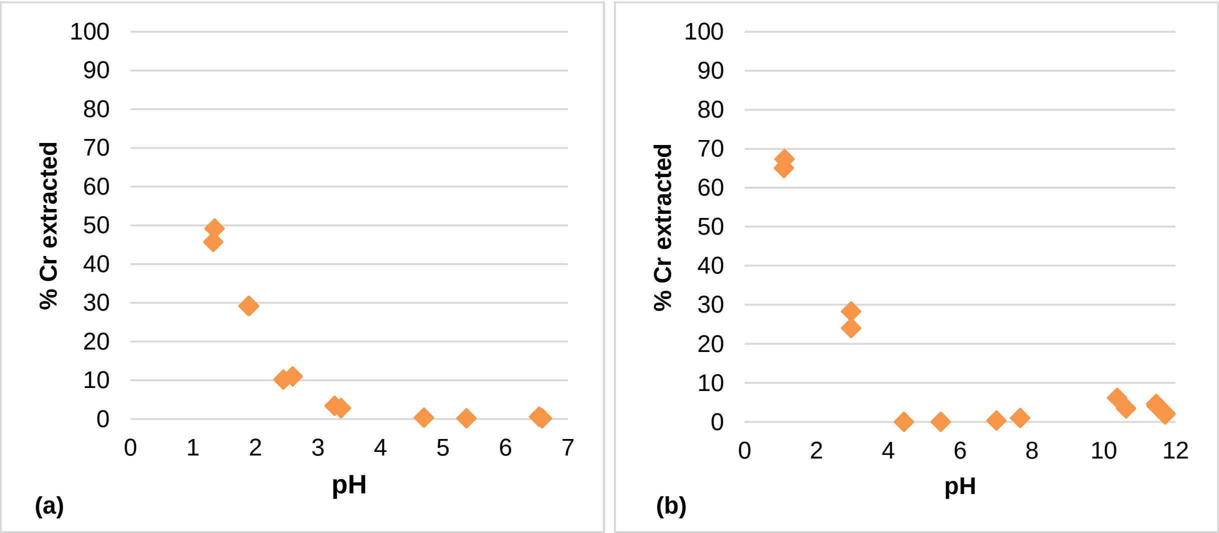

Figure 5.1: Desorption of Cr as a function of pH: (a) soil and (b) fly ash

Figures 5.2 and 5.3 show the pH desorption curves for the Al, Ca, Fe and K, Mn, Na in comparison with the curves obtained for Cr, in soil and fly ash, respectively. A very strong relation ($0.90 < R^2 < 1.00$) was observed between Cr and Fe, for both matrices, and between Cr and Al, for the fly ash, which might mean that they are linked. A strong relation ($0.70 < R^2 < 0.90$) was also seen between Cr and Al, for the soil, and between Cr and Mn, for the fly ash, which can also represent some affinity between these elements. Regarding Ca, K, and Na, for both matrices, and Mn for the soil, no evident relation was observed between these elements' desorption curves and Cr.

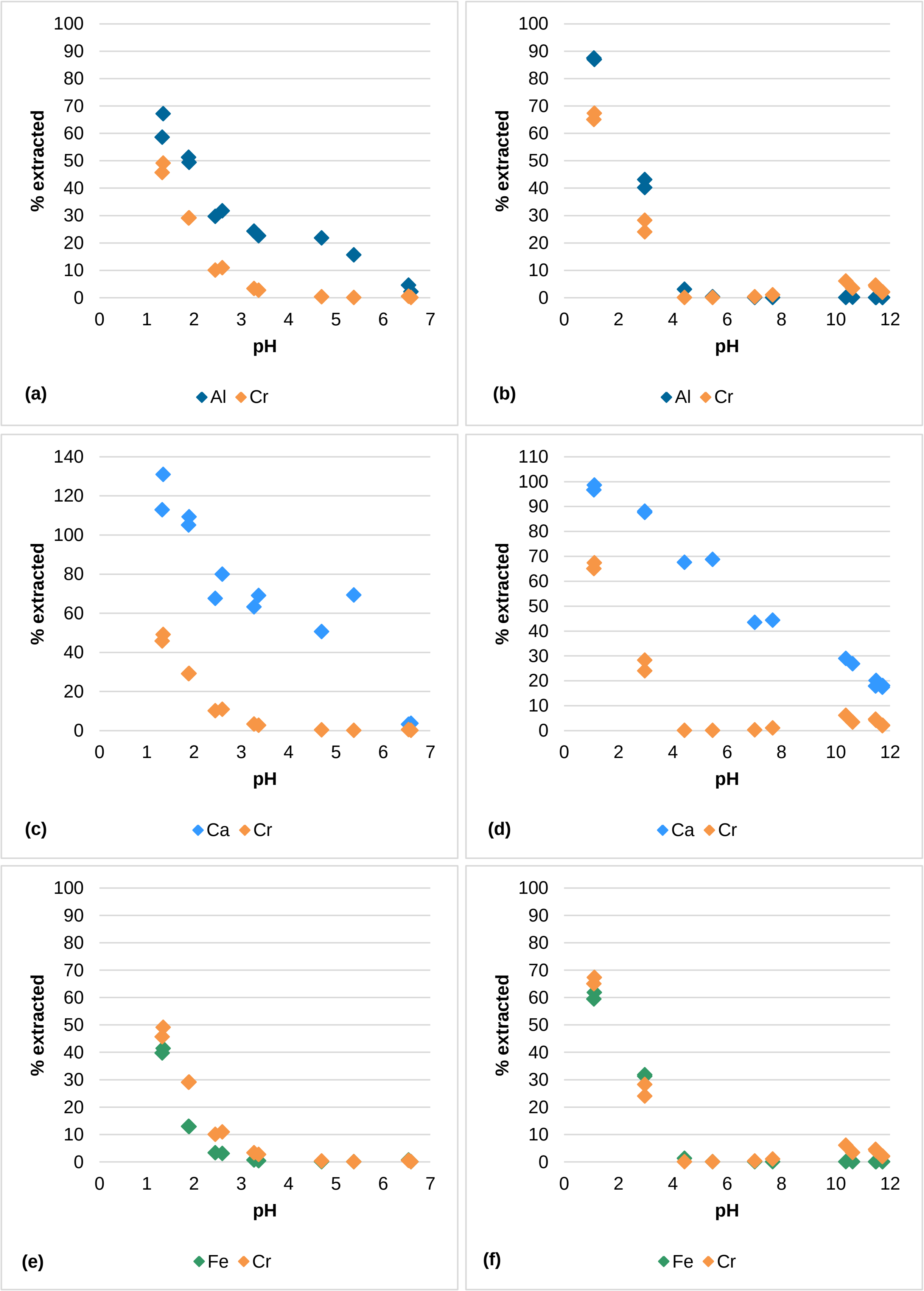

Figure 5.2: Desorption of Al, Ca and Fe vs Cr as a function of pH: (a) (c) (e) soil and (b) (d) (f) fly ash

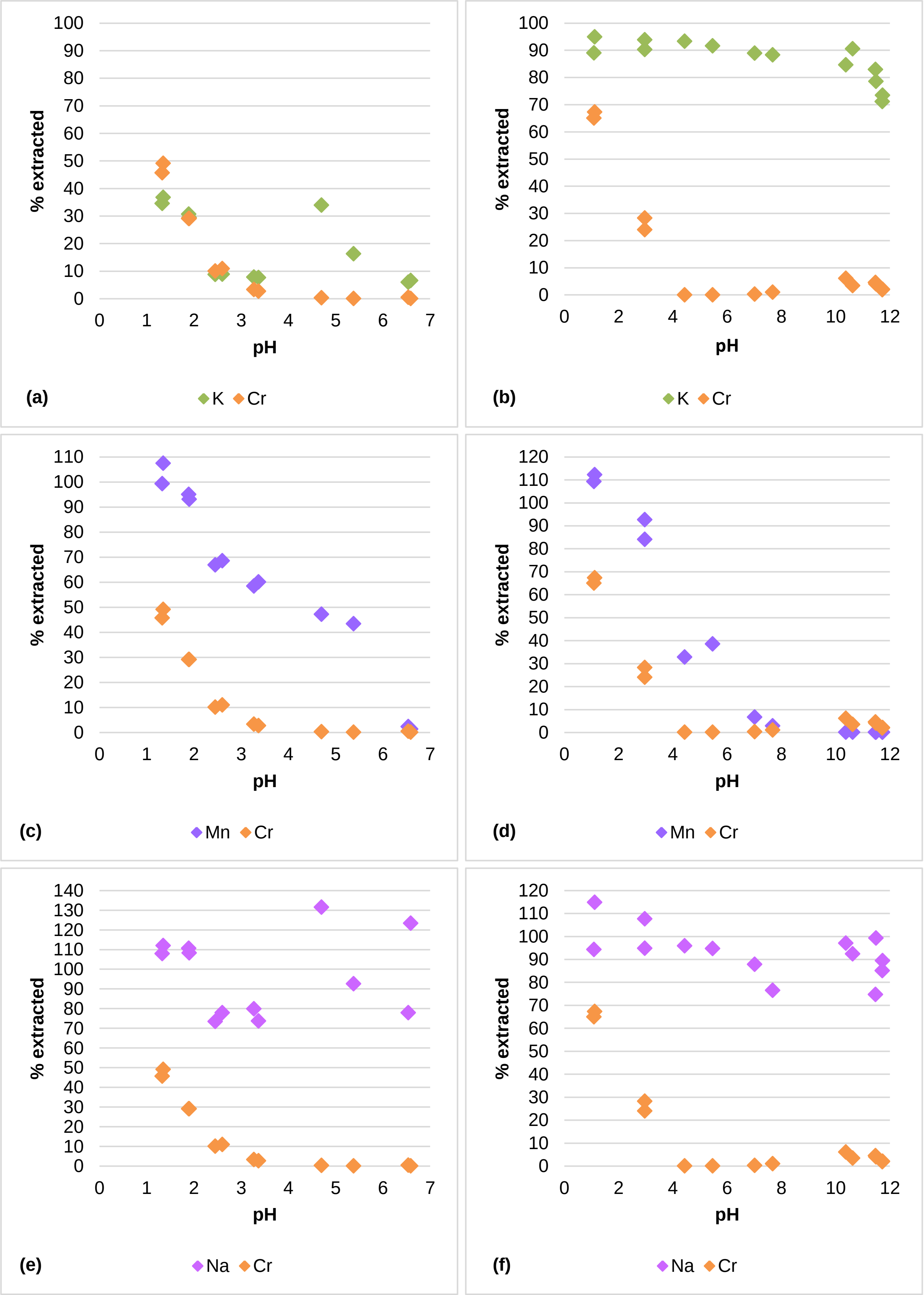

Figure 5.3: Desorption of K, Mn and Na vs Cr as a function of pH: (a) (c) (e) soil and (b) (d) (f) fly ash

5.2 ED experiments

5.2.1 pH and conductivity

The pH and conductivity in the suspensions over time are illustrated in two figures each, one regarding the experiments with 13 days and the other with 26 days. For soil, the pH is presented in Figures 5.4 and 5.5, and the conductivity is presented in Figures 5.8 and 5.9. For the fly ash, the pH is presented in Figures 5.6 and 5.7, and the conductivity is presented in Figures 5.10 and 5.11. The voltage drop for the soil, with an applied current density of 0.2 mA/cm^2, was between 2.8-70 V. For the fly ash, with an applied current of 1 mA/cm^2, the voltage drop was between 2.8-12.2 V. Since all the experiments were carried out under constant current, the voltage profile directly reflects the conductivity and resistivity of the suspensions. For the soil, the high voltage drop is a result of the high resistivity and low conductivity of the suspension. On the contrary, for the fly ash, the low drop in voltage is due to the low resistivity and high conductivity of the suspension.

The combined cell (2/3C or 3/2C) functioned in the following way: when the 2/3C or 3/2C cell was working as a 2C cell, it caused the acidification of the suspension as a consequence of the direct supply of H^+ into the suspension; contrarily, when the 2/3C or 3/2C cell worked as a 3C cell, there was an increased removal of anions from the suspension.

pH

The differences in the pH development for both matrices are related to their initial pH and their carbonate content, as it indicates the buffering capacity of the matrix. Thus, the buffering capacity was much higher for the fly ash, due to its higher carbonate content, and slowed the decrease of the pH. The duration of the remediation affects the final pH of the suspension, consequently affecting the heavy metals removal. Longer remediation times increase the acidification of the suspension, decreasing the final pH and allowing a higher removal of heavy metals.

Regarding the soil, the initial pH was neutral and decreased to acidic values during the treatment. For the 13 days experiments, the lowest final pH (2.3) was achieved with the 2C and 2/3C cells (Figure 5.4). For the 26 days experiment, since the alternating current frequency of the combined cell 2/3C was every day, the differences in the functioning of this new set-up were accentuated and caused an irregular evolution between pH 2 and pH 4 (Figure 5.5). The lower pH values were observed when the combined cell 2/3C was working as a 2C cell, and the increase in pH was seen when the combined cell 2/3C was working as a 3C cell. The final pH of this experiment was 2.1.

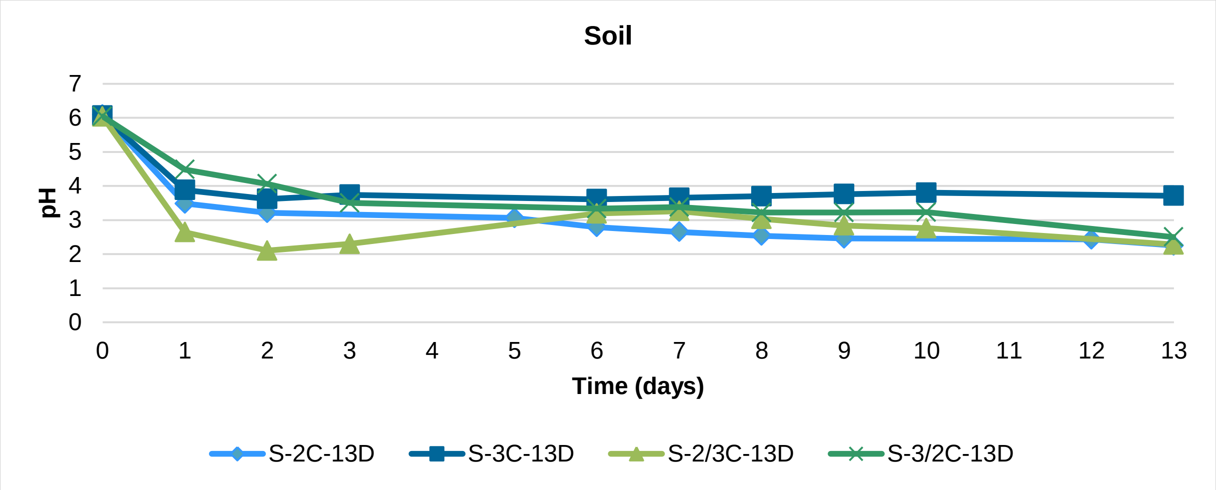

Figure 5.4: pH of the suspension for the soil experiments with 13 days duration

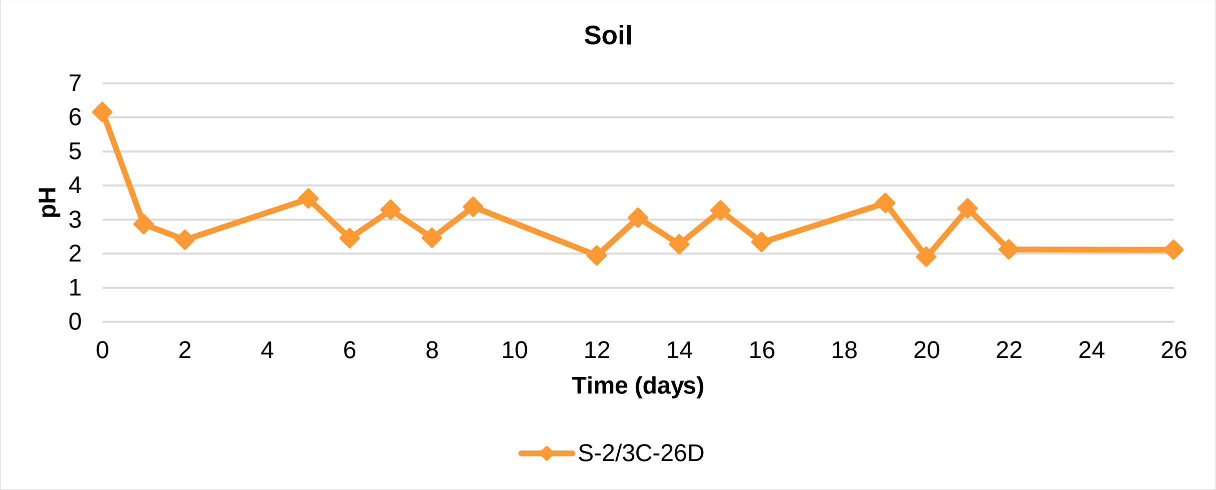

Figure 5.5: pH of the suspension for the soil experiment with 26 days duration

Regarding the fly ash, the initial pH was alkaline and decreased to neutral pH values in the 13 days experiments (Figure 5.6). For these experiments, the lowest final (3.7) pH was achieved with the 2C cell. For the fly ash, the 26 days experiment allowed a higher mobility of the heavy metals in suspension due to the decrease in pH achieved by the longer duration of the treatment (Figure 5.7). The final pH of this experiment was 1.5. A very strong relation between the pH and the duration of the treatment was observed for all the 13 days experiments ($R^2 > 0.91$) and for the 26 days experiment ($R^2 = 0.95$).

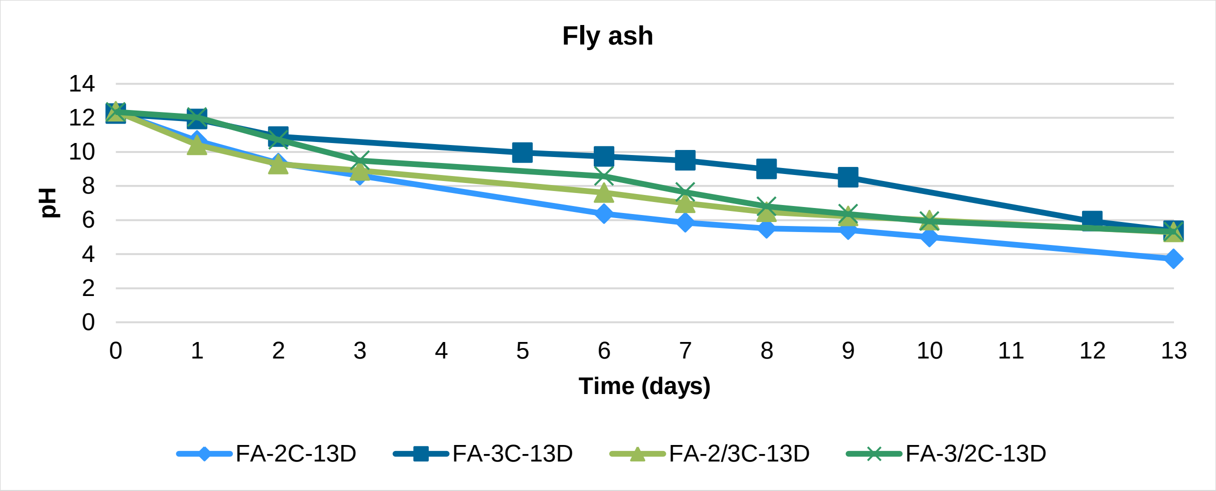

Figure 5.6: pH of the suspension for the fly ash experiments with 13 days duration

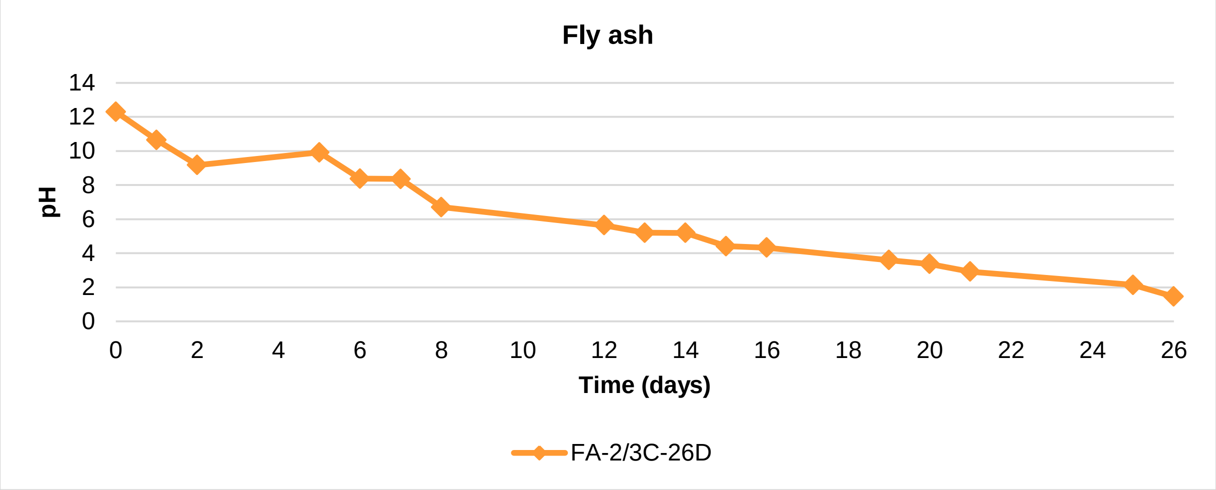

Figure 5.7: pH of the suspension for the fly ash experiment with 26 days duration

Conductivity

At the beginning of the experiments, the transport of soluble ions and the desorption of heavy metals by H^+ are the dominant processes and result in decreasing conductivity. At the end of the experiments, the transport and removal of the desorbed species becomes more important than desorption, producing a constant increase in conductivity. Furthermore, as the pH in the suspension decreases with time, it results in a higher dissolution of the matrix that can be seen as a higher electrical conductivity at the end of the experiments.

Regarding the soil, the initial conductivity was low and increased slightly during the treatment in the 13 days experiments. For these experiments, the highest final conductivity (3.4) was achieved with the 2C cell (Figure 5.8). For the 26 days experiment, an irregular evolution of the conductivity, around 0.15 and 3.70 mS/cm, occurred due to the alternating current frequency, as explained previously (Figure 5.9). The increase in conductivity was observed when the combined cell 2/3C was working as a 2C cell due to the direct supply of H^+ into the suspension that caused its acidification. The final conductivity of this experiment was 2.9.

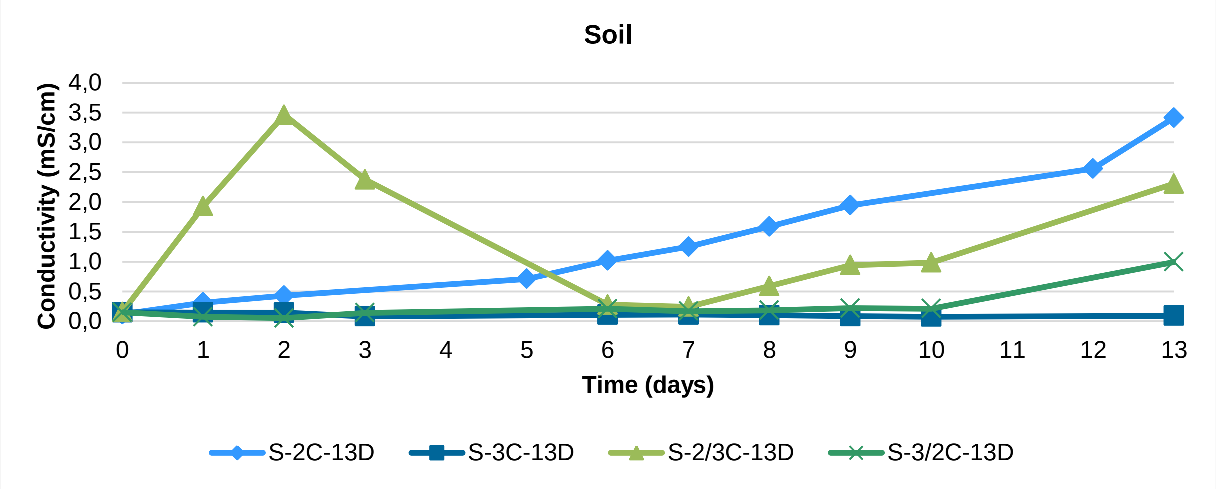

Figure 5.8: Conductivity of the suspension for the soil experiments with 13 days duration

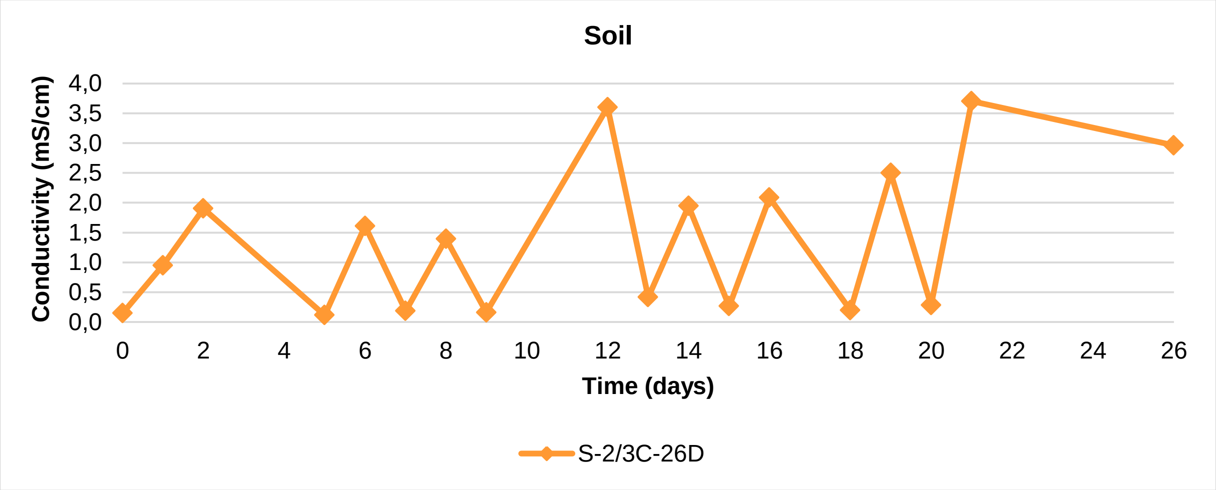

Figure 5.9: Conductivity of the suspension for the soil experiment with 26 days duration

Regarding the fly ash, the initial conductivity was high and decreased with treatment in the 13 days experiments. For these experiments, the highest final conductivity (46) was achieved with the 2C cell (Figure 5.10). For the 26 days experiment, the conductivity decreased until the middle of the treatment and then increased until the end of the treatment, reaching a value close to the initial conductivity (45.4) (Figure 5.11).

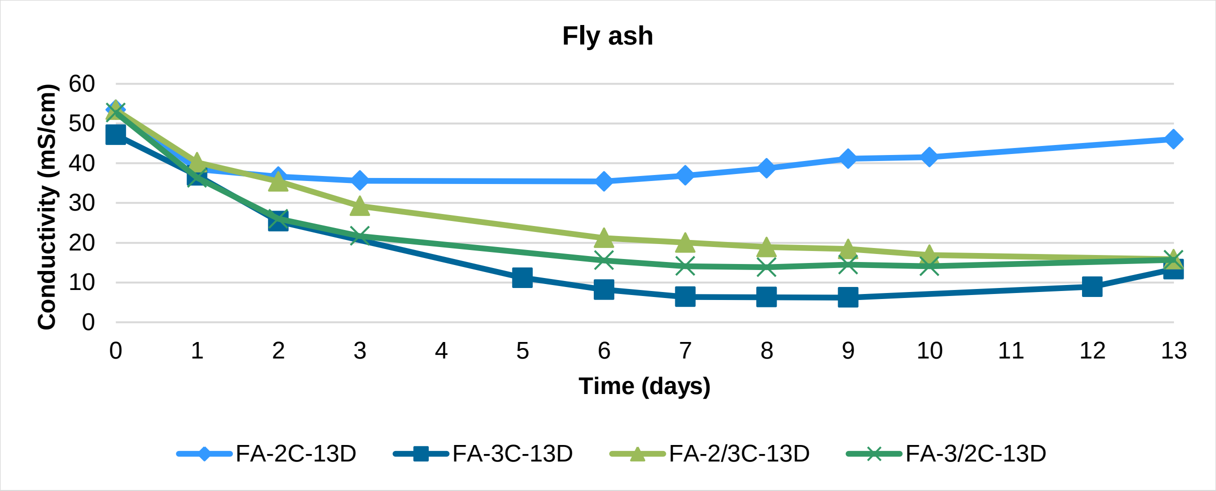

Figure 5.10: Conductivity of the suspension for the fly ash experiments with 13 days duration

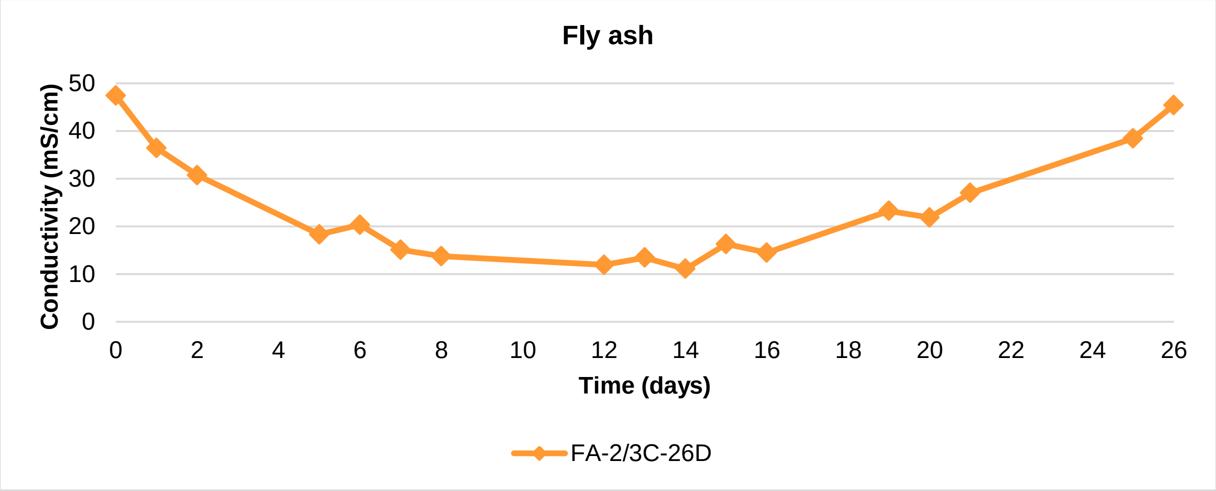

Figure 5.11: Conductivity of the suspension for the fly ash experiment with 26 days duration

5.2.2 Chromium distribution, recovery and removal

Cr distribution

The distribution of Cr in the cell after ED experiments was calculated and is presented in Table 5.2 and illustrated by Figure 5.12a, for the soil, and Figure 5.12b, for the fly ash. For simplification, the Cr that was found in the anolyte and anode A is described as anode end; the Cr that was found in the catholyte and cathode is described as cathode end; and the Cr that was found in the suspension, stirrer and anode B is described as suspension.

The majority of Cr was found, after the treatment, in the matrix, for both soil (63-90%) and fly ash (81-99%). For the soil, a small amount of Cr was transported towards the anode end (1%), being the main transport of Cr towards the cathode end (4-22%). There was also adsorption of Cr species on the membranes (5-13%) (Figure 5.12a). On the contrary, for the fly ash, although the transport of Cr was low, it occurred mainly towards the anode end (1-3%) for the 13 days experiments. For the 26 days experiment, the situation changed and the main transport of Cr occurred towards the cathode end (7%). This experiment also showed the highest amount of Cr in suspension after the treatment (6%), probably due to the dissolution of the fly ash that occurs at low pH values. For the fly ash, adsorption of Cr species on the membranes was very low (1%) and it was only present for the experiments conducted with the combined cells 2/3C and 3/2C (Figure 5.12b).

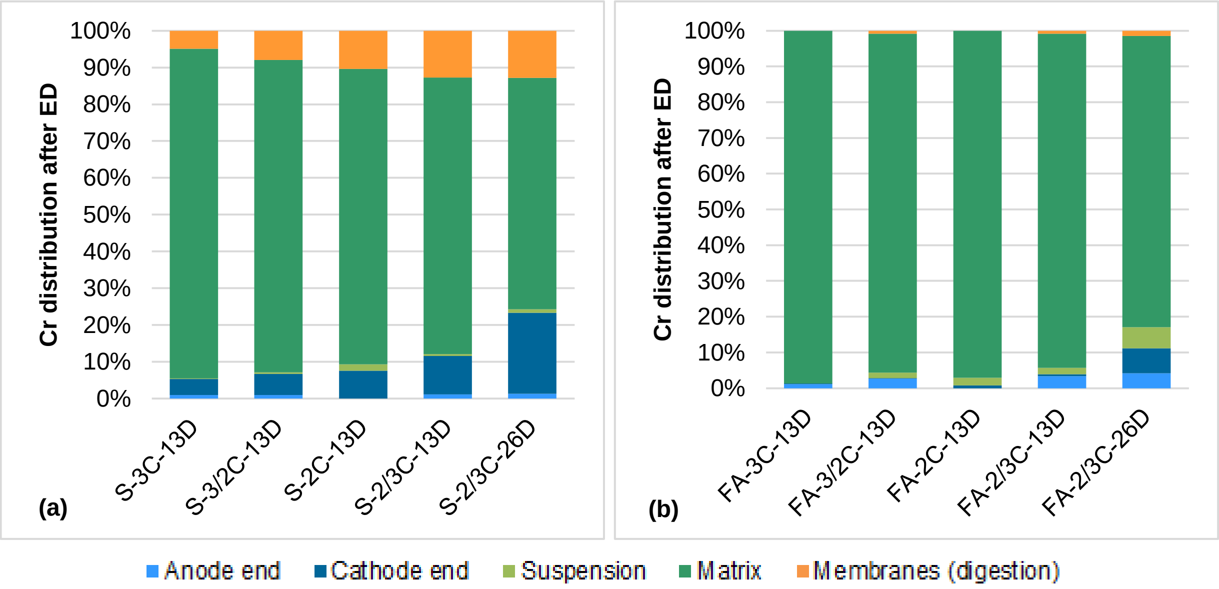

Figure 5.12: Final distribution of Cr (%) after ED experiments: (a) soil and (b) fly ash

Table 5.2: Final distribution of Cr after ED experiments for soil and fly ash

Experiments		Cr distribution after ED (%)				
		Anode end	Cathode end	Suspension	Matrix	Membranes (digestion)
Soil	**S-3C-13D**	1	4	0	90	5
	S-3/2C-13D	1	6	0	85	8
	S-2C-13D	-	8	2	80	10
	S-2/3C-13D	1	10	1	75	13
	S-2/3C-26D	1	22	1	63	13
Fly ash	**FA-3C-13D**	1	0	0	99	0
	FA-3/2C-13D	3	0	2	95	1
	FA-2C-13D	-	1	2	97	0
	FA-2/3C-13D	3	1	2	93	1
	FA-2/3C-26D	4	7	6	81	1

Cr recovery

The final pH of the suspension, the recovery of Cr, the total removal of Cr and the removal of Cr towards the anode side and the cathode side are shown in Table 5.3.

The recovery is a mass balance defined as the total mass of heavy metal measured after ED divided by the mass of heavy metal measured in the matrix before EDR. The total mass of heavy metal after ED is measured in the electrolytes, electrodes, membranes, stirrer and matrix. For an optimal recovery, this mass balance rate should be close to 100%, but values between 80-120% are also considered to be acceptable recoveries. Previous EDR studies have shown great value variations on the recovery of Cr (Ottosen et al., 2009). In this study, a new procedure for the analysis of the membranes was used in order to investigate if better recoveries could be achieved. It was thought that the heavy metals adsorbed on the membranes were not being successfully extracted and that values obtained were in fact lower than in reality.

However, this new procedure for the analysis of the membranes did not improve the recoveries for the experiments. As shown in Table 5.3, most of the recoveries were not within the 80-120% range. For the soil, most of the recoveries were below 80%, probably due to the heterogeneous distribution of Cr in the contaminated soil. For the fly ash, the situation was the opposite as the recoveries, for the 13 days experiments, were all over 120%. This was due to a significant dissolution of the fly ash (24-40%) caused by the wash out of salts (Chen et al., 2015; Kirkelund et al., 2015) as well as the dissolution of carbonates due to acidification of the suspension during the ED process (Kirkelund et al., 2010). For the 26 days experiment, the removal during EDR was sufficient for the concentration not to increase as a result of fly ash dissolution, resulting in an acceptable value for the recovery (116%).

Table 5.3: Cr recovery and removal after ED experiments for soil and fly ash

				Removal (%)		
Experiments		**Final pH**[(1)]	**Recovery (%)**	**Total**	**To anode side**	**To cathode side**
Soil	**S-3C-13D**	3.7	66	10	14	86
	S-3/2C-13D	2.5	62	15	12	88
	S-2C-13D	2.3	103	18	-	100
	S-2/3C-13D	2.3	80	24	7	93
	S-2/3C-26D	2.1	64	36	5	95
Fly ash	**FA-3C-13D**	5.4	123	1	86	14
	FA-3/2C-13D	5.3	125	4	93	7
	FA-2C-13D	3.7	155	1	-	100
	FA-2/3C-13D	5.3	139	5	88	12
	FA-2/3C-26D	1.5	116	13	34	66

(1) Final pH measured in the suspension

Cr removal

The removal is defined as the mass of heavy metal measured in the electrolytes, electrodes and membranes after ED divided by total mass of heavy metal measured after ED. The removal can occur either towards the anode side or cathode side and the percentages are calculated based on the removal as 100%. The anode side refers to the anode end and the anion exchange membrane. The cathode side refers to the cathode end and the cation exchange membrane.

Previous studies on the influence of Cr speciation on stationary EKR showed that removal of Cr(III) occurred only under highly acidic conditions, while removal of Cr(VI) was observed to increase at neutral/alkaline conditions (Reddy & Chinthamreddy, 2003; Jensen et al., 2012). Furthermore, studies on Cr speciation made with soils spiked with Cr(III) and Cr(VI) on EKR and EDR have shown that the removal of Cr is towards the cathode, when the soil is spiked with Cr(III) (Weng & Yuan, 2001), and towards the anode, when the soil is spiked with Cr(VI) (Reddy et al., 1997; Reddy & Chinthamreddy, 2003; Nieto Castillo et al., 2008).

Table 5.3 shows that the highest total Cr removals were obtained in the experiments with the lowest final pH in the suspension, which correspond to the 26 days experiments for both soil (36%) and fly ash (13%).

For the soil, in the 13 days experiments, the set-up that achieved the highest removal was the combined cell 2/3C (24%). The order of Cr removal for the soil was the following: 3C < 3/2C < 2C < 2/3C. Cr removal rates were between 10-36%, which is an usual range of values for a CCA contaminated soil with unenhanced ED treatment (Section 3.5, Table 3.1). The removed Cr was mainly transported towards the cathode side, revealing Cr(III) since this species is positively charged for this pH range and is only removed under highly acidic conditions.

For the fly ash, in the 13 days experiments, the set-up that achieved the highest removal was the combined cell 2/3C (5%). The order of Cr removal for the fly ash was the following: 2C ≤ 3C < 3/2C < 2/3C. Cr removal rates were very low (1-13%), but these values are also usual for MSWI fly ash with unenhanced ED treatment (Section 3.6, Table 3.3). For the 13 days experiments, the removed Cr was mainly transported towards the anode side, revealing Cr(VI) since this specie is negatively charged and the pH conditions of the suspension during ED were alkaline to neutral. However, for the 26 days experiment, 34% of Cr was removed towards the anode side and 66% of Cr was removed towards the cathode side, revealing the removal of both Cr(III) and Cr(VI) respectively, due to the change in pH conditions of the fly ash suspension from alkaline to highly acidic during EDR.

Influence of the membranes on Cr removal

To further evaluate the significance of the Cr that remains adsorbed on the membranes, the removals of the experiments have been illustrated specifying the removals obtained at the anode end and cathode end and the removals obtained at the membranes. Therefore, Figure 5.13 illustrates Cr removal rates in the cathode end, cation exchange membrane, anion exchange membrane and anode end, in real percentages. Table 5.4 presents the same data but the percentages are calculated based on the removal to each side as 100%.

Although the new procedure for the analysis of the membranes did not improve the recoveries for the experiments, it proved to be a good tool to assess the amount of Cr that remained adsorbed on the membranes after ED and include it in Cr removal. For the soil's 13 days experiments, the Cr adsorbed on the cation exchange membrane represented more than 50% of the Cr removed to the cathode side. Regarding the fly ash, the Cr adsorbed on the membranes after ED was not a significant part of the Cr removed.

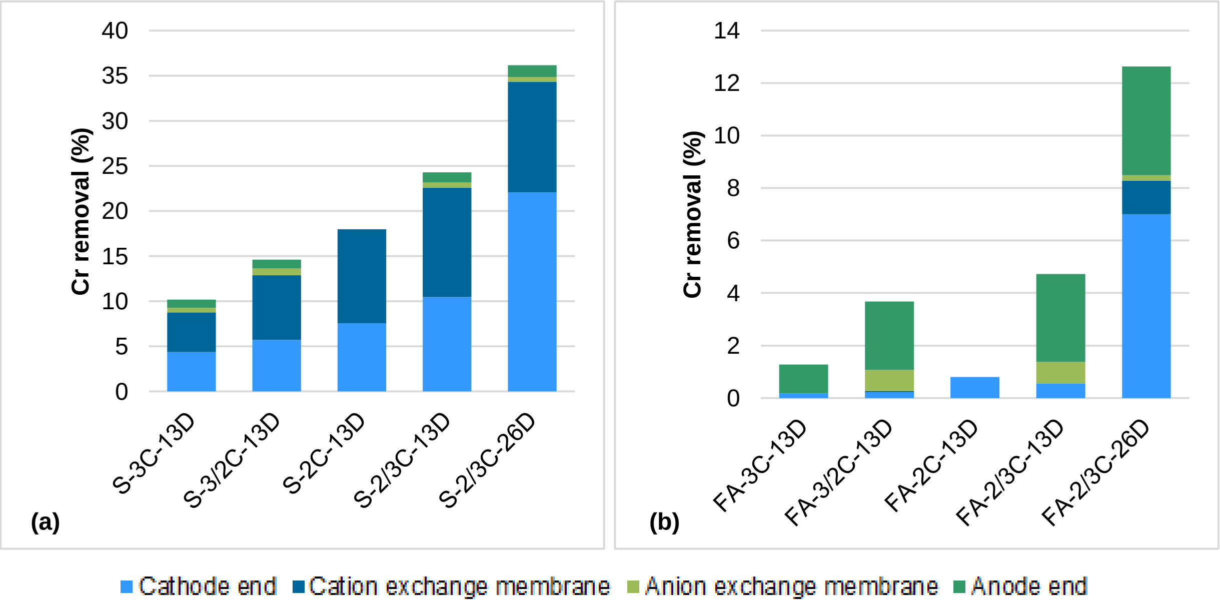

Figure 5.13: Cr removal (%) after ED experiments: (a) soil and (b) fly ash

Table 5.4: Cr removal in the anode and cathode ends and membranes (%) regarding Cr total removal to anode side and cathode side

		Removal to anode side (%)		Removal to cathode side (%)	
Experiments		Anode end	Anion membrane	Cathode end	Cation membrane
Soil	**S-3C-13D**	66	34	50	50
	S-3/2C-13D	56	44	44	56
	S-2C-13D	-	-	42	58
	S-2/3C-13D	65	35	46	54
	S-2/3C-26D	70	30	64	36
Fly ash	**FA-3C-13D**	100	0	100	0
	FA-3/2C-13D	77	23	82	18
	FA-2C-13D	-	-	100	0
	FA-2/3C-13D	80	20	100	0
	FA-2/3C-26D	95	5	85	15

5.3 Study of Cr(VI)

Cr(VI) extraction was performed, with slight modifications, following USEPA Method 3060A, that was adopted, in 2006, as the basis for the European Standard EN 15192. The method uses an alkaline digestion procedure for extracting Cr(VI) from soluble, adsorbed and precipitated forms of Cr compounds in soils, sludges, sediments and similar waste matrices. In order to quantify total Cr(VI) in solid matrices, three criteria must be satisfied: the extracting solution must solubilize all forms of Cr(VI); the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III); and the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). The method 3060A meets all the criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal Cr(III)-Cr(VI) interconversions have been observed and reported, except in matrices with high concentrations of Mn, amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$ (USEPA, 1996). Therefore, Cr(III)-Cr(VI) interconversions were not expected to occur in the alkaline digestion of the soil and fly ash.

Cr(VI) detection was performed following Hach Company Method 8023, a DPC based method that measures the amount of solubilized Cr(VI) that is present in the alkaline digestate through UV-VIS spectrophotometry.

For both matrices, Cr(VI) analysis was carried out before and after ED experiments. The concentrations of Cr total and Cr(VI) obtained are shown in Figures 5.14 and 5.15, for the soil and fly ash, respectively. Since Cr(III) and Cr(VI) are the two most stable species of Cr, the value of Cr total in this study was considered as the sum of Cr(III) and Cr(VI). Therefore, the amount of Cr(III) present in the matrices was estimated through the difference between Cr total and Cr(VI) values.

Even though the concentration of Cr(VI) in the soil was already low before ED experiments (Figure 5.14), the use of the ED process helped to remediate Cr(VI) from the soil, resulting in a decrease in its concentration after all the experiments. For most of the soil experiments, Cr(VI) concentration after EDR was below the detection limit of the method (2 mg/kg). According to the criteria for Cr contaminated soil and its different pollution classes applicable in Denmark and to the experimental data, before and after EDR, the soil under study can be classified as unpolluted (Cr total < 500 mg/kg and Cr(VI) < 20 mg/kg).

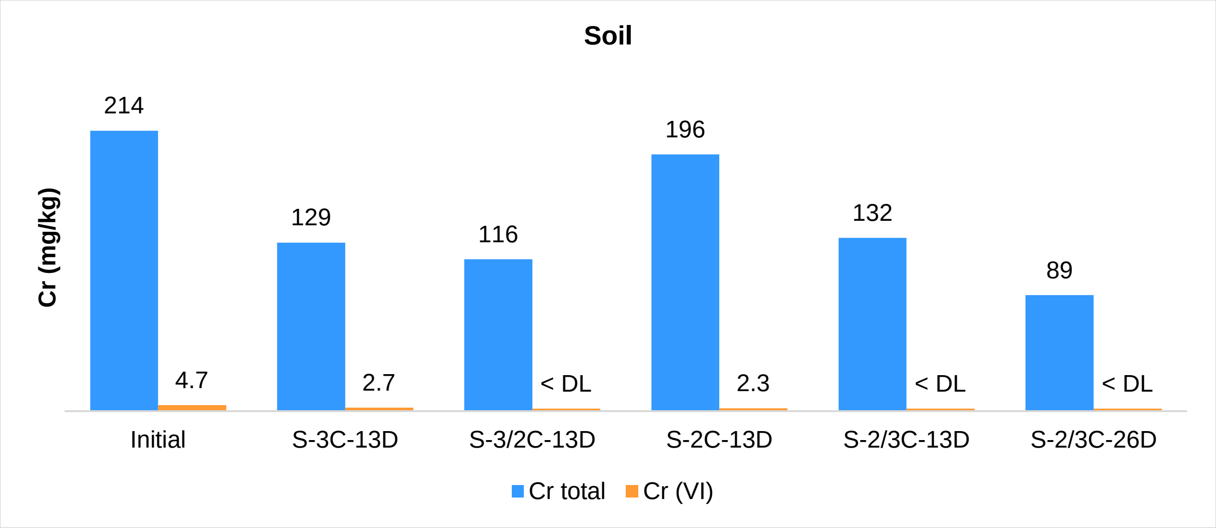

Figure 5.14: Cr total and Cr(VI) concentration (mg/kg) before and after ED experiments for soil

(1) The value 2.7 mg/kg obtained for S-3C-13D reports the value of one of the three samples, the other two values were also below the lower detection limit of the method.

In the CCA preservative solution, Cr is present in the form of Cr(VI), as chromate (CrO_4^{2-}). However, Cr(VI) mobility in the soil is highly dependent on the content of organic matter. In loamy soils, such as the soil in study, the organic matter will react with chromate to chromite, resulting in the formation of insoluble Cr(III) oxides at pH above 6 (Nielsen, 2013). Table 5.5 shows the Cr valence speciation for the soil experiments, where Cr(III) was the predominant specie present, confirming that Cr(VI) was reduced in the soil by organic matter, as expected, although its low content.

Table 5.5: Cr speciation (%) before and after the ED experiments for soil

	Cr valence speciation (%)	
Experiments	**Cr(VI)**	**Cr(III)**
Initial	2.2	97.8
S-3C-13D	2.1	97.9
S-3/2C-13D	1.7	98.3
S-2C-13D	1.2	98.8
S-2/3C-13D	1.5	98.5
S-2/3C-26D	2.3	97.7

Figure 5.15 shows an increase in Cr total concentration in fly ash after the 13 days experiments, due to the dissolution of fly ash during ED, as previously referred. However, for the 26 days experiment, the removal during EDR was sufficient for the concentration not to increase as a result of fly ash dissolution, resulting in a slightly lower Cr total concentration after ED. The initial concentration of Cr(VI) in the fly ash was already below the detection limit of the method (2 mg/kg). For all experiments, Cr(VI) final concentration, after ED, remained below the detection limit.

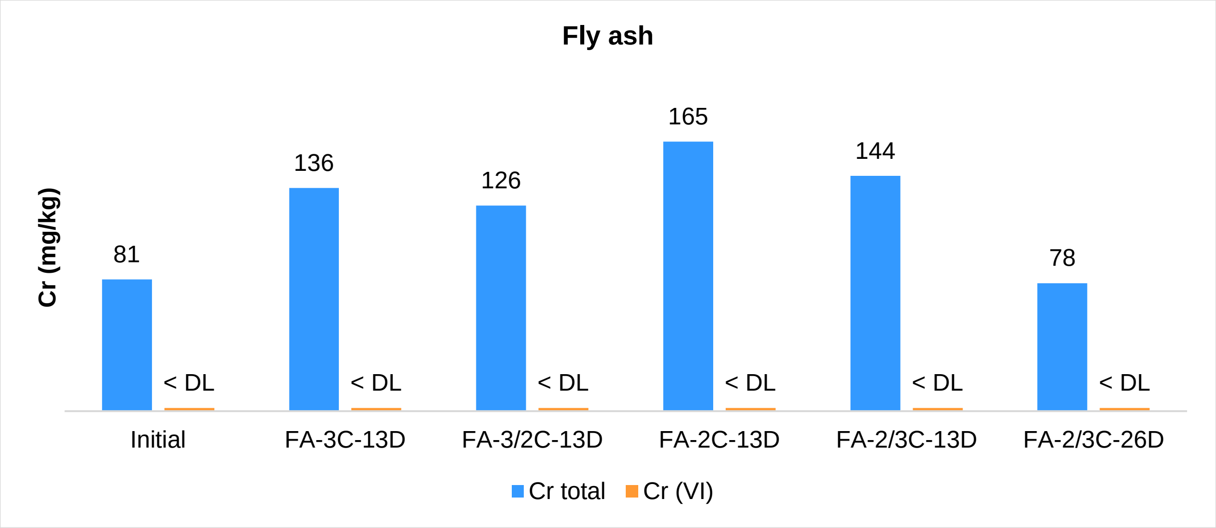

Figure 5.15: Cr total and Cr(VI) concentration (mg/kg) before and after ED experiments for fly ash

In MSWI residues, Cr was thought to be present mainly as Cr(VI) due to the oxidation of Cr(III) to Cr(VI), that takes place during the combustion of the waste and its alkaline pH (Astrup et al., 2005). However, a study on the impact of solid fuel combustion technology on valence speciation of Cr in fly ash showed that, for MSWI fly ash and other types of examined fly ashes, the dominant form of Cr present was Cr(III) (Świetlik et al., 2014). This study also showed a significant difference between Cr total (97.3 mg/kg) and Cr(VI) (6.3 mg/kg). Table 5.6 shows the Cr valence speciation for the fly ash experiments, where Cr(III) was the predominant species present. The percentages obtained for Cr(VI) and Cr(III) are consistent to those obtained by Świetlik et al. (2014) (6.5% for Cr(VI) and 93.5% for Cr(III)). However, the values obtained for Cr(VI) in this study, which are all below the detection limit of the method (2 mg/kg), are lower than those reported by other authors: 7.4 mg/kg (Hu et al., 2013) and 6.3 mg/kg (Świetlik et al., 2014).

Table 5.6: Cr speciation (%) before and after the ED experiments for fly ash

	Cr valence speciation (%)	
Experiments	**Cr(VI)**	**Cr(III)**
Initial	2.5	97.5
FA-3C-13D	1.5	98.5
FA-3/2C-13D	1.6	98.4
FA-2C-13D	1.2	98.8
FA-2/3C-13D	1.4	98.6
FA-2/3C-26D	2.6	97.4

5.4 Sequential extraction

Sequential extraction is widely used to investigate heavy metals associated with mineral and organic phases and can help indicate bioavailability and mobility of heavy metals, as opposed to total heavy metal concentrations (Kirkelund et al., 2010).

IAWG (1997) hypothesized that the results of sequential extraction might not necessarily reflect the associations with the claimed phases, but rather represents the different leaching conditions within a landfill over time. The carbonates and exchangeable phase is available under neutral conditions; the reducible phase and the oxidizable phase are potentially available under reducing conditions; the residual phase is unavailable for leaching (Wan et al., 2006).

Figure 5.16 shows Cr initial distribution (%) for the soil and fly ash. Although the organic matter content was low in both matrices, Cr was mainly found in the oxidizable phase for both of them, suggesting that it is difficult to remove by electromigration (Kirkelund et al., 2010) and potentially available for leaching under reducing conditions. For the soil, 70% of Cr was in the oxidizable phase bound to organic matter, whereas 20% of Cr was found in the reducible phase, which is a more accessible phase to electromigration. Regarding the fly ash, 70% of Cr was found in the oxidizable phase and 20% in the residual phase, resulting on a difficult removal by electromigration.

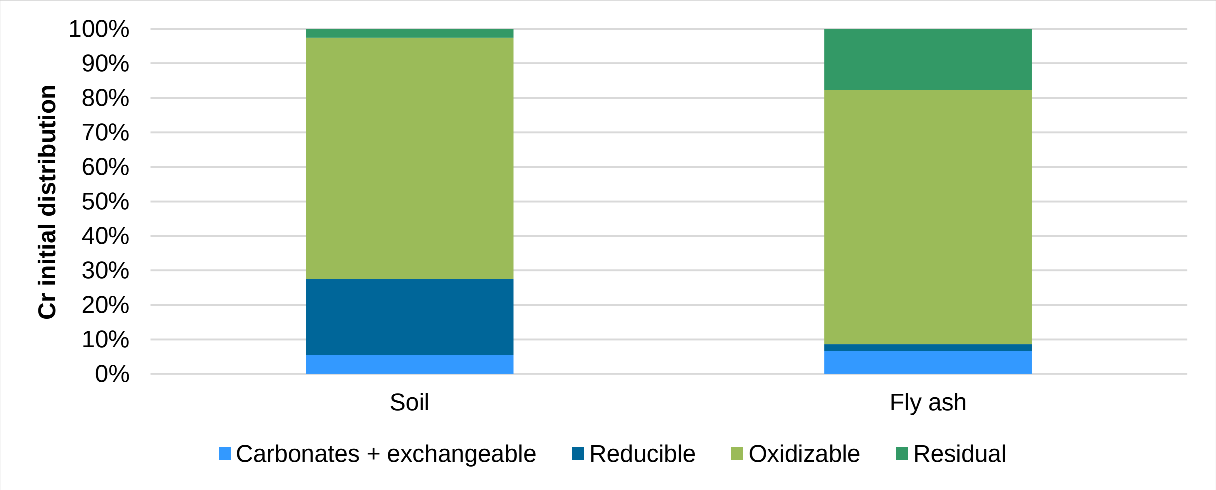

Figure 5.16: Cr distribution (%) determined by sequential extraction before ED for soil and fly ash

The distribution (mg/kg) of Cr and the Al, Ca, Fe, K, Mn and Na was determined by sequential extraction for the soil and fly ash, before and after selected ED experiments. The combined cell experiments, 2/3C-13D and 2/3C-26D, were selected, for both matrices, to evaluate the changes in the elements distribution that occurred with the use of this new set-up, after 13 and 26 days. The 2C-13D experiments were also selected, for both matrices, because the lowest final pH values were achieved with this set-up for the 13 days experiments. Regarding the initial concentration for all the elements in both matrices, the values obtained by sequential extraction varied from those measured by ICP-OES, after pre-treatment according to DS 259, due to the differences between the methods (multi step vs single step).

Figure 5.17 shows Cr distribution (mg/kg) in the soil and fly ash. For the soil, Figure 5.17a shows a redistribution of Cr to the reducible phase, in the 2C cell, and to the oxidizable phase, for both experiments made with the combined cell 2/3C. Regarding the fly ash, even though a low percentage of Cr was removed, its concentrations in the different experiments after ED increased, due to the dissolution of the fly ash, as previously referred. Figure 5.17b also shows a redistribution of Cr to the reducible phase and to carbonates and exchangeable phase, resulting in an increase of the leaching potential for the fly ash after EDR.

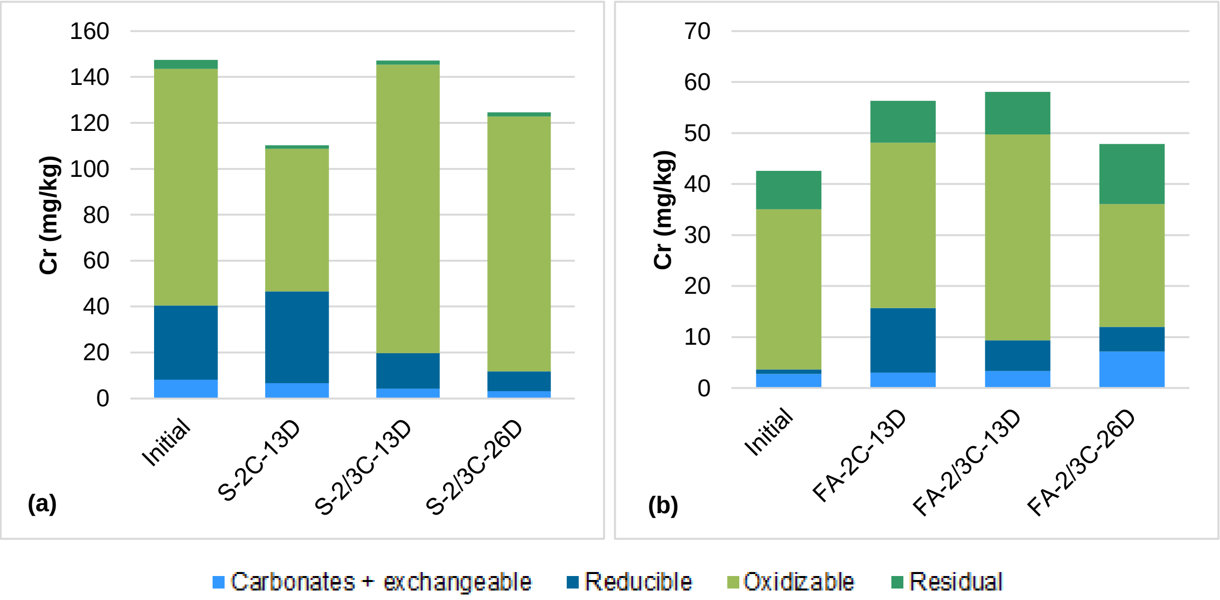

Figure 5.17: Cr distribution (mg/kg) determined by sequential extraction before and after ED for: (a) soil and (b) fly ash

Regarding the sequential distribution of the other elements, shown in Figures 5.18 and 5.19, removals were not observed for all the elements, but only for Ca, K and Mn for both matrices, Al and Fe for the soil, and Na for the fly ash. The increase in concentration of Al and Fe, for the fly ash may be due to either the fly ash dissolution, as seen for Cr, or to non-dissolution of the elements during EDR. The increase in concentration of Na, for the soil, might be a consequence of the electrolytes that were used ($NaNO_3$). Some of the elements presented the same distribution of phases after EDR, although with lower or higher concentrations. The elements that had a redistribution of phases were predominantly found in the carbonates and exchangeable, and reducible phases before ED. These phases are considered to be more accessible for dissolution and removal during ED experiments.

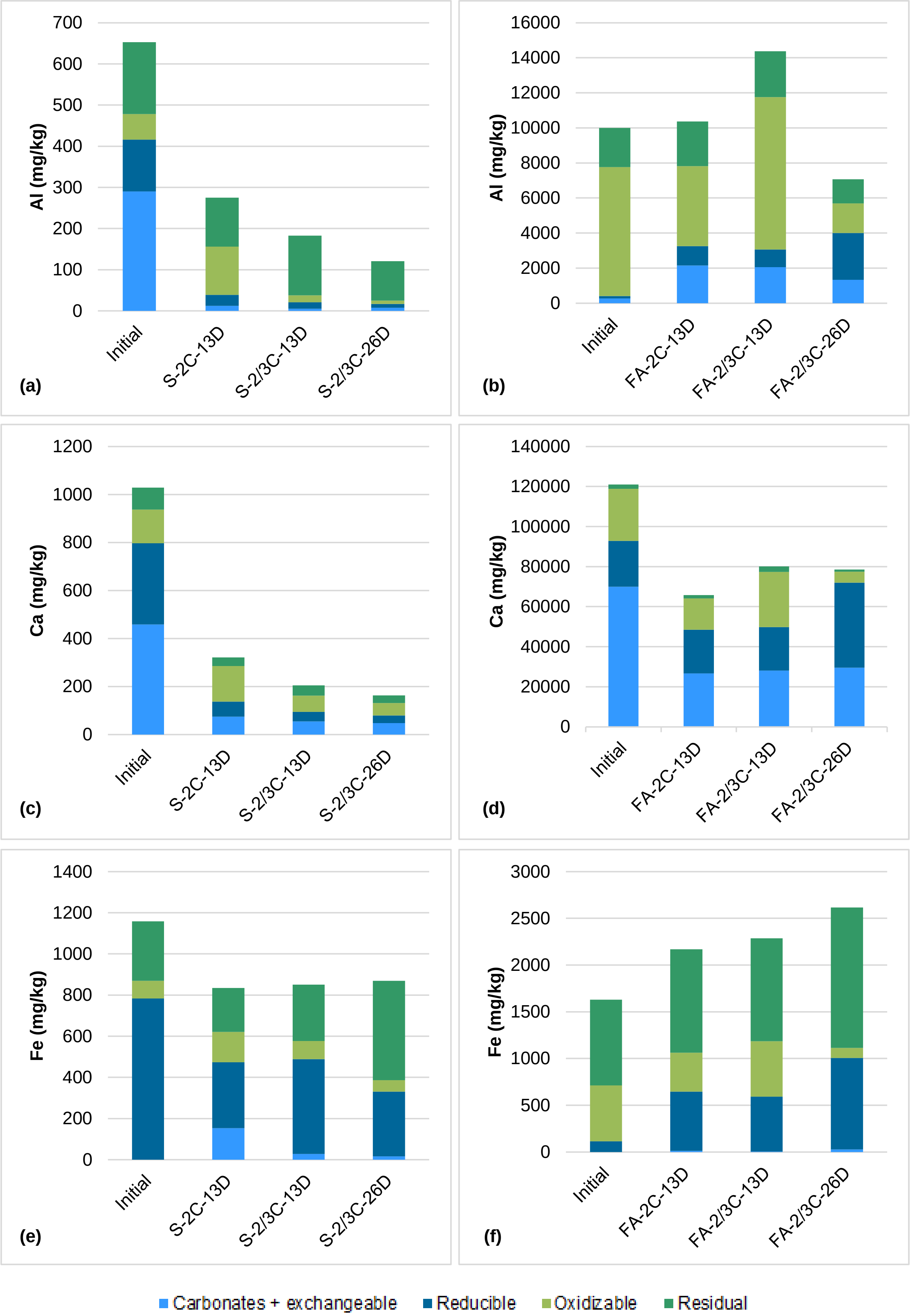

Figure 5.18: Al, Ca and Fe distribution (mg/kg) determined by sequential extraction before and after ED: (a) (c) (e) soil and (b) (d) (f) fly ash

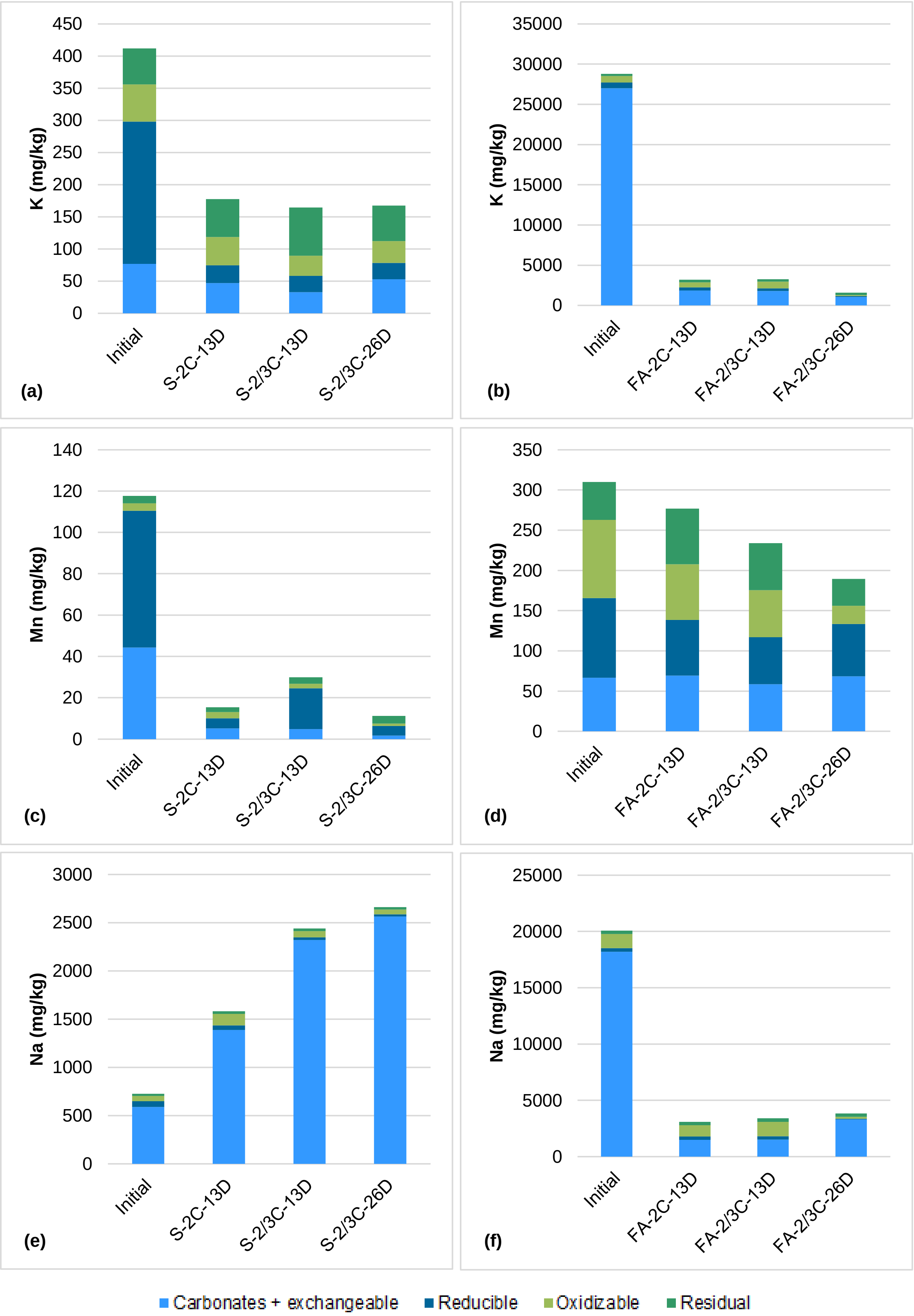

Figure 5.19: K, Mn and Na distribution (mg/kg) determined by sequential extraction before and after ED: (a) (c) (e) soil and (b) (d) (f) fly ash

5.5 Leaching of chromium in fly ash

Interest in the leaching behaviour of heavy metals has been growing over the last decade, mainly due to the European Directive 2003/33/EC that established criteria and procedures for the acceptance of waste at landfills. Many consider that the release of heavy metals from the reuse and disposal of MSWI ashes through leaching represents the greatest potential threat, regarding the environment and human health. Therefore, it is not only important to know the concentration of heavy metals present in the fly ash but also their leaching potential, i.e. to measure their readily soluble phases.

The amount of leached heavy metals is directly related with the pH of the leachate. In the presence of some oxides (e.g. Fe or Mn oxides), the amount of leached heavy metals may be reduced, especially for pH<7, due to their high adsorption capacity (Quina, 2005). However, in general, the mobility of heavy metals increases at more acidic pH, resulting in an increased leaching, as seen in the pH desorption.

Since the reuse of MSWI fly ash in construction is still generally forbidden, no limits have been defined for it. However, to assess the possibility of using this residue in construction, the leaching values obtained for the fly ash were compared with the Danish regulation BEK 1662/2010 for the use of other types of waste materials in construction in Denmark (Miljøministeriet, 2010). This regulation has three categories: C1 (free use), which is defined by a low total content of contaminants, C2 (restricted use) and C3 (severely restricted use). C2 and C3 are based on water leachability of the contaminants. The limits for these categories are given in Table 5.7. Table 5.7 also shows the measured total content and leachability for Cr total and Cr(VI) obtained for the fly ash.

Regarding Cr total and Cr(VI) contents (mg/kg), the values before and after ED were within C1 range (Table 5.7). As for leaching, Cr total met the threshold values for category C1 before ED. However, during ED treatment, the leaching of Cr total increased, although not enough to exceed the value range for category C2. These findings indicate that, regarding to Cr content and leaching, the fly ash could be used as a construction material.

Table 5.7: Cr content (mg/kg) and leaching (mg/L) before and after ED experiments for fly ash. Categories of Danish regulation (BEK 1662/2010) for the use of other types of waste materials in construction for comparison

		13 days				**26 days**	**Categories (BEK 1662/2010)**		
Cr content and leaching	**Initial**	**3C**	**3/2C**	**2C**	**2/3C**	**2/3C**			
pH(1)	12.32	7.57	7.25	5.66	6.69	3.78	**C1**	**C2**	**C3**
Cr total content (mg/kg)	80.5	136.3	125.6	164.6	143.7	78.2	0-500	>500	>500
Cr(VI) content (mg/kg)	<DL(2)	<DL(2)	<DL(2)	<DL(2)	<DL(2)	<DL(2)	0-20	>20	>20
Cr total leached (mg/L)	0.01	0.11	0.26	0.05	0.27	0.04(3)	0-0.01	0.01-0.5	>0.5

(1) pH measured in the leachates
(2) Value below the detection limit of the method (2 mg/kg)
(3) L/S=4

5.6 Relations between chromium and other elements (Al, Fe, Ca, K, Mn and Na)

Although the pH desorption curves and sequential extractions that were carried out for the Al, Fe, Ca, K, Mn and Na provided information about the elements' mobility, distribution of phases and removal as a consequence of ED, they were not sufficient to extrapolate the existing relations that affected Cr speciation. Literature on this subject was reviewed to further understand Cr relations with these elements.

Ottosen et al. (2009) studied a CCA contaminated soil from another wood preservation site in Denmark. In their study, they used SEM/EDX to analyse soil particles and observed a CCA-oxide solid phase cementing the soil particles together. All the particles that were investigated showed similar composition, except regarding Cr, because not all of them contained a measurable amount of Cr, leading to the conclusion that Cr in industrially contaminated soil is, in general, distributed heterogeneously and not fully associated to soil constituents.

Lima et al. (2008) characterized different fly ashes from bio and municipal waste. XRD analysis was performed to determine media composition and crystalline compounds. The crystalline minerals found were anhydrite ($CaSO_4$), calcite ($CaCO_3$), hematite (Fe_2O_3), sylvite (KCl), magnesite ($MgCO_3$) and halite (NaCl). A similar characterization was obtained by Kirkelund et al. (2015) for MSWI fly ash, also with the use of XRD analysis, where the crystalline minerals found were anhydrite, sylvite, calcite and quartz (SiO_2). In a different study, Cornelis et al. (2008) analysed the leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes. The leaching of oxyanions was found to be usually lower than what was expected on the basis of pure-phase solubility in alkaline wastes, possibly due to mechanisms such as surface adsorption and solid solution formation with minerals containing Ca, present in the alkaline waste. Calcite is often considered as a possible sink for oxyanions in waste. Another conclusion was that, in most cases, adsorption by Fe and Al oxides, which are reducing agents for Cr, will only be important in weathered wastes where these oxides have sufficient positive charge. In a study about geochemical modelling of leaching from MSWI APC residues, Astrup et al. (2006) concluded that Cr leaching from APC residues was affected by mechanisms other than solubility control. Therefore, for understanding the leaching behaviour of Cr, precipitation/dissolution and surface complexation mechanisms should also be studied.

6. Conclusions and future developments

This study aimed to understand if ED is an appropriate treatment for remediating Cr. For that purpose, special attention was paid to Cr speciation, before and after ED experiments, to evaluate if Cr(III)-Cr(VI) interconversions occurred during the treatment.

In general, Cr is present in contaminated matrices as a minor element, except in contaminated matrices resulting from direct Cr contamination. Thus, ED was applied to two types of matrices that contained different amounts of Cr: CCA contaminated soil and MSWI fly ash. Ten ED experiments were carried out, five for a soil with a current density of 0.2 mA/cm^2, and five for a MSWI fly ash with a current density of 1 mA/cm^2. Three ED set-ups were used in the experiments to evaluate the differences in Cr removal and recovery rates.

The relation between the three different set-ups used and the removal rates proved that the most important factor in Cr removal is the pH. As the pH decreases, the extraction of Cr increases. For both matrices, as observed in the pH desorption curves obtained, the extraction starts at pH around 4, but the highest extraction percentages are achieved at pH 1. Therefore, the closer the pH in the ED experiments reaches 1, the higher the Cr removal rates will be. The set-ups that achieved the lowest final pH were the 2C cell and 2/3C cell, for the soil, and the 2C cell, for the fly ash. However, the higher removal rates for Cr, for both the soil (24%) and the fly ash (5%), were only achieved with the combined cell 2/3C, due to the influence of speciation on Cr removal. Since the 2C cell does not have the anolyte compartment, it will only remove Cr as cations, remaining the Cr anions in the suspension in the matrix compartment. The combined cell 2/3C with alternating current is the most efficient set-up in Cr remediation, because it improves Cr mobility, with the decreasing pH effect of the 2C cell, and Cr removal to the anode and cathode sides, characteristic of the 3C cell.

The analysis of Cr(VI), before and after ED experiments, was the used tool to interpret the changes that occurred in Cr speciation. This analysis was conducted by two methods: USEPA Method 3060A, for the extraction of Cr(VI), and Hach Company Method 8023, for the detection of Cr(VI). In this study, the value of Cr total was considered as the sum of Cr(III) and Cr(VI). Hence, Cr(III) was calculated as the difference between Cr total and Cr(VI). Despite the differences in Cr total concentrations, both matrices presented a similar speciation, before and after ED, with Cr(III) as the main species found and Cr(VI) less than 3% of Cr total. Oxidation of Cr(III) to Cr(VI) did not occur during ED since there was no increase in Cr(VI) after the treatment. For the fly ash, Cr(VI) values remained below the lower detection limit of the method. For the soil, Cr(VI) values decreased after the treatment due to removal. Therefore proving that the ED process does not influence Cr speciation through Cr(III)-Cr(VI) interconversions.

The main environmental impact from utilization and disposal of MSWI residues arises from the release of contaminants to the surrounding environment by leaching. Cr leaching tests were performed on the fly ash to assess the possibility of using this matrix in construction, by complying with the leaching values for Cr, present in the Danish regulation BEK 1662/2010, for the use of other types of waste materials in construction in Denmark. It was seen an increase in Cr leaching values after treatment that confirms that the ED process influences the leaching of Cr. Nonetheless, the values obtained after ED did not exceed the value range for category C2 (restricted use), what indicates that this matrix can be used as a secondary resource in construction, with restrictions.

Further analyses were conducted on Al, Fe, Ca, K, Mn and Na, through pH desorption curves and sequential extractions, to understand how their compounds affected the speciation of Cr. These analyses provided information about the elements' mobility, distribution of phases and removal as a consequence of ED, but no evident relation was able to be extrapolated from them.

This study is the first to provide knowledge about the changes in Cr speciation that occur in industrially contaminated matrices after the use of ED as a treatment technique. The results indicate that the ED process is an appropriate technique for remediating matrices containing Cr, because it contributes to Cr removal, without causing Cr(III)-Cr(VI) interconversions.

Future developments

I. Analysis of the membranes

A new procedure for the analysis of the membranes was carried out in this study to further evaluate the significance of the Cr that remains adsorbed on the membranes. To determine if this procedure is in fact a good tool to assess the amount of Cr that remains adsorbed on the membranes after ED and include it in Cr removal, ED experiments should be made in duplicate with the same experimental conditions and the analysis of the membranes should be tested, through the comparison between the values obtained with the new procedure and the ones obtained with the traditional procedure.

II. Alternating current set-up frequency

The combined cell 2/3C was found to be the most efficient set-up for Cr remediation. Although two alternating current frequencies were tested (every minute and every day), the duration of the experiments in which they were tested was different and the removal rates could not be compared. Therefore, different alternating current frequencies, e.g. every minute, every hour and every day, in ED experiments with the same matrix and duration should be tested, in order to compare the removal rates and see which frequency maximizes Cr removal.

III. Minimum remediation time

In order to achieve a highly acidic final pH in the minimum possible remediation time, a pre-treatment to decrease the initial alkaline pH of MSWI fly ash should also be used in the experiments.

IV. Cr(VI) analysis for the MSWI fly ash

Regarding Cr(VI) analysis for the fly ash, a different detection method should be used to achieve measurable Cr(VI) values within the detection limit of the method.

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