

**Electrokinetically induced removal of heavy metals from an aged,  
contaminated sludge – a laboratory experiment**

MSc thesis  
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Universiteit Utrecht  
2011

Final

## **Abstract**

Soil pollution is a universal environmental issue and the clean-up of such contaminated soils can be a costly and time consuming task. Traditional methods such as pump and treat or soil flushing may not provide an effective solution, in particular for fine grained, clayey and highly impermeable soils and contaminants that are relatively immobile. The aim of this study was focused on the removal of heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) from a coagulant treated, aged, contaminated sludge by means of electroremediation. Also a side experiment has been conducted in which the use of coagulant polymers on the removal of heavy metals from a soil spiked with Cd, Cr, Cu, Ni, Pb, Zn was investigated. A sequential extraction was conducted in order to study the metal distribution of both the contaminated sludge and the spiked soil. Maximum removal percentages during the experiment using a constant current of 1 mA/cm<sup>2</sup> over ~180 hours with a corresponding 0.5 V/cm potential gradient were > 15 % for Cd (21%), Cu (15%), Zn (23%); Ni and Pb showed removal < 10%; Cr demonstrated no removal. Varying the electrode material was of no influence for the transfer of current from the power supply into the system. In contrast, absence of NaCl in the electrode reservoirs demonstrated a major decrease in the efficiency of the applied current on the removal of heavy metals from the contaminated sludge. A difference between the direction of electroosmosis in presence and absence of coagulant polymers in the spiked soil sample was observed on the direction of electroosmosis. However, the effect of the opposite electroosmotic movement of water on the contaminant transport was not quantified. With this study it was impossible to extrapolate the effect of the electrical current and potential gradient due to multiple parameter changes per experiment. It was recommended that batch-scale on-site application of electroremediation is preferred above in-situ field implementation, since more control, with emphasis on pH, of the system environment, i.e. the contaminated sample including electrolyte fluids and electrodes, is possible during batch-scale on-site application of electroremediation.

### *Keywords:*

*electroremediation; electrokinetic remediation; contaminated aged sludge; contaminated soil; heavy metal contamination*

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## Introduction

Soil pollution is a universal environmental issue. It is often a historical burden due to previous agricultural or industrial activities and at various places around the world there is still ongoing pollution of the subsurface. Nowadays, the subsurface is intensely used and is an important source for various resources, such as groundwater for drinking and irrigation purposes, crop cultivation, nature areas, building and urban exploitations, etcetera. Strict maximum levels of harmful constituents in drinking water, groundwater and soil are legally established to protect human health and ecological risks.

The clean-up of contaminated soils can be a costly and time consuming task. Often a combination of both heavy metals and organic compounds are found, hence the necessity of developing effective solutions that are capable of dealing with multiple types of pollution simultaneously. Since the subsurface is in principle very inhomogeneous, site-specific solutions are to be made. Traditional methods such as pump and treat or soil flushing may not provide an effective solution, in particular for fine grained, clayey and highly impermeable soils and contaminants that are relatively immobile. Simply digging and removing contaminated soil from the site is generally too costly and merely relocates the problem rather than providing a systematic solution. Also, the processing of these vast volumes of soil is very costly. Dewatering and size and density separation of the soil may diminish the final weight and volume of the contaminated soil and increases the, economically interesting, reuse of clean soil; it does not result in a sustainable solution.

For subsurface heavy metal pollution, specifically, limited remediation methods are available. Immobilization and in-situ retention of metals in soil by sulfides or oxides is most widely applied. It may remove immediate threat of the pollution but it does not remove the subject itself: the heavy metal contaminants. Remediation by electromigration is another very promising technique that is, however, still under development.

Since the 1980's (Yeung, 2011) the remediation of contaminated soils based on electrokinetics has evolved into a very well applicable and widely studied method. Although it has been used for a while now for small scale in-situ remediation, the hinter lying principles are not fully understood and therefore mixed results and removal efficiencies have been found.

The aim of this study is to evaluate on-site application of electroremediation on a contaminated sludge. The sludge is aged and originates from river bottom and floodplain deposits and is contaminated with both a variety of heavy metals, such as Cd, Cr, Cu, Ni, Pb and Zn, as well as with organic contaminants like mineral oil.

This study is divided into 5 sections. The *background* section will treat the theory on the mechanisms that play a role during the application of an electrical current through a contaminated soil. It includes a short state of the art literature review. Subsequently in the *results* and *discussion* sections, the results of the laboratory experiment are presented and discussed. To finalize, some conclusions are given together with recommendations in the *conclusion* and *recommendations* sections.

This study is submitted as my thesis for obtaining the grade of MSc Earth Sciences at Universiteit Utrecht and is executed at the Universiteit Utrecht in cooperation with BioSoil R&D, B.V.. The supervisors for this thesis are dr. ir. J.P.G. Loch (UU), dr. A.T.

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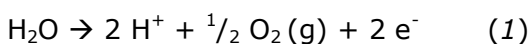
## Background

The geochemistry of soils is of great importance for the speciation and mobility of contaminants, both for heavy metals (e.g. Eykholt and Daniel, 1994; Reddy *et al.*, 1997; Reddy and Chinthamreddy, 2003) and organics (e.g. Lima, *et al.*, 2011; Ribeiro *et al.*, 2011) as well for the various mechanisms that play a role in the net transportation of contaminants through the soil system. All natural soils, at the scale of soil pollution, are heterogeneous and host a wide variety of soil-contaminant interactions. These interactions are of major importance for the understanding of the geochemical reactions and mechanisms during electrokinetic remediation, as well for the practical aspects on the removal of subsurface pollution, i.e. predicting the movement and directions, removal efficiencies, etcetera (Reddy *et al.*, 1997; Alshawabkeh, 2009).

In this section the mechanisms of contaminant transport through soil by electroremediation and the possible effects of chemical soil characteristics on the removal of contaminants will be discussed. It will be followed by a short overview of the state of the art. For a more complete literature review, please refer to Page and Page (2002), Alshawabkeh (2009), Reddy and Cameselle (2009), and Yeung (2011).

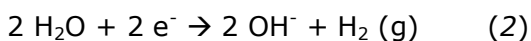
### *Current application*

When a current is applied to any type of electrodes in a water based solution, the principle reaction will be electrolysis of H<sub>2</sub>O (figure 1) (Acar and Alshawabkeh, 1993). At the anode the following reaction takes place



The oxygen atom of the water molecule principally provides the electrons, resulting in an oxidizing environment.

At the cathode electrons are available in excess, creating a reducing environment. The following reaction occurs:



As can be seen from the above chemical reactions, H<sup>+</sup> is produced at the anode, whereas OH<sup>-</sup> is generated at the cathode. These ions will start to move through the soil as induced by the application of an electrical current (see *Mechanisms for contaminant transport* section below) affecting the pH of the pore water of the sample in between the electrodes. The infiltration of the electrolyte solutions into the soil will affect soil chemistry and the removal of any constituent from the soil (see *pH and buffer capacity* section).

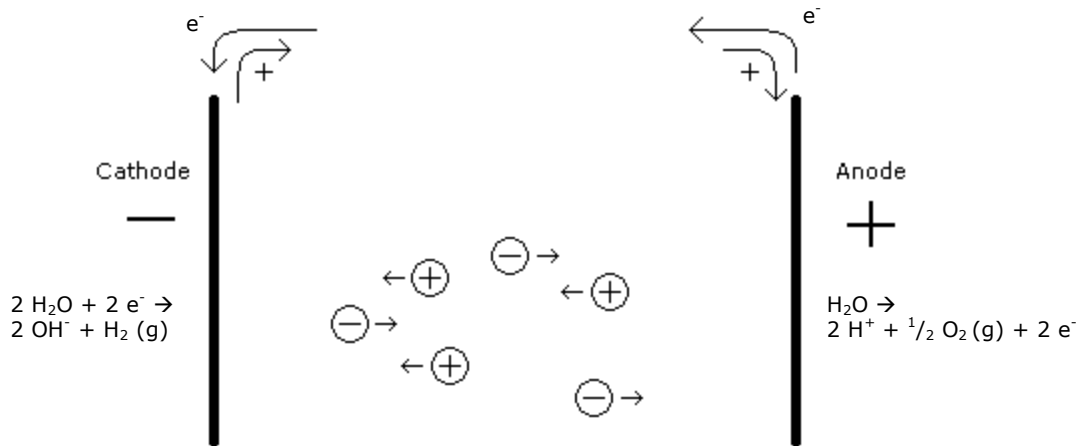


Figure 1: Schematic drawing of current application over electrodes placed in a water based solution

### *Mechanisms for contaminant transport*

There are four principle mechanisms of contaminant transport under an applied electrical field (Probstein and Hicks, 1993; Acar and Alshawabkeh, 1993): (1) electromigration, i.e. the movement of an ion in solution due to the electrical current; (2) electroosmosis, i.e. the movement of water with respect to the solid particles and matrix of the soil; (3) electrophoresis, i.e. the movement of charged solid particles relative to the solution; and (4) molecular diffusion of constituents in solution.

Electromigration (1) is the movement of charged species in a solution due to the electrostatic attraction by the electrodes. This results in anions that will be attracted towards a positively charged anode. Cations will be drawn towards the negatively charged cathode. The velocity of electromigration  $v_{em}$  is given by the relation

$$v_{em} = u_i |z_i| FE \quad (3)$$

with  $u_i$  being the ionic mobility of species  $i$  in solution;  $z_i$  the valence of species  $i$ ;  $E$  the applied potential gradient; and  $F$  Faraday's constant. In porous media such as soils  $u_i$  is a macro parameter and should incorporate soil specific properties such as porosity and tortuosity (Acar and Alshawabkeh, 1993).

With the electromigration of ions, the water incorporated in the ion hydration shell will move along. This will create drag force on the water molecules surrounding the moving ions, pulling the water and its constituents along (figure 2). This induces the movement of water: electroosmosis (2).

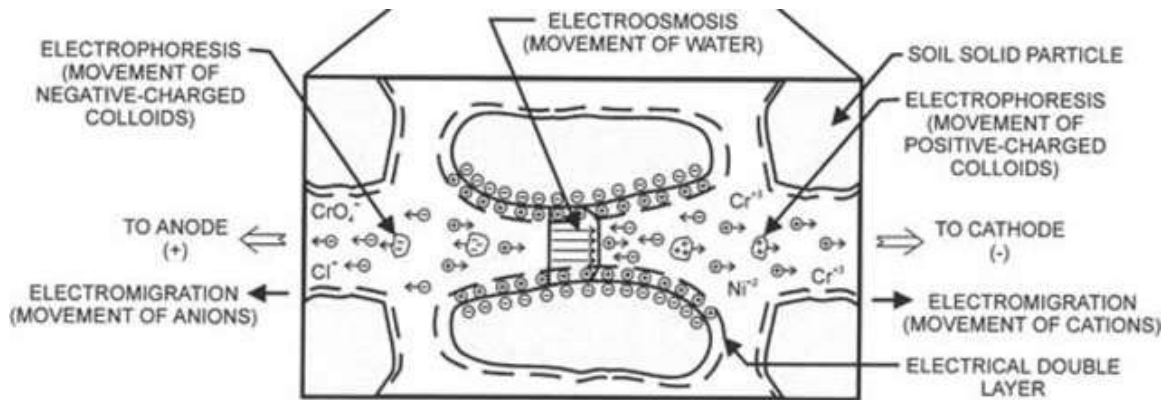


Figure 2: Overview of the mechanisms occurring inside the pore space during electrokinetic remediation. Source: Reddy et al. (1997)

The formula that describes the volumetric flow rate of water by electroosmosis is as follows (Yeung, 2011):

$$Q_e = k_e EA \quad (4)$$

where  $Q_e$  is the electroosmotic volumetric flow rate;  $k_e$  the electroosmotic conductivity coefficient; and  $A$  the surface through which the current is applied.

Various models have been proposed in order to define the value for the conductivity coefficient  $k_e$  and the directly related electroosmotic water velocity  $v_e$ . The Helmholtz-Smoluchowski equation is the most commonly accepted model (Mitchell, 1993; Eykholt and Daniel, 1994). This equation relates the velocity of electroosmosis to the properties of the fluid and the solid surface:

$$v_e = (- (D\epsilon_0\zeta) / \eta) * E \quad (5)$$

where  $D$  is the dielectric constant of the fluid medium;  $\epsilon_0$  the permittivity of a vacuum;  $\zeta$  is the zeta-potential, i.e. the electrical potential at the slip plane of the solid particle double layer and the ions in solution (Eykholt and Daniel, 1994); and  $\eta$  the viscosity of the fluid medium.

Due to the internal mineral structure of clay minerals, a charge deficit is apparent at the particle surface. In order to neutralize the charge deficit, the double layer will contain more cations than anions. In a fine grained soil, containing clay minerals, the solid particles will be, mostly, negatively charged. If electroosmosis occurs due to the movement of ions, the excess cations over anions in the double layer will generate a net flow of water in the direction of the cathode. The opposite may occur if the solid particles are positively charged. Since clay mineral soil particles are, at pH values > 4, generally negatively charged, movement of cations will create most drag force, resulting in a net flow of water towards the cathode (Mitchell, 1993).

Electrophoresis (3) is the movement of charged particles, induced by the electrostatic attraction generated by the electrodes. Since there are hardly any free floating particles available in compacted soils, this mechanism is considered to be of minor importance in soil systems (Acar and Alshawabkeh, 1993).



The driving force behind molecular diffusion (4) and the diffusive flow of constituents is a chemical potential gradient, i.e. concentration differences (Mitchell, 1993). This process is a general process, in contrast to the above transport mechanisms that will only occur in a soil system with an electrical current applied. Typical values for the above mechanisms in clays are presented in table 1.

Table 1: Typical values for the parameters of the mechanisms that play a role during electroremediation in clays. *Adapted from Mitchell (1993).*

parameter	symbol	minimum	maximum	units
hydraulic conductivity	$k_h$	$1 * 10^{-11}$	$1 * 10^{-6}$	m/s
electroosmotic conductivity	$k_e$	$1 * 10^{-9}$	$1 * 10^{-8}$	$m^2/Vs$
diffusion coefficient	$D$	$2 * 10^{-10}$	$2 * 10^{-9}$	$m^2/s$
ion mobility	$u$	$3 * 10^{-9}$	$1 * 10^{-8}$	$m^2/Vs$

The equation relating the ionic mobility to the molecular diffusion coefficient is known as the Nernst-Townsend-Einstein relation and is defined:

$$u_i = (D_i F) / (RT) \quad (6)$$

where  $D_i$  is the diffusion coefficient of species  $i$  in solution;  $R$  the gas constant; and  $T$  the absolute temperature (Acar and Alshawabkeh, 1993). Both the effective ionic mobility and effective diffusion coefficient are macro parameters and include porosity and tortuosity of the porous medium.

#### *Soil mineral and pore water solution composition*

The mineral clay content of soils is an important parameter for electroosmosis to occur. Only a few percent clay might already induce electroosmosis (Grundl and Michalski, 1996) contributing to the total transport of solution and its constituents through the soil system. Electroosmosis, however, might only be observed in fine-grained and low permeable soils. A highly permeable soil will create the ability for the hydraulic force to counteract the electroosmotic force; moreover, in a coarse grained soil the double layers do not dominate the pore space.

Calcium carbonate has proven to be a major factor to take into account during electroremediation. Some studies have shown that the presence of carbonate (Suèr *et al.*, 2003) or bicarbonate ions (Hicks and Tondorf, 1994), in pore water is affecting the movement of metals in solution. Its relation to the buffer capacity and metal transport will be elaborated in the *pH* subsection.

The presence of organic matter in soils is another major geochemical factor affecting the transportation mechanisms during electrokinetic remediation. Organic molecules may contain many active surface sites, available for buffering pore water solutions or complexation with heavy metal constituents (van der Perk, 2006). Complexation with dissolved organic molecules may greatly alter the solubility and mobility of metals present in the pore water solution (van der Perk, 2006; Hicks and Tondorf, 1994). The possible effects on pH buffering by organic substances will be treated in the following *pH* subsection.

Aside from organic matter, the presence of various inorganic substances or co-contaminants, such as metalsulfides (Hicks and Tondorf, 1994; Suèr *et al.*, 2003),

metaloxides (Reddy *et al.*, 1997; Suèr *et al.*, 2003), Cr(III) and Cr(IV) co-contaminants (Reddy and Chinthamreddy, 2003), sulfate (Hicks and Tondorf, 1994; Suèr *et al.*, 2003), chloride (Hicks and Tondorf, 1994; Suèr *et al.*, 2003), Al-polymers (Putra and Tanaka, 2011), may have a major effect on the mobility and solubility of metals.

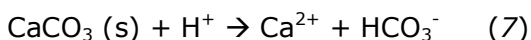
#### *pH and buffer capacity*

The pH of the soil and pore water is of great importance for the speciation, precipitation and dissolution and therefore the mobility of metals in soil (Acar and Alshawabkeh, 1993; Hicks and Tondorf, 1994). Depending on the characteristics of specific metals present in the soil, a change in pH may lead to dissolution, precipitation or complexation. Metals having a low solubility and that are available in solution may form precipitates at changing pH. Precipitates may clog soil pores, inhibiting electroosmotic and electrokinetic movement. Precipitated metals will be immobile and therefore removal from the soil will be hard to accomplish (Hicks and Tondorf, 1994; Reddy, 2010).

The buffer capacity of the soil is determined by the amount of protons the soil may take up before changing the pH of the solution. Protons can either be taken up or released by cation exchange, by protonation and deprotonation of carboxyl groups at the surfaces of organic substances, or by dissolution of various constituents present in the soil (Sposito, 2008).

Cation exchange is the ability of a soil to exchange protons and other cations present in the pore water with the surfaces of soil particles. This may occur at the surface of clay minerals, organic matter and metal(hydr)oxides (van der Perk, 2006). The cation exchange capacity of a soil (CEC) is determined by the availability of these surface sites. If acid is added to the pore water, cations situated at the cation exchange sites of soil particles will compete with H<sup>+</sup> for adsorption at these sites. Protons will exchange with the available cations, of which Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Al<sup>3+</sup> are the most important cations, depending on the soil type (Sposito, 2008).

Another contributor to pore water buffering is the presence of calcium carbonate (CaCO<sub>3</sub>) in the soil. On reaction with H<sup>+</sup>, carbonate will dissolve, releasing bicarbonate (HCO<sub>3</sub><sup>-</sup>) and calcium (Ca<sup>2+</sup>) into solution.



This reaction will continue to take up protons as long there is CaCO<sub>3</sub> available, preventing the solution to acidify. The highest buffer capacity of this buffer is around neutral pH values.

A third buffer might be present in soil in the form of organic compounds such as humic and fulvic acids, which are widely available in organic rich soils. In contrast to the buffering by cation exchange and dissolution of carbonates, these organic acids will keep the pH at lower values, around pH = 3 (Sposito, 2008).

If present, the dissolution of Al-hydroxides and aluminosilicates will add to the buffering of the pore water solution as well. The maximum dissolution of hydroxides will occur around pH = 3 - 6. The buffer capacity of this process, is, however, an order of magnitude smaller than the buffer capacity due to protonation and

deprotonation of humic substances (Sposito, 2008) and therefore negligible if organic matter is present.

Aside from the effects on precipitation and dissolution, pH also plays a significant role in the surface charge of solid particles, e.g. Al, Fe and Mn (hydr)oxides (Sposito, 2008; Mitchell, 1993). Depending on the surface charge, ions, such as metal contaminants, will be attracted or repelled from mineral surfaces. Their mobility in pore water will be greatly affected by attraction and adsorption by charged surfaces (Yeung *et al.*, 1997). Two main factors are involved in the net surface charge of soil particles: (1) structural charge; (2) pH.

The structural charge (1) is applicable to clay minerals. The structural charge of clay mineral particles is inherent to their mineral structure and therefore not dependent on the pH of the surrounding pore water solution. Clay minerals may have various isomorphous substitutions of metals (van der Perk, 2006), that result in an internal charge deficit, rendering the clay mineral particles with a negative structural charge. Contrary to the internal charge of clay minerals, the surface charge of organic molecules and metalhydroxides alike, is pH dependent (2). As explained above, not only clay surfaces are capable of exchanging protons, also organic matter (e.g. humic acids) and metalhydroxides have readily exchangeable protons available at their surfaces, e.g. in the form of loose-end mineral structures or active proton exchangeable sites, for example R-OH groups, of organic molecules (Sposito, 2008). Changing pH values, i.e. proton concentrations, in the pore water solution, will force active sites to release or take up additional protons, resulting in a change of the net surface charge of solid particles.

#### *Redox potential*

The initial form and redox state of various heavy metal contaminants can be of influence for their mobility (Hicks and Tondorf, 1994). Different metals can occur in various redox states, depending on the overall redox state of the soil. For example, chromium occurs in natural soil as Cr(III) or Cr(VI) (Reddy *et al.*, 1997; Reddy and Chintamreddy, 2003), of which Cr(III) is generally less soluble and Cr(IV) the more mobile state. The complexes in which the species can be found in solution are either oxyanions, for Cr(VI), and positively charged hydroxides for the more reduced state, Cr(III). This will be of great effect for its behavior in soils during electrokinetic remediation (Reddy *et al.*, 1997). The same principle holds as well for some other, in natural soils abundant metals and metalloids such as Mn, Fe, As, Cu (van der Perk, 2006).

#### *Contaminant ageing*

Ageing of contaminated soil can be an important factor for the mobility of metal contaminants present in soil. Metal contaminants can be adsorbed and incorporated into inorganic and organic substances present in the soil. For example, Ni can be incorporated into kaolinite clay or adsorbed on humic acids (Nachtegaal and Sparks, 2003). It may form stable complexes, increasing with exposure time of the soil to the metal in solution. With ageing of contaminants in soil, co-precipitation and incorporation with inorganic minerals will occur; cavities inside mineral lattices will be filled and solid solutions may occur (van der Perk, 2006; Eick *et al.*, 2001; Ford *et al.*, 1997; Ma *et al.*, 2006). Metals that have been diffused and incorporated into minerals will be less prone to desorption (Eick *et al.*, 2001) and are thus less

available for plants, reducing toxicity levels (Oorts *et al.*, 2006), but are also less mobile, reducing removal efficiencies during remediation attempts.

### *State of the art<sup>1</sup>*

Although the development in the application of electrokinetics on the remediation of contaminated soils has only been recent, the first experiment on electrokinetics was conducted already in 1802 by Reuss (Yeung, 2011). This is considered to be the first experiment in which electroosmosis was observed. In Reuss' experiment, at the bottom of a U-shaped glass tube filled with water, fine quartz powder was put. On each side of the powder, platinum wires were connected to the water inside the tube. With the application of a direct current over the two wires, a rise of water was observed at the cathode side of the setup.

The electroosmosis as observed in the above experiment lead to an interest in the application of an electrical current over a porous medium by various research areas. With the aim of stabilizing hill sides, slopes and the urban subsurface, experiments were conducted on reversing flow directions of groundwater by electroosmosis (Yeung, 2011). In the 1930's an experiment on the application of an electrical current through a soil system has been applied for desalination purposes (Page and Page, 2002). This is considered the first study on the removal of excess concentrations of unwanted substances from the subsurface by electroremediation.

From the extraction of excessive salts from soil, research on the topic of electroremediation has shifted towards the removal of organic and heavy metal contaminants. In the 1980's studies on the removal of heavy metals were conducted, including pilot-scale field experiments (Lageman, 1993; Page and Page, 2002). Plenty of laboratory studies, many of which used spiked and artificial soil samples, have shown removal of heavy metals to be feasible with the application of a direct current through the sample (Alshawabkeh, 2009; Ottosen *et al.*, 2009).

Laboratory setups have been rescaled to fit in-situ removal experiments. These, mainly pilot-scale, field experiments have had various results. Some studies stated to have found removal efficiencies up to 90% (e.g. Lageman, 1993; Yeung *et al.*, 1997; Lageman and Pool, 2009) whilst others are coping with a wide variety of practical issues and unexpected results and behavior of the subsurface (e.g. Miani *et al.*, 2000; Oonnittan *et al.*, 2009; pers. com. Lima *et al.*, 2011). The latter, in part, comes forth from the inability to adequately scale important parameters such as the difference in mobility and availability of metals between spiked soil samples and aged *in-situ* contamination (Oonnittan *et al.*, 2009; Ma *et al.*, 2006). Also, the lack of understanding in the principle mechanisms in the subsurface during electroremediation and the inability of models to handle the complex coupled transport processes occurring during field applications can result in unpredictable behavior in field situations (Yeung, 2011). This implies, as supported by the closing of dr. ir. Loch at the 2011 EREM International Symposium on Developments in Electrokinetic Remediation of Soils, Sediments and Construction Materials at Utrecht University, The Netherlands, that further research should be conducted in

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<sup>1</sup> For an extensive overview on the state of the art of the literature, please refer to literature review articles by Page and Page (2002), Alshawabkeh (2009), and Yeung (2011). Also the book edited by Reddy and Cameselle (2009) provides an extensive review on the literature and overview of the various processes during electroremediation, as well as practical applications and its issues.

understanding the fundamental principles that are applicable to the porous medium during electroremediation, with the aim to obtain sufficient knowledge for analytical modeling on the micro pore scale for predictions on removal and transport.

Although laboratory experiments are yet to prove consistently scalable towards field applications, enhancement methods and more advanced application techniques have been investigated.

Electrolyte enhancement fluids with the aim of improved complexation and mobility of both metals and organic contaminants such as citrate for Pb and Cu (Chang *et al.*, 2010), acetate for e.g. Cu (Chen *et al.*, 2010), EDTA for heavy metals in general (Yeung, 2009; Chang *et al.*, 2010; Reddy and Chintamreddy, 2003), ammonia for e.g. Cu (Chen *et al.*, 2010), Tween 80 for PAHs (Lima *et al.*, 2011; Karagunduz, 2009), among many and with mixed results, have been added to laboratory setups and field situations.

Another explored technique is bio-enhanced electroremediation or electrokinetic-bioremediation (Wick, 2009). It consists of a mix between biodegradation of the organic contaminant and applied electrokinetics. The electroremediation part encompasses the movement of bacteria and nutrients throughout the contaminated porous medium in order to enhance bioavailability and bioaccessibility. Also, other parameters for effective bioremediation of organic pollution may be positively affected by the application of an electrical current, e.g. oxygen availability, subsurface heating, pH changes (Wick, 2009).

The use of electrokinetic barriers has been surveyed and various positive results have been found. Vulnerable areas downstream of pollution sources such as mine tailings have been protected from infiltration by contaminated groundwater by redirecting the flow by electroosmosis (Lynch, 2009). The combination of electrokinetics and a permeable reactive barrier downstream of a pollution source on a bench-scale test lead to enhanced removal of TCE and additional adsorption of Cd onto the reactive barrier (Chung and Lee, 2007). Another result on the idea of an electrokinetic barrier is the so-called electrokinetic biofence, developed by Lageman and Pool (2009). This fence is a combination of an electrokinetic barrier with bio-enhanced electroremediation by injecting additional nutrients. The barrier is placed downstream of a contaminant source and nutrients are injected just upstream of the barrier for optimal distribution of the nutrients for the degradation of the organic contaminant.

Also explorations have been made on the subject of the supply of an electrical current into the contaminated soil system. This includes electrode spacing and setup, electrode design and semi-permeable ion selective membranes (Alshawabkeh and Yeung, 1999; Yeung, 2011), and pulsed current treatment (Ryu *et al.*, 2010). A 2-dimensional electrode setup rather than a 1-D setup may be installed if a non homogeneous potential gradient is necessary, for example for the treatment of specific highly contaminated spots. Ion selective membranes may be useful to install for avoiding penetration of, e.g.  $\text{OH}^-$  generated by the cathode (Alshawabkeh and Yeung, 1999). Pulsed application of the electrical current into the system is demonstrated by a bench-scale experiment by Ryu *et al.* (2010). Overall removal percentages were low throughout the experiment, but pulsed application did result in an enhanced removal efficiency of Cd and Zn from a mining waste area soil sample.

## Materials, methods and experimental

### *Sample description*

The contaminated soil is a mixture of removed soil from 2 sites in the Netherlands. The first originates from the floodplains of the Meuse, close to the city of 's Hertogenbosch, Noord Brabant. The major part of the mixture, however, comes from a small river, the Esschestroom, at Oisterwijk, Noord Brabant. In this area tanneries and zinc smelters were active in the past.

Before application in this research, the bulk soil, as it has been removed from the site, has been pretreated with a soil washing installation. This pretreatment consists of density and particle size difference based separation of the size fractions. After the treatment, the residual sludge should contain particles with a maximum size of 50  $\mu\text{m}$  only. Due to this density and particle size difference method, the sludge is enriched in organic matter. The principle behind this is that most contaminants are mainly attached to both the organic material and clay parts. Therefore, once the soil is separated in the various fractions, the large, coarse particle size can be reused on-site. The much smaller volume of strongly contaminated clay, silt and organic matter can either be treated or disposed in a landfill. Table 2 gives an overview of the sludge properties.

The second step of the pretreatment process is the dewatering of the sludge. It has passed a press after the addition of both anionic and cationic polyacrylamide to coagulate and flocculate the sludge. This process results in a total moisture content of around 50 wt%. Subsequent to the pretreatment processes, the sludge was analyzed on major metals and organic contaminants and has been stored in open air. The sample as it has been used in this experiment, originates from this final, pretreated bulk sludge. In the first experiment (I), a first batch of the sludge has been used. In the later experiments (II to IV), a second batch has been used. Both initial batches have been analyzed. The results are shown in table 4.

The contaminated sludge is dark brownish, blackish in color. It contains some coagulations of soil material, small roots, pieces of wood, plastics and other bits of organic material. Inorganic material, such as pebbles are present as well. A number of small seedlings have developed on the sludge. In comparison to the first batch of sludge, the second batch contains more organic root material over other soil material and holds less coagulations. It is also less compressible than the first batch.

Before application, the sludge sample is generally homogenized by hand, removing seedlings and pieces  $> \sim 2$  cm in size.

To investigate the possible influence of the polymers present in the sludge, a side experiment was set up. For this side experiment, a soil sample, similar in mineral composition to the contaminated sludge from the river Dommel, was taken from the field, at a location close to De Uithof, Utrecht at the higher parts of the riverbank of the river Kromme Rijn (see table 2 for properties).

In order to simulate contamination, the soil was spiked in the laboratory with various heavy metals. A 2 L glass bottle was filled with 250 mL solution containing Cd, Cr, Cu, Ni, Pb and Zn (see table 5 for concentrations). The heavy metal cocktail together with  $\sim 100$  g of soil was brought into suspension by thoroughly stirring and was left

Table 2: Initial properties of sludge and spiked Kromme Rijn river soil. The latter is denoted KRsoil in the text and tables.

<sup>1</sup>: Over the interval of the initial sample pH down to 3.75.

<sup>2</sup>: Particle size analysis has been done prior to spiking of the KRsoil.

sample	pH	organic matter	dry content	fraction <2 $\mu$ m	buffer capacity <sup>1</sup>	CEC					
						total	Ca	Mg	K	Na	Al
		[wt%]	[wt%]	[wt%]	[ $\Delta$ mmolH <sup>+</sup> / $\Delta$ pH]	[mmol <sub>e</sub> /100g]	[mmol <sub>e</sub> /100g]	[mmol <sub>e</sub> /100g]	[mmol <sub>e</sub> /100g]	[mmol <sub>e</sub> /100g]	[mmol <sub>e</sub> /100g]
sludge	5.73	22	51	3.2	0.26	2.01	1.83	0.05	0.02	0.01	0.09
KRsoil	5.83	6	86	4.2 <sup>2</sup>	0.23	15.32	12.43	2.19	0.40	0.00	0.31

Table 3:

In this table, an overview of the experimental parameters for each experiment is given. The experiments that were executed in the Perspex box are denoted by roman numbers I to IV. The 2 cells of the side experiment are denoted by S1 and S2.

<sup>1</sup>: This is the potential gradient over the sample, as measured by the Ag/AgCl reference electrodes.

<sup>2</sup>: See table 3 for details on the properties of the samples.

Experiment <sup>2</sup>	buffer	NaCl	sample weight	total electrolyte volume	buffer volume	current	current density	output potential	potential <sup>1</sup>	runtime	electrode material	electrode dimensions	sample	sample application details	equilibrium time
		[M]	[g]	[mL]	[mL]	[mA]	[mA/cm <sup>2</sup> ]	[V]	[V]	[h]		[cm]			[h]
I	A	-	4616	9253	1982	6 - 9	0.075 - 0.112	4.25 - 4.45	1.5	191:00	carbon bar	20x1 (lxd)	sludge batch 1	compacted	24
II	B	0.100	3487	3500	1000	40	0.5	6,25 - 7,75	4.55 - 5.80	167:00	carbon bar	20x1 (lxd)	sludge batch 2	compacted	0
III	B	0.032	1650	3200	1000	80	1	9,75 - 13,47	7.5 - 10.1	174:45	titanium grid	5x8 (lxw)	sludge batch 2	saturated	72
IV	B	-	1626	3500	1000	80	1	12.60 - 17.16	9.3 - 12.8	197:45	carbon bar	20x1 (lxd)	sludge batch 2	saturated	72
S1	B	0.064	9.76	350	350	20	1	3.75 - 3.91	-1.413 - 3.68	168:00	gold ring plate	0.1x3 (wxd)	KRsoil	dry; compacted	672
S2	B	0.064	6.20	350	350	20	1	3.19 - 3.34	0.05 - 0.17	168:00	gold ring plate	0.1x3 (wxd)	KRsoil + polymers	dry; compacted	192

Table 4: Initial metal and organic contaminant content of both sludge batches and spiked Kromme Rijn river soil. A blank field indicates the constituent is not measured.

constituent	sludge batch 1	sludge batch 2	KRsoil
	[ppm]	[ppm]	[ppm]
Al	22000	14000	16088
Ca		8900	2325
Cd	24	15	66
Cr	1300	940	584
Cu	340	190	2185
Fe	35000	27000	21530
K		1200	3314
Mg		1700	3622
Mn		460	436
Na		210	413
Ni	65	38	1249
Pb	250	130	2485
Zn	740	490	3070
total C10-C40	990		
total PAH	< 0.050		
BTEX	< 0.25		
Naftalene	< 0.010		

Table 5: Heavy metal concentrations of spiking solution.

constituent	concentration	complex
	[ppm]	
Cd	47	Cadmium chloride
Cr	70	Chromium (III) chloride
Cu	537	Copper (II) chloride
Ni	643	Nickel (II) chloride hexahydrate
Pb	844	Lead (II) nitrate
Zn	1248	Zinc acetate
pH	4.7	

Table 6: Buffer concentrations.

buffer	pH	couple	concentration
			[M]
A	3.97	Na-acetate	0.008
		Acetic acid	0.035
B	3.95	Na-acetate	0.051
		Acetic acid	0.234

to react for 5 days. The solution-soil mix was separated by centrifuging at 2800 rpm for 15 minutes. Around 1 mL and 1 mg of the anionic and cationic polymer, respectively, has been added to the solid phase. The solid material, afterwards, has been put to dry at 65°C and is homogenized using agate mortar and pestle.

### Laboratory setup

See table 6 for details on the buffers and see table 3 for an overview of the characteristics of each experiment. Two different setups have been used in this



research. One setup was used for the contaminated sludge from the river Dommel, whereas the other setup was used for the side experiment on spiked soil and the addition of polymers. The first setup (figure 3 & 4) consists of a Perspex container of 78x20x25 cm (l<sub>x</sub>w<sub>x</sub>h). The dimensions of the sludge in the central container are 23x20x4 cm (l<sub>x</sub>w<sub>x</sub>h). The central container is delimited by glass fiber mesh.

For experiment I and II, the central compartment was filled with sample, firmly compressed and tightened against the sides of the container and the filters. Then, the electrode compartment was filled with demineralized water and buffer solution up to around 2 cm below the surface of the sludge. For the 3<sup>rd</sup> and 4<sup>th</sup> experiment (III and IV), the sample was only compressed lightly. The electrode compartments were slowly filled with demineralized water and buffer solution up to the surface of the sample.

For experiment I, II and IV, bar shaped carbon electrodes were used to transmit electrical current into the system. Titanium, grid shaped electrodes were employed for the 3<sup>rd</sup> run (III). In experiment I, a constant potential gradient of 0.065 V/m over the sample was applied. A constant current of 40, 80 and 80 mA was applied for experiments II, III and IV, respectively.

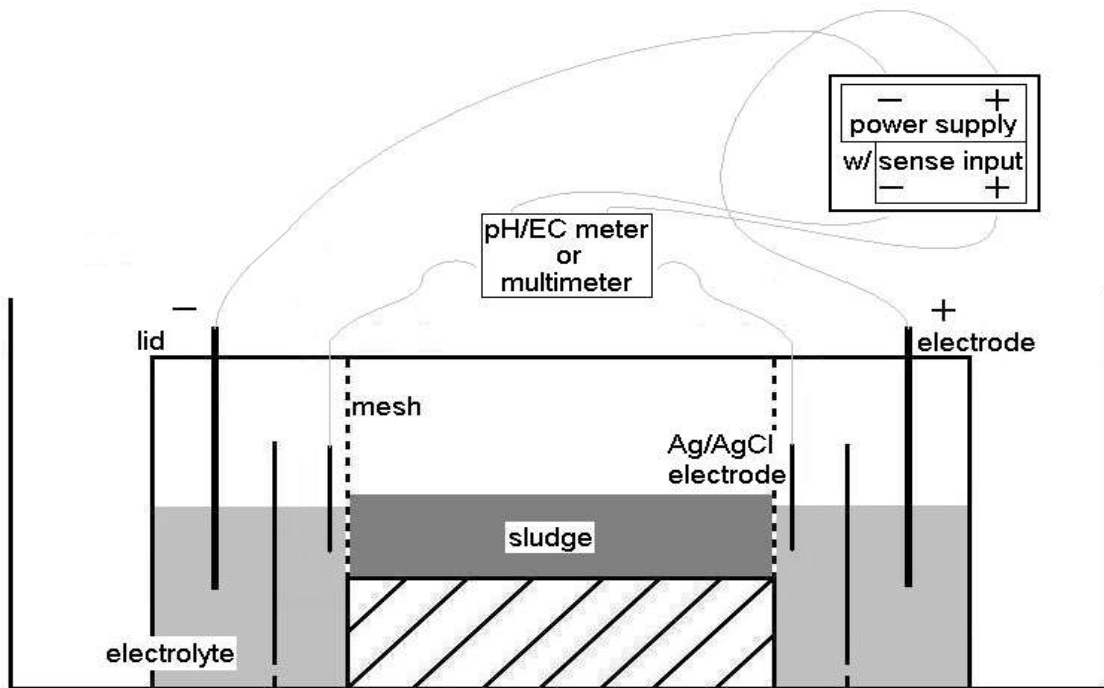


Figure 3:  
Schematic overview of laboratory setup, as used during experiment I. The dimensions of the container are 78x20x25 cm (l<sub>x</sub>w<sub>x</sub>h), the sludge compartment is 23x20x4 cm (l<sub>x</sub>w<sub>x</sub>h).

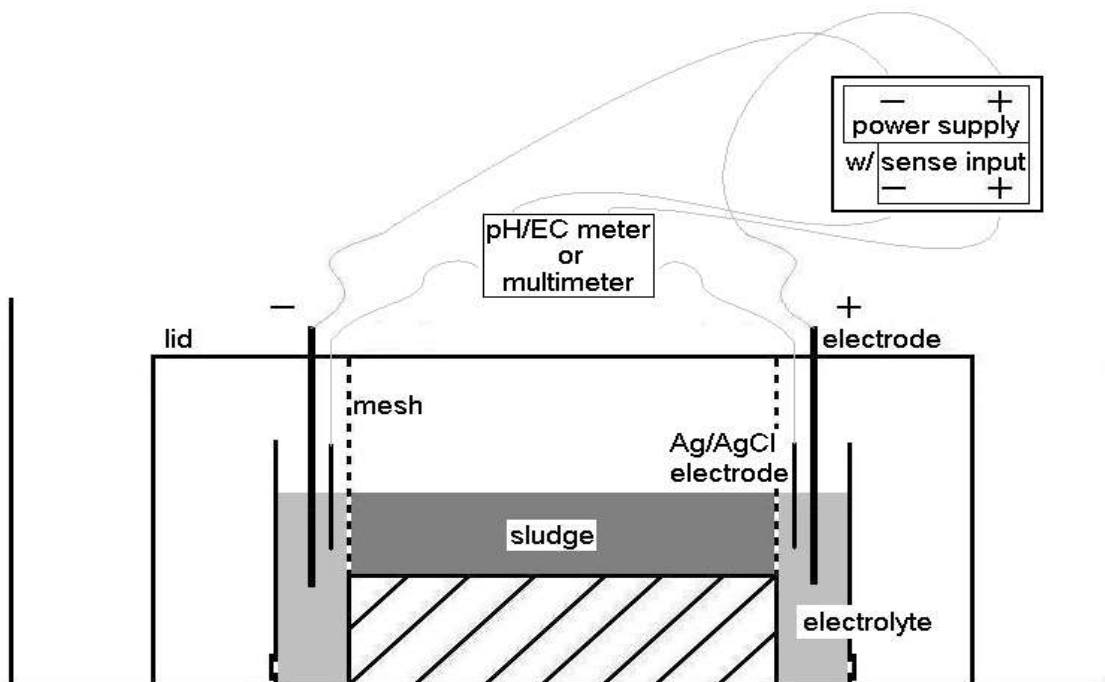


Figure 4:  
Schematic overview of laboratory setup, as used during experiment II, III and IV. The dimensions of the container are 78x20x25 cm (l<sub>x</sub>w<sub>x</sub>h), the sludge compartment is 23x20x4 cm (l<sub>x</sub>w<sub>x</sub>h).

The second setup designed for the side experiment is adapted from Loch *et al.* (2010) (figure 5). It consists of two cylindrical cells made from PVC, with both a diameter and thickness of 8 cm. One cell was filled with dry spiked Kromme Rijn river soil, the other cell contained the same sample, but with addition of two ionic polymers. Each cell holds a central compartment (diameter 5 cm) in which the sample was placed. The total thickness of the sample inside the cell was around 1 mm. The sample was delimited by cellulose filters (0.45 µm) that were in direct contact with a cylindrical shaped plate gold electrode. The electrode is attached to a piece of porous stone and connected to the electrical output via wiring through the lid of the cell. Both the top and bottom lid, with the porous stone attached to it and the sample in between, were firmly screwed onto the central compartment. The lid can hold a small volume of solution. The electrolyte volume was extended by external reservoirs connected via tubing and was flushed by a peristaltic pump at a rate of 10.0 mL per hour.

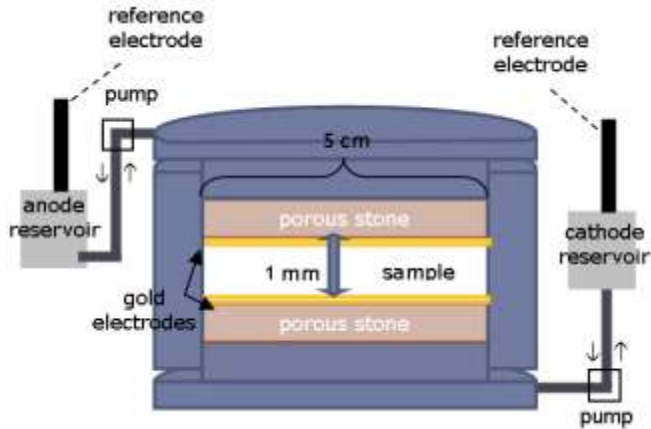


Figure 5:  
Schematic overview of laboratory setup as used during experiment S1 and S2. Source: Adapted from Loch et al. (2010)

### *Sludge and soil ion and elemental content analyses*

The initial heavy metal concentrations of the sludge have been analyzed using *aqua regia* extraction method and subsequently Inductive Coupled Plasma – Mass spectrometry (ICP-MS) analysis on the fluid as produced by the *aqua regia* method. Data on organic matter content and dry weight were produced using Thermogravimetric Analysis (TGA). Analysis on Benzene, Toluene, Ethylbenzene, Xylene and Naftalene (BTEXN) constituents was done using Head Space-Gas Chromatography-Mass Spectrometry (HS-GC-MS), whereas Gas-Liquid Partition Chromatography-Flame Ionization Detector (GLPC-FID) technique was used for the analysis on mineral oil constituents. At the end of each experiment, the sludge compartment of the setup was divided in 5 parts along the direction of the current. Each part of treated sludge was homogenized during sampling. The samples were analyzed on dry weight and organic matter content, as the initial sludge, using TGA. *Aqua regia* extraction method, followed by Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis, was used for elemental determination.

### *Mineral content*

The initial organic matter content and dry weight of both the first and second batch of sludge were analyzed using TGA. Analysis on the overall crystalline mineral content of the second batch of sludge and the spiked Kromme Rijn soil was done using X-Ray Diffraction (XRD) analysis technique.

### *Particle size*

The contaminated sludge was sorted on density differences during pretreatment. The particle size distribution afterwards was determined using a Malvern particle sizer. The spiked river Kromme Rijn soil was analyzed as well, using the same apparatus.

### *CEC analysis*

The CEC of the sludge is determined using a silver-thiourea method (van Reeuwijk, 2002). This method is based on the strong affinity of  $\text{Ag}^{3+}$  ions for negatively

charged soil particles. The silver ions will compete for adsorption on the solid particles with the readily exchangeable cations  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$  and  $K^+$ . The affinity of silver ions for the soil particles is higher than the affinity of the exchangeable cations, indicating desorption of the readily exchangeable cations and adsorption of the silver ions. The sludge has been put into suspension in 40 mL 0.01 M AgCl, 0.1 M thiourea solution. The suspension has been in reaction for 4 hours on a shaker, followed by a 10 minute centrifuging at 2800 rpm. After separation of the solid and fluid, the supernatant solution is analyzed by ICP-OES.

#### *pH and buffer capacity*

The buffer capacity of the sludge was analyzed using HCl. 10 gram of homogenized sludge was mixed with 25 mL, 0.1 M KCl in a 50 mL Greiner tube. An additional 5 tubes were mixed with both 25 mL 0.1 M KCl solution and either 2.5, 5, 7.5, 10 or 12.5 mL 0.1 M HCl. All tubes were placed on a shaker for 24 hours, after which the pH of the sludge-solution mixture was measured using a glass electrode. The buffer capacity of the sample for the side experiment, the soil originated from the banks of the river Kromme Rijn, was determined using 2 g of sample mixed with 5 mL 0.1 M KCl. The mixture was put on a shaker for 1 hour and, 4 times consequently, 0.5 mL 0.1 M HCl was added, up to 2 mL in total.

For determination of the pH of the sludge as it was sampled at the end of each experiment, a 50 mL Greiner tube was filled for 1/3<sup>rd</sup> with sample and 2/3<sup>rd</sup> demineralized water. The tube was thoroughly mixed and placed on a shaker for 2 hours. Subsequently, the pH of the sludge/water mix was determined by using a glass Ag/AgCl electrode.

#### *Sequential extraction of metals*

On both the contaminated sludge and spiked river Kromme Rijn soil, a sequential extraction was done in order to investigate the speciation of metals - 6 fractions were determined in total. The method was carried out *in duplo* and is adapted from Buykx *et al.* (2000), based on the extraction method as developed by Tessier *et al.* (1979). At first, 5.00 gram of both air dry sludge and oven dry soil were weighed in 50 mL Greiner tubes. Following the addition of each extractant, the tubes were placed on a shaker. After the reaction time specified for each step (table 7), the tubes were centrifuged for 20 min at 2800 rpm. Afterwards, the liquid was separated from the solid for analysis with ICP-OES. The remaining solid was used for the next step.

The first step (I) of the extraction procedure is the addition of 30 mL ultrapure UHQ water, to extract the readily soluble metals. Secondly (II), 10 mL 1 M  $MgCl_2$  was added with the purpose of extracting the exchangeable metals. The 3<sup>rd</sup> step (III) will dissolve the metals bound to carbonates using a 10 mL 1 M Na-acetate/acetic acid buffer at a pH of 4.75. Then (IV), 25 mL 0.1 M  $NH_2OH \cdot HCl$  was added to each sample, releasing metals that are bound to Fe and Mn (hydr)oxides. The 5<sup>th</sup> and last step (V) will release the metals bound to organic matter and sulfides. This was done by adding a mixture of 10 mL 30%  $H_2O_2$  and 3.75 mL 0.02 M  $HNO_3$ . After the required reaction time, an additional extractant was added to this step by the addition of 25 mL 3 M  $NH_4$ -acetate as to prevent the released metals to be scavenged by the remaining solid phase. Fraction VI was calculated from the metal concentrations of the sample as done by *aqua regia* analysis minus the concentrations of fractions I to

V. This fraction contains all metals included in primary and secondary minerals that were soluble by *aqua regia*.

*Fluid ion and elemental content analyses*

Before and during each experiment, the processing solution was sampled and analyzed. ICP-OES analysis was used for elemental determination, where IC analysis was done for producing data on major anionic constituents. Total DOC content was analyzed as well.

Table 7: Overview of the fractions and extractants of the sequential extraction method.

Fraction #	Extractant	Concentration	Reaction time [h]	Fraction
I	UHQ water	30 mL	44:00	in solution
II	MgCl <sub>2</sub>	10 mL 1M	2:15	exchangeable
III	Na-acetate/Acetic acid	10 mL 1M	3:30	carbonates
IV	NH <sub>2</sub> OH HCl	25 mL 0.1M	17:00	Fe & Mn (hydr)oxides
V	H <sub>2</sub> O <sub>2</sub> + HNO <sub>3</sub>	10 mL 30% + 3.75 mL 0.02M	71:00	organic matter & sulfides
	NH <sub>4</sub> -acetate	25 mL 3M	1:30	scavenging prevention
VI	residual			mineral inclusions

## Results

### *Sequential extraction*

For the characterization of both the contaminated sludge and the spiked soil sample, a sequential extraction has been conducted. The extraction provides an overview of the distribution of the metals present in the sample. The distribution of the metals in the various fractions as generated by the sequential extraction may provide some insight in the binding, or mobility, of the metals present in the sample. The first extraction steps will release the more readily soluble and more mobile metals, whereas every sequential step will release the more firmly attached or incorporated metals. Refer to table 7 in the above *Materials, method and experimental* section for an overview of the fractions extracted by this procedure.

The metal distribution of the contaminated sludge is shown in figure 7. All metals, except for Cd, were mainly present in the residual fraction. Ca and K were the only species available in the water soluble phase. Almost 20% of the total fraction of Ca and Cd was present in the readily exchangeable phase. In addition, K and Ni were available in this fraction as well, however in minor percentages of their total distribution only. Ca, Cd and Zn, were located significantly in the carbonate fraction, besides Mn, Ni, K, Cu and Pb that were occurring in this fraction in minor quantities only. Mn, Zn, Cd and Ca were mostly present in the oxide fraction of the sludge. Minor amounts of K, Ni, Fe and Pb were found in the oxide fraction as well. Besides the residual fraction, Cr was only found in the oxidizable organic/sulfide fraction. Significant percentages of Cu, Pb, Ni, Zn, Al, Fe, Cd and Mn were present in the oxidizable part of the sludge as well.

The results of the sequential extraction of the spiked soil are presented in figure 8. The residual phase is the most important fraction in which Al, Fe and K were situated. Cd, Ca, Mn, Zn and Ni were significantly present in the water soluble fraction. Together with Pb and Cu and Cr to a lesser extent, they were also highly present in the exchangeable fraction. Excluding Al, Fe and K, all metals were present in the carbonate phase, ranging from around 5% up to 20% of their total mass. All metals, except for Al were present to some extent in the oxide fraction of the sludge, with Zn, Mn and Cu being the most significant metals. Cr and Cu were significantly present in the organic/sulfide fraction, 46 and 37%, respectively, together with minor percentages of Pb, Ni, Zn and Mn.

### *Experiment II*

Experiment II was conducted to investigate the electromigration of heavy metal contaminants in pretreated sludge. It was performed in the Perspex box setup using carbon bar electrodes, a constant current of 40mA and had a total runtime of 167 hours. Refer to table 3 for more details of this experiment.

Figure 6 represents the voltages applied for each experiment. Experiment II is given in blue. A decrease was visible during the experiment with exception of a small increase during the last 48 hours. The difference between the output voltage and the potential over the reference electrodes (ref-ref) remained equal in time.

The results on the removal of metals from the sludge after treatment are given in table 8. The pink lines in figure 7 represent the total removal after experiment II as well. Metals that showed removal < 0% are not included in the metal distribution figure (figure 7).

Cu is the only contaminant metal that showed a net extraction from the sludge after the second (II) experiment. As can be seen from figure 7, this removal percentage corresponds to the organic/sulfide fraction. Non contaminant metals Ca, Mn and Fe were also extracted from the sludge. Where Ca removal coincided majorly with the water

soluble fraction, Mn extraction corresponded to the oxide fraction, and Fe to the organic/sulfide fraction.

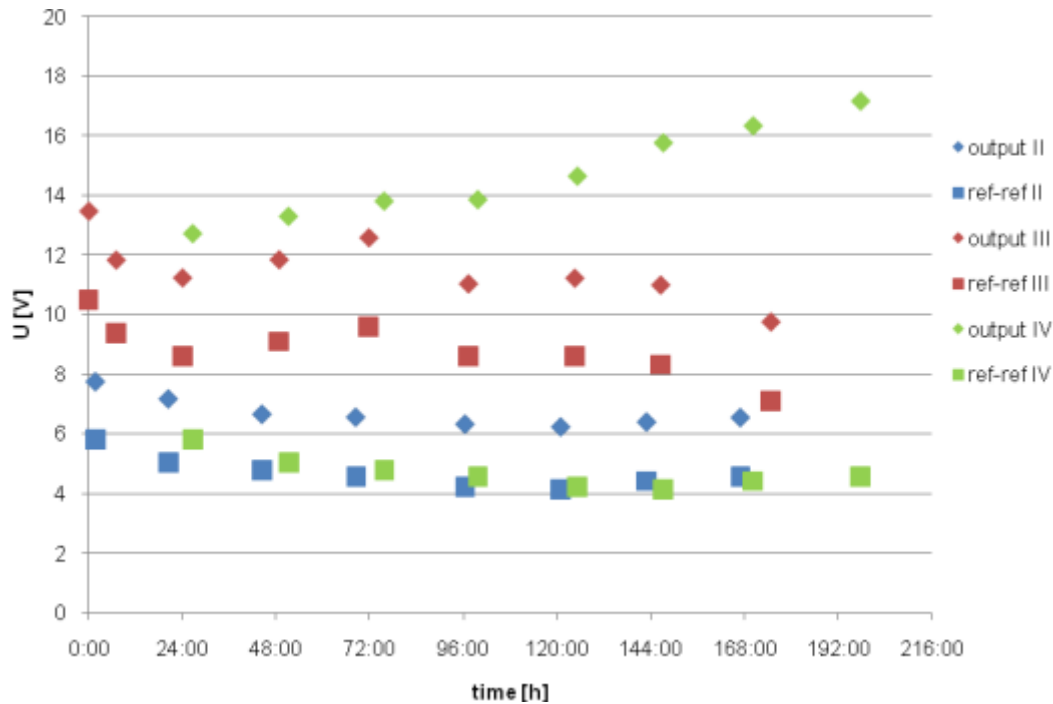


Figure 6: Voltages applied during each experiment. Output represents the output given by the power supply; ref-ref indicates the voltage over the double junction reference electrodes. Refer to figure 4 for the laboratory setup.

Table 8: Removal percentages of metals from the contaminated sludge sample after treatment.

constituent	experiment		
	II	III	IV
Mn	7	43	38
Ca	8	39	25
Zn	0	23	16
Cd	0	21	16
Cu	10	15	0
Ni	-2	9	1
Fe	3	8	-5
Pb	-11	9	-18
Cr	-3	1	-15
Mg	-6	-2	-41
K	-8	-1	-3

Figures 9 and 10 illustrate the removal of each species from the sludge per sample. Cd was not removed from the sludge, but it showed redistribution with an increase in section 2 and a decrease in the section closest to the cathode (section 5). The negative removal percentage of Cr indicated enrichment throughout the sample. Only section 5 contained a relative concentration  $< 1$ . For Cu, general removal occurred and all sections demonstrated values  $< 1$  for  $C/C_0$ , with the lowest value at section 1 and 5 and the highest in section 2. Ni concentrations after treatment are slightly higher than the initial concentration. Section 5, however, did illustrate a removal of Ni. Except for the section closest to the anode (section 1), Pb showed a negative removal percentage throughout the sludge after

treatment. Overall, comparable to Cd, no Zn was removed after treatment. At the cathode side (section 5) most Zn was removed, whereas enrichment was found in section 2.

A general loss of Ca from the sludge was observed after experiment II, with lowest concentrations in the section closest to the anode (section 1, figure 10). Both K and Mg were enriched in the full sample, with maximum relative concentrations in the 3<sup>rd</sup> and 4<sup>th</sup> section. Mn is one of the 4 components that exhibited overall removal and was removed most in both sections closest to the electrolyte solutions, section 1 and 5.

The pH of the sludge samples is visualized in figure 11. In the section closest to the anode (section 1) the observed pH was lowest: pH = 5.11. The other sections demonstrated pH values between 6.6 and 6.2.

Refer to the appendices for figures of the dissolved metal, anion and DOC concentrations in the anode and cathode electrolyte compartments (page 50).

Figures A.1 and A.2 visualize the data on the metal concentrations in the electrode compartment solutions over time for experiment II.



metal distribution; sludge

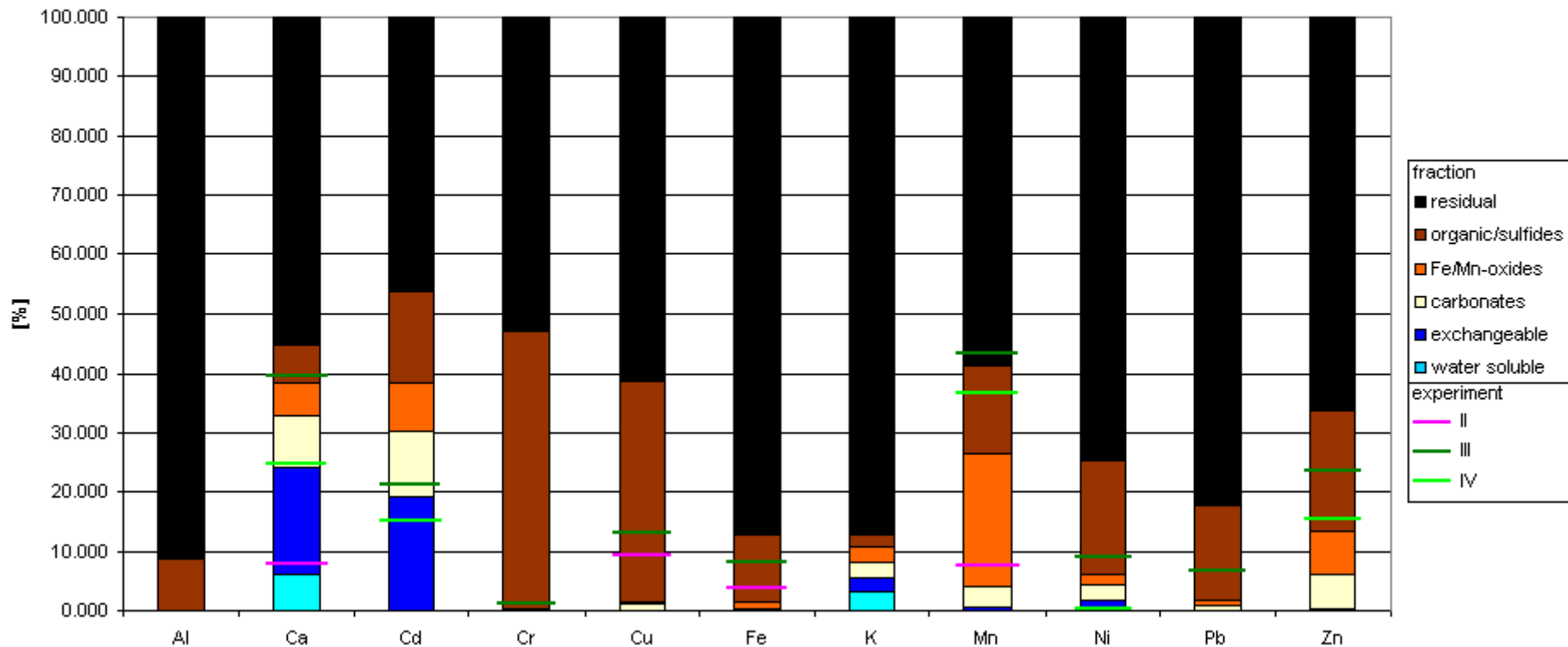


Figure 7: Metal distribution of the contaminated sludge generated from sequential extraction data. Removal per experiment is visualized using colored bars. These represent the total removal percentage after treatment, as is presented as well in table 8.

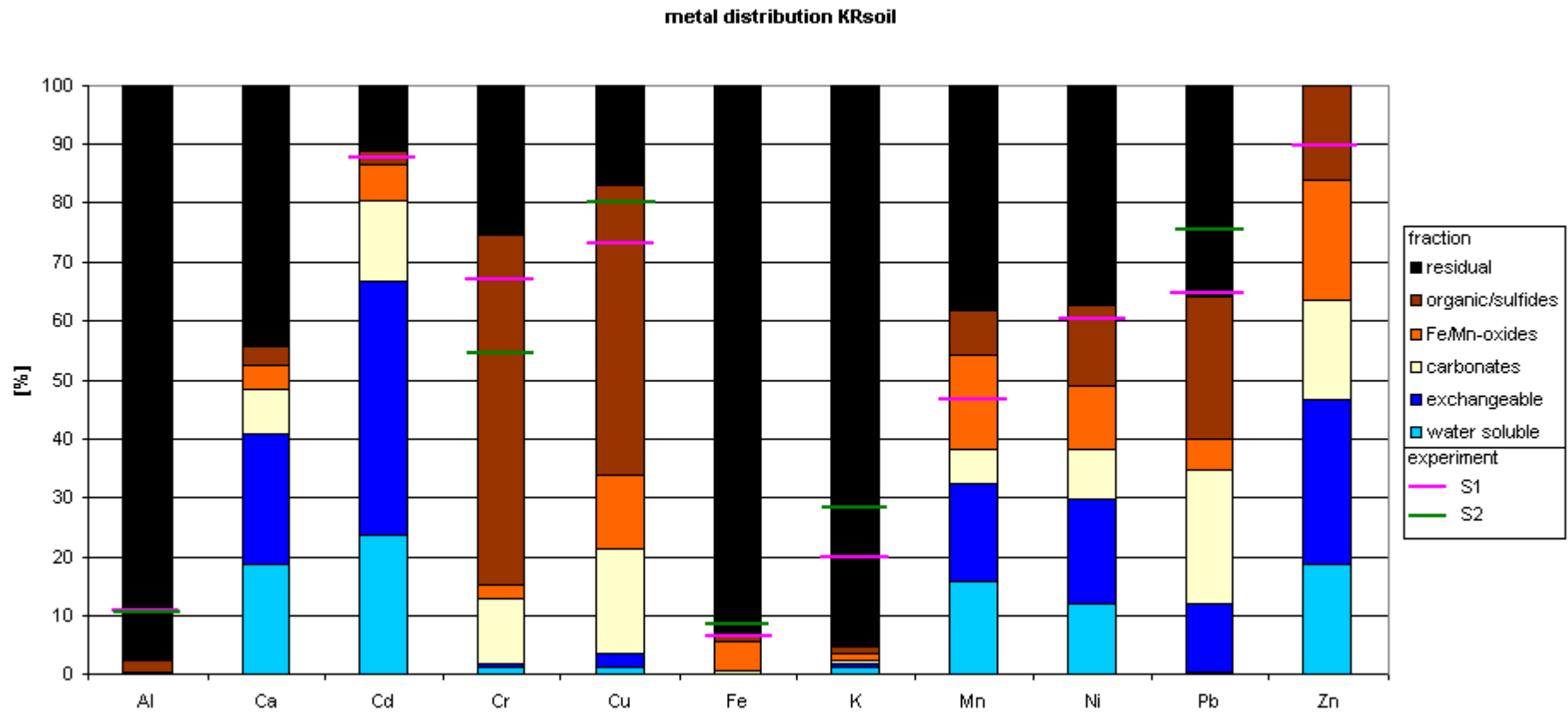


Figure 8: Metal distribution of the KRsoil generated from sequential extraction data. Removal per experiment is visualized using colored bars. These represent the total removal percentage after treatment, as is presented as well in table 8.

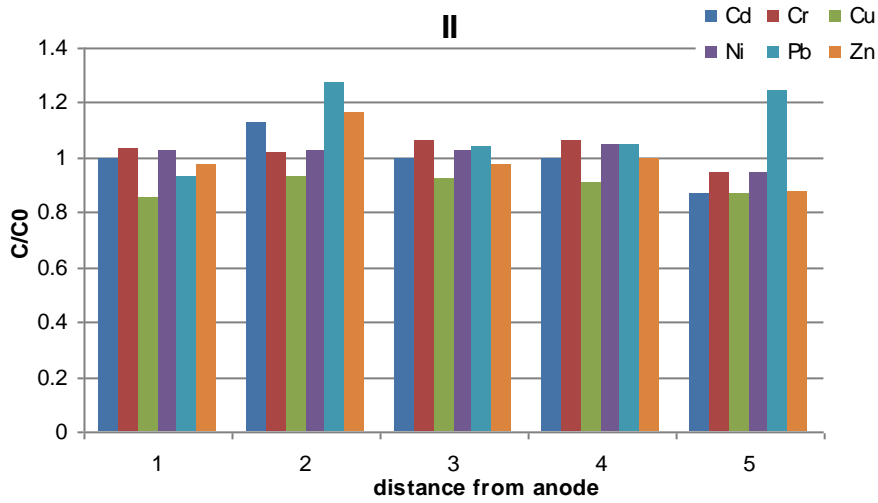


Figure 9: Relative concentrations  $C/C_0$  of heavy metals in the contaminated sludge after experiment II

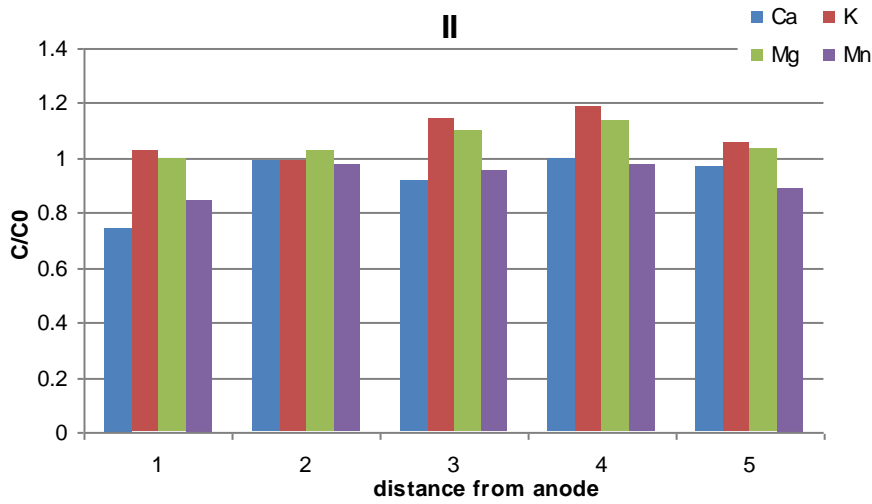


Figure 10: Relative concentrations  $C/C_0$  of non-contaminant metals in the contaminated sludge after experiment II

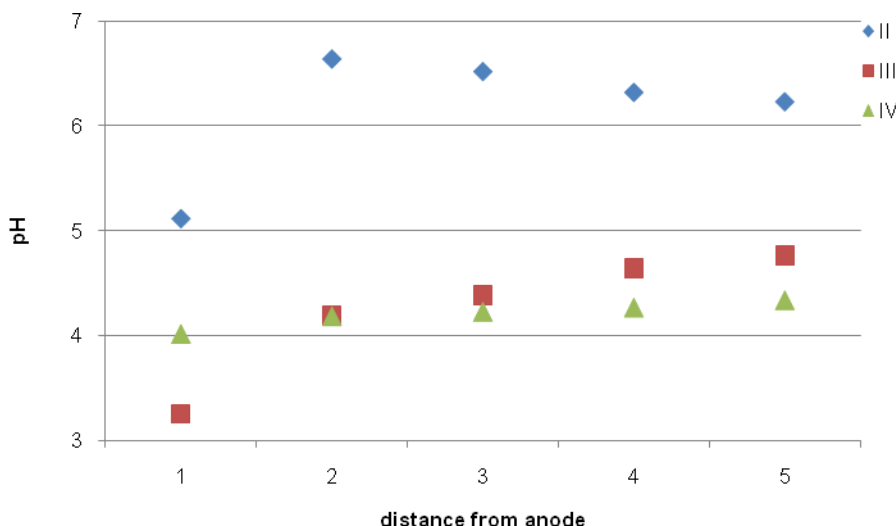


Figure 11: pH values for experiments II, III and IV of the contaminated sludge after treatment

Anolyte concentrations for all heavy metals were equal or below 1 ppm. The concentration of Na was decreased during the experiment to almost half the initial concentration at the end of the run. K, Si, Ca, Fe, and Al showed increasing concentrations throughout the experiment.

In the cathode compartment, Zn is the only contaminant that visibly showed increasing concentrations during the experiment, all other heavy metals stayed below 1 ppm. Na only increased slightly with time. Of the other metal constituents, Ca, Mg, K, Mn, Fe, and Si demonstrated progressing increased concentrations.

Major anion content,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , of the electrolyte fluids are plotted against time in figures A.9 and A.11.  $\text{Cl}^-$  showed diminishing trends in concentration through time in both reservoirs, with the greatest decrease in the anode reservoir. In contrast,  $\text{SO}_4^{2-}$  concentrations increased in both reservoirs, where the catholyte concentrations increased most.  $\text{NO}_3^-$  was only present in the anolyte, sustaining an increasing trend towards the end of the experiment.

Acetate and DOC concentrations are visualized in figures A.10 and A.12. Opposite behavior between the anode and cathode reservoir concentrations were observed. In the anolyte, acetate diminished, whereas in the catholyte concentrations showed a general decrease with time. DOC content of both reservoir solutions demonstrated a trend equal to the acetate data.

### Experiment III

In this experiment a constant current of 80mA has been applied using titanium grid electrodes with the aim of enhancing the removal of contaminants and comparing the efficiency of the electrode material. Table 3 contains more details on the experiment.

Table 8 illustrates the removal percentages of the metal constituents from the sludge and the dark green lines in figure 7 illustrate the removal in framework with the metal distribution.

The voltages applied for each experiment are illustrated in figure 7. Red color represent experiment III. An overall decrease in time was demonstrated. Voltages over the reference electrodes (ref-ref) and the output electrodes showed similar behavior during the experiment.

Experiment III demonstrated removal of all heavy metal contaminants of which Zn, Cd and Cu showed removal percentages of >15%. Ni, Pb and Cr were extracted during treatment and showed removal percentages < 10%. The extraction percentage of Cd corresponded to the carbonate fraction, whereas removal of the other contaminant metals coincided with the organic/sulfide fraction. The non-contaminant metals Mn and Ca showed highest removal of all metals, and were corresponding to the residual and organic/sulfide fraction, respectively. Also, some Fe was removed and removal coincided with the organic/sulfide fraction.

Figures 12 and 13 illustrate the concentrations of metals in the sludge at the end of experiment III. Removal of Cd throughout the whole sludge compartment was observed, with lowest relative concentrations at the section closest to the anode (section 1) and the highest in section 5. Cr removal was marginal and mainly redistribution took place. In section 1 an enrichment was found, whereas the other sections values for  $C/C_0$  were <1. A general extraction of 15% was demonstrated for Cu. The lowest relative concentration was observed in the central section (section 3). Ni showed removal from sections 1 to 4, and a slight enrichment in section 5. A decrease in Pb concentration was observed in the central sections 2 to 4. Both sections 1 and 5 did not show any concentration difference. With the highest removal percentage of the contaminant metals (23%), Zn demonstrated values <1 for  $C/C_0$  throughout the whole sludge, which was lowest in section 1.

With Ca removal of almost 40%, all sections of the sludge showed  $C/C_0$  values < 1 with an increasing trend towards the cathode. Relative K concentrations remained about equal throughout all sections of the sludge, with most removal from the central section (section 3); the same holds for Mg. Maximum extraction of Mn occurred in section 1, and values for  $C/C_0$  were increasing towards the cathode.

pH values of the sludge after treatment were increasing from anode, pH = 3.25, to cathode, pH = 4.75 (figure 11).

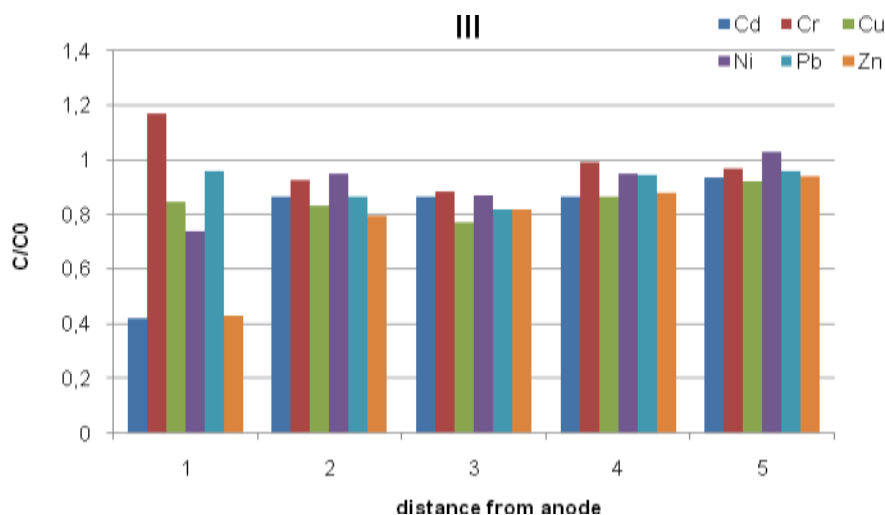


Figure 12: Relative concentrations  $C/C_0$  of heavy metals in the contaminated sludge after experiment III.

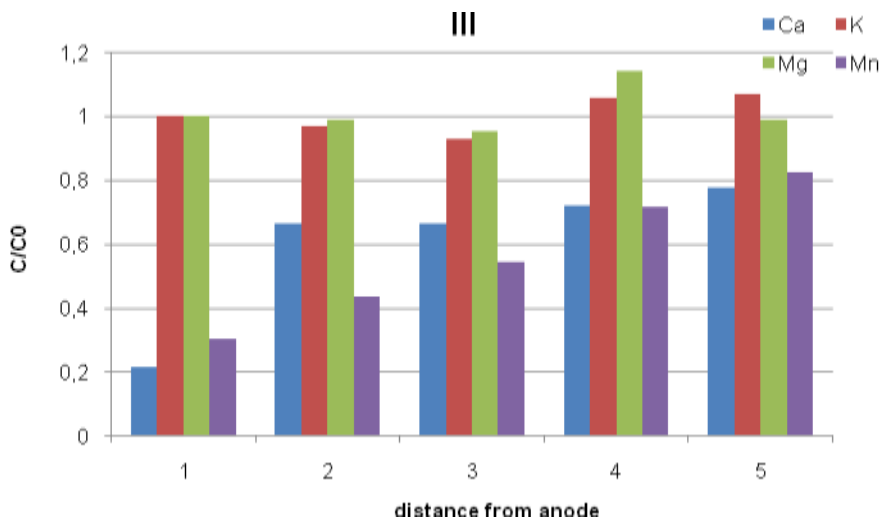


Figure 13: Relative concentrations  $C/C_0$  of non-contaminant metals in the contaminated sludge after experiment III.

Figures B.1 and B.2 illustrate the concentrations of metals in the anode and cathode reservoir fluids of experiment III.

In the anolyte, concentrations of all heavy metals remained below 1 ppm, except for Zn; it increased in time. Non-contaminant metals Na, Ca, Mg, Mn and K showed a downward trend during the experiment. An overall increase in time was observed for Si, Fe and Al.

As were anolyte concentrations, all heavy metal constituents in the catholyte, except for Zn, did not exceed 1 ppm. Zn was fluctuating heavily, with notable drops down to almost 0 ppm. Na, Ca, K and Mg showed an increase in time, whereas Mn, Si and Fe demonstrated fluctuating concentrations, as did Zn.

A plot of the major anions,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , for the anode reservoir solution is shown in figure B.9.  $Cl^-$  concentrations rose continuously in time, where  $NO_3^-$  only increased in the latter half of the experiment. The concentrations of  $SO_4^{2-}$  remained fairly constant during the experiment.

Catholyte anion concentrations are visualized in figure B.11. A concentration decrease in time was observed for  $Cl^-$  and a small decrease of  $SO_4^{2-}$  was found. As in the anolyte,  $NO_3^-$  concentrations increased majorly after half the runtime.

Acetate concentrations and DOC content are demonstrated in figure B.10 and B.12. A decrease in concentrations in the anode reservoir and opposite behavior in the cathode reservoir was observed. The total DOC content closely followed the acetate concentrations in both reservoirs.

#### Experiment IV

Experiment IV was conducted using a constant current of 80mA and carbon bar electrodes in order to compare with the results of experiment III where titanium electrodes were used. Please note that in this experiment, by accident, no NaCl has been added. Refer to table 3 for more details of the experiment.

Table 8 contains the removal percentages of the metals from the sludge after treatment. The bright green lines in figure 7 represent the removal in combination with the metal distribution.

Figure 7 shows the voltages applied during all experiments. Experiment IV is shown in green. The output voltage increased in time, opposite to the ref-ref voltages that illustrated an decrease during the experiment.

Similar to experiment III, Cd and Zn were extracted from the sludge by > 15%. However, no other heavy metals were removed in experiment IV. The removal percentages of Cd and Zn corresponded to the exchangeable and organic/sulfide fractions, respectively. Mn, followed by Ca were the metals that showed greatest removal from the sludge. Their removal percentages coincided with the organic/sulfide and carbonate fraction, respectively.

In figures 14 and 15, the results on the metal content of the sludge are presented. Both extracted heavy metals Cd and Zn are removed throughout the whole sludge, where section 1 exhibited the lowest concentrations. The  $C/C_0$  values for both heavy metals increased towards the cathode in each subsequent section (section 2 – 5). Cr was enriched in all sections with section 3 containing the lowest relative concentration. Cu did not show a net removal, but demonstrated redistribution, where most removal occurred in sections 1 and 3; this holds for Ni as well.  $C/C_0$  values for Pb were > 1 for all sections, with maximum enrichment found in the central section (section 3).

Equal to experiment III, Ca and Mn demonstrated highest removal percentages in experiment IV. Both non-contaminant metals exhibited  $C/C_0$  values < 1 throughout all sections of the sludge. Fluctuating throughout the sections, lowest relative concentrations for Ca and Mn were found in section 1. K was slightly enriched throughout all sections, whereas Mg showed significance enrichment in all sections of the sludge, with section 2 containing most Mg.

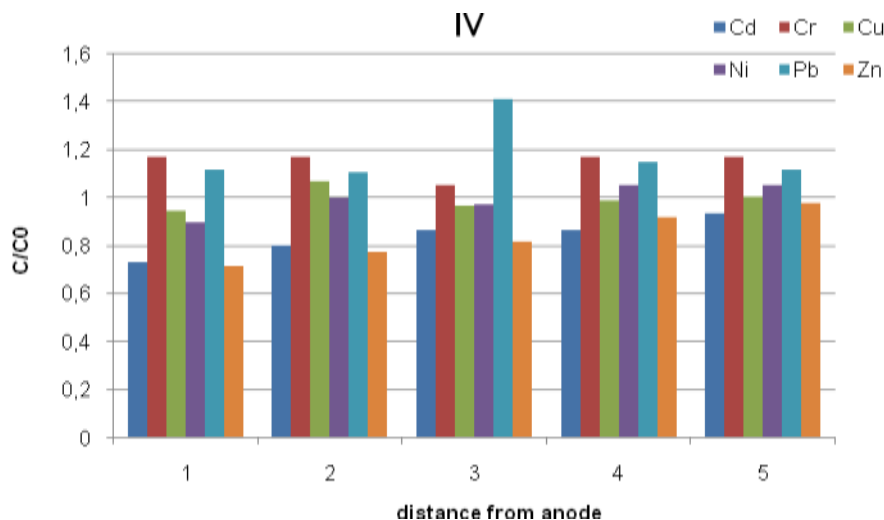


Figure 14: Relative concentrations  $C/C_0$  of heavy metals in the contaminated sludge after experiment IV.

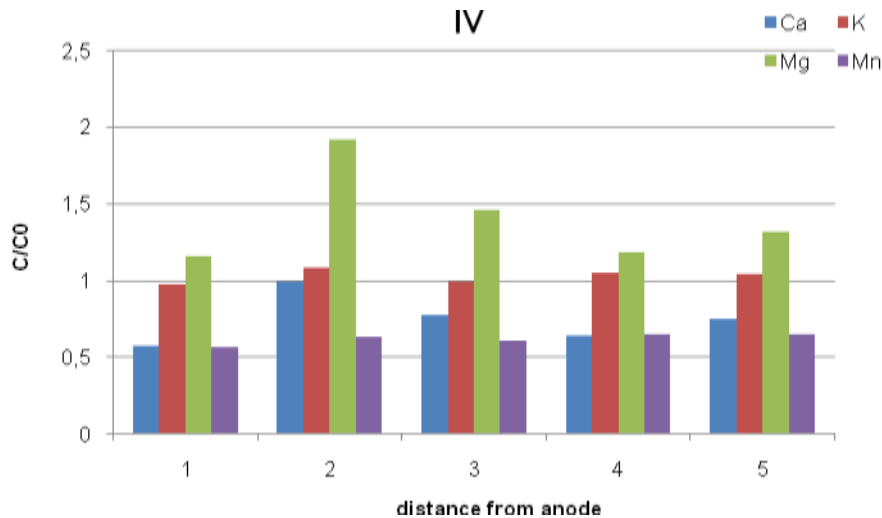


Figure 15: Relative concentrations  $C/C_0$  of non-contaminant metals in the contaminated sludge after experiment IV.

Results on pH are illustrated in figure 11, they ranged from pH = 4, at section 1, to pH = 4.3 closest to the cathode (section 5).

In figures C.1 and C.2, electrolyte metal concentrations are presented. Except for Zn, all heavy metal contaminant concentrations in the anode reservoir were below 1 ppm. Zn showed a decrease during the experiment. Ca, Mg, Na, K, Mn and Al content in the anolyte demonstrated a decrease in time. Both Fe and Si were increasing during the experiment.

In the cathode reservoir, and of the heavy metal constituents, only Zn showed concentrations above 1 ppm, with a maximum half way through the experiment. Na, Ca and K, demonstrated increasing catholyte concentrations in time. Mg, Mn, Si and Fe demonstrated a peak between half way and  $2/3^{\text{rds}}$  in time.

Figure C.9, demonstrates major anion concentrations in the anode reservoir. An overall decrease of both  $\text{Cl}^-$  and  $\text{NO}_3^-$  was visible, whereas  $\text{SO}_4^{2-}$  increased in time. The catholyte (figure C.11) contained decreasing trends for all three anionic species.

In the anolyte, acetate concentrations (figure C.10) exhibited an overall increase during the experiment. An opposite trend was observed in the cathode reservoir (figure C.12), DOC concentrations showed similar behavior to the acetate concentration.

### Experiments S1 and S2

The side experiments S1 and S2 were conducted with a spiked soil sample using a setup different from experiments II – IV (table 3 and figure 5). They were designed for making a comparison in the removal of metals between the spiked soil with (S2), and without (S1) the addition of the anionic and cationic polymers. These polymers were added during the pretreatment of the contaminated sludge in order to extrude water from and compact the sludge. Therefore, similar to the sludge, a soil sample was spiked with the same heavy metal contaminants and addition of polymers to one cell in order to investigate the possible influence of these polymers on electroremediation. For these experiments, removal percentages are generated using



electrolyte concentration data rather than direct analysis on the content of the sludge after treatment.

The removal percentage from the spiked soil after treatment is presented in table 9. The pink (S1) and green lines (S2) in figure 8 represent the removal of the metals from the spiked soil sample in combination with the sequential extraction. Elements that showed removal percentages > 100% are not incorporated in figure 8.

In experiment S1, all heavy metals were removed > 50% and corresponded to the organic/sulfide fraction, except for Pb that was from residual fraction. Ca removal exceeded 500% and removal of Mg coincided with the organic fraction. Removal percentages of Mn, K, Al and Fe corresponded to the residual fraction.

Table 9: Removal percentages of metals from the spiked soil sample after treatment.

constituent	experiment	
	S1	S2
Zn	89	165
Cd	88	195
Cu	73	81
Cr	67	55
Pb	65	75
Ni	59	116
Ca <sup>2</sup>	508	504
Mg	58	80
Mn	46	113
K	20	28
Al	10	11
Fe	8	8

Figures D.1 and D.2 visualize the data of the electrolyte concentrations of cell 1 (S1). The anode reservoir showed an increase in time for Zn and fairly constant concentrations of Pb, Cu, Cr and Ni, however with an initial increase and small fluctuations. Na, Ca, and Mn concentrations decreased in time, whereas K, Mg Al, Fe and Si showed an increase.

In the catholyte, a general rise in concentration was visible in time for all metal constituents, including a small rise for the heavy metal contaminants.

Concentrations of major anionic species are represented in figures D.9 and D.11. In the anolyte of cell 1, all three species, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, demonstrated a general increase. Concentrations of the three species in the cathode reservoir fluctuated during the experiment.

In the anode reservoir an increase in acetate (figure D.10) concentrations was observed through time. The catholyte (figure D.12) showed varying acetate content with an increasing trend. Total DOC concentrations demonstrated a small increase and decrease in the anode and cathode reservoir, respectively. In the cathode reservoir it did not follow the acetate concentrations as was observed in experiments II – IV.

Equal to experiment S1, in S2, heavy metal contaminant removal exceeded 50%, with Cd, Zn and Ni removal > 100%. Extraction of Cu and Cr corresponded to the organic/sulfide fraction, whereas Pb coincided with the residual fraction. Ca and Mn removal percentages were > 100% and Al, Fe and K removal corresponded to the residual fraction.

In figure E.1, metal concentrations in the anolyte of experiment S2 are presented. Cd, Ni, Pb and Zn demonstrated a decrease in concentration, whereas Cr exhibited a slight decrease. Cu concentrations remained equal in time. Increased concentrations were observed for Ca, Mg, K, Al, Fe and Si. Decreasing trends were found for Na and Mn.

<sup>2</sup> It is suspected that an error occurred during the analysis on Ca content of the initial spiked soil.

In the cathode reservoir of cell 2 (S2) (figure E.2), as was observed in S1, an increase of all metal concentrations was exhibited, including heavy metals.

Figure C.9 and C.11 are representing the concentrations of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  in the anode and cathode reservoir. The anolyte contained increasing amounts of all three species, however heavily fluctuating in time. The cathode reservoir showed decreasing concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , and increasing amounts of  $\text{NO}_3^-$ .

Acetate concentrations in the anolyte (figure C.10) showed a general increase in time, again heavily fluctuating. The cathode (figure C.12) contained an overall concentration decrease. DOC content in both reservoirs did not show a significant change in concentrations. It did not closely follow the acetate concentrations.

## Discussion

### *Sequential extraction*

In the results of the sequential extraction a clear distinction was visible in the metal distribution between the contaminated sludge and the spiked soil (figure 7 and 8). In the sludge the residual and the organic/sulfide fractions are the predominant fractions in which the metals were distributed, whereas metals in the spiked soil were found to a lesser extent in these fractions. They were significantly present in the water soluble, exchangeable and carbonate fractions, which are the more mobile fractions.

Since the sludge has been retrieved from a flood plain after years of continuous supply of contaminated water, the metal constituents both present in solution and in solid form have had time to come into equilibrium with the solid particles. As treated in the *background* section, the process of ageing may lead to more stable chemical bonds between the contaminants and the sediment due to the formation and incorporation of metals into the mineral structure and lattice of silicates and carbonates and into organic structures (van der Perk, 2006; Eick *et al.* 2001; Ford *et al.*, 1997; Ma *et al.*, 2006). This has resulted in a higher content of the heavy metals present in the residual and organic phase and less in the readily exchangeable or water soluble fraction of the sludge. Therefore comparison of the results on heavy metal removal from the aged sludge and the spiked soil will not be valid in relation with applied current. However, it demonstrated clearly the effect of aged versus spiked contamination on the removal.

In the contaminated sludge, only Cd and Zn were, besides in the residual fraction, significantly present, respectively in the exchangeable and carbonate fraction or the carbonate fraction only. This may be explained by the fact that both Cd and Zn have high affinities for incorporation in and strong adsorption onto  $\text{CaCO}_3$  minerals (van der Perk, 2006). The overlapping nature of the sequential extraction steps might give an explanation for the major presence of Cd in the readily exchangeable fraction. It can be overestimated and part of the Cd may also be present in the carbonate phase.

Both the initially spiked KRsoil and contaminated sludge demonstrated below neutral pH values (table 3), indicating very low or zero carbonate content. This was reflected in the metal distribution: the carbonate phase was a minor fraction for all metals.

The relatively high amounts of metals that were present in the organic/sulfide fraction might be due to the high affinity of these metals for organic matter (van der Perk, 2006). Also, in the sludge, organic matter was abundant (table 3), providing ample possibilities for complexation of metals with organic matter.

In both samples the metals Al, Fe and K were found predominantly in the residual fraction. This is in agreement with the expectation that these elements are primarily present in the mineral structures of either crystalline clay minerals (aluminosilicates), for Al and K, or ironoxides, for Fe. K is most probably part of the interlayer between clay platelets (Buykx *et al.*, 2000).

A discrepancy in the data was found for the CEC measurements (table 2) and the sequential extraction (figure 7 and 8). The data generated by the CEC analysis showed consistently lower values, a >7-fold difference, for the readily exchangeable

K and Ca. However, the general distribution expectation is in agreement with the CEC results: with the exception of the residual fraction, Ca and K were mostly available in the water soluble and exchangeable fraction. The dissimilarity in data might be due to differences in methodology. The CEC was determined using Ag-thiourea solution with 4 hour reaction time. While the exchangeable phase in the sequential extraction was determined using  $MgCl_2$  extractant for 2:15 hours, subsequent to 44 hours of shaking reaction with UHQ demineralized water. The longer reaction time of the sequential extraction method may have resulted in enhanced release of Ca and K into the supernatant fluid. Also, the overlapping nature of the sequential extraction method, as might be the case with Cd, may have lead to overestimation of the metals present in the exchangeable phase.

### *Removal*

In table 8, the removal percentages of the metals from the sludge for the different experiments are presented. Some elements showed negative removal, i.e. an enrichment, after treatment. This might be due to heterogeneity of the sludge and sampling. During sampling, the sludge has been homogenized before analysis. Not all sludge from each compartment, however, is sampled for analysis. Therefore, an inhomogeneous distribution of metals in the contaminated sludge might lead to over or underestimation of metal removal, possibly resulting in the removal percentages  $< 0\%$  or  $> 100\%$ . Another explanation for negative removal, or enrichment, after treatment might arise from the limitation of the *aqua regia* method. *Aqua regia* is used for the analysis of the solid sludge, both before and after the experiments. It does not dissolve the constituents present in crystalline minerals. Possibly, during treatment constituents might have been redistributed in the solid phase from the insoluble, residual fraction, to a more readily soluble fraction, i.e. metals that were initially not dissolved with *aqua regia*, might have dissolved after the experiment. This will result in higher concentrations in the supernatant fluid after *aqua regia* dissolution and therefore may give negative removal rates. A sequential extraction of the sludge after treatment might give more insight in the possible fraction redistribution that took place during the experiments.

### *Experiment II*

Experiment II was conducted to investigate the electromigration of heavy metal contaminants in pretreated sludge. It was performed in the Perspex box setup using carbon bar electrodes, a constant current of 40mA and had a total runtime of 167 hours. Refer to table 3 for more details of this experiment.

During experiment II, Cu was the only contaminant metal that demonstrated a net removal from the sludge (table 8). Figure 9 showed that not only a net removal took place, also redistribution of Cu occurred. Although Cd and Zn did not show a net removal, redistribution took place as well. This redistribution pattern observed for Cu, Cd and Zn, a decreasing trend in  $C/C_0$  values towards section 5, can give a hint on the transport direction of these metals. The contamination in sections 2 to 5 indicate transport towards the anode (section 5 is closest to the cathode reservoir), and the removal from section 1 might be partly explained by diffusion into the anode reservoir due to concentration differences between the sludge and the electrolyte. Even though Ni and Cr demonstrated removal  $< 0\%$ , the same redistribution pattern was visible. Metal concentrations in the electrolytes, however, are not necessarily in agreement with this redistribution pattern (see below).

By comparing removal with distribution (figure 7), the observed removal percentages did not seem to coincide with the distribution pattern, i.e. the metals that are in the most readily available fractions (water soluble, exchangeable, carbonate) are not the ones that are represented by highest removal rates. For example, no net removal of Cd was observed, despite the fact that it is the only heavy metal that is significantly present in the readily exchangeable and carbonate phase – fractions that are considered from which metals are most easily leachable from solid into solution. This does not imply that the removal percentage as plotted in figure 7 and 8 mean that necessarily only the metals present in these fractions are removed fully. As mentioned above, in order to gain more insight in metal redistribution during treatment, a sequential extraction of the sludge at the end of each experiment can provide relevant information.

In the electrolytes during experiment II no significant increase in metal concentrations was found. With the exception of Zn, all metals remained below 1 ppm (figures A.5 and A.8). According to the data from the sludge analysis, no Zn removal was observed. In table 10 the removal percentages from the sludge, calculated from both the sludge analyses and the metals present in the electrolyte solution are compared. The total amount of Zn present in both the electrolytes is only 1% of the total amount of Zn initially present in the sludge. Therefore it might be very well possible that no net removal of Zn from the sludge was visible in the analysis of the sludge, despite an observed, small, increase in the solution.

For Cu it is the other way around: no Cu has been found in the electrolytes, although analysis of the sludge did show removal of Cu (10%). It may be due to heterogeneities in the sludge, as explained above. But another reason might be that Cu has been removed from the solution by electroplating or precipitation. The latter, however, has not been observed during experiment II. Electroplating, however, due to the redox transformation of Cu(II) to Cu(0), might have occurred at the cathode. Since the electrodes in experiment II are porous graphite bars, the occurrence of electroplating might not have been visible, because of plating taking place inside the pores of the carbon electrode. Therefore electroplating may be an explanation for the Cu missing in the solution.

Table 10: Comparison of removal percentages calculated from both sludge analysis and electrolyte solution results.

constituent	sludge	solution
Cu	10	0
Zn	0	1
Ca	8	7
Mn	7	4
Fe	3	0

The addition of acetate for the buffering of the electrode fluid is another factor that can be of major importance to the extraction and transport of metals from the sludge during treatment. Various heavy metals, e.g. Cd, Cr, Cu, Ni, Pb and Zn, show high affinities for organic molecules, including acetate. The release of organic acids, e.g. humic acids, during treatment may induce formations of dissolved complexes. The addition of acetate to the pool of organic acids in the system increases the availability of organic surface site for complexation. Therefore, the addition of acetate may enhance metal extraction from the solid phase, resulting in improved mobility and possible removal. Moreover, with the addition of NaCl to the electrode solutions, metal-chloride complexes will form during the experiment. So, similar to acetate complexation, enhancement of the extraction of metals from the solid fraction due to metal-chloride complexation might occur. The formation of various complexes may change the valence and mobility of the dissolved metals. From this study, it is impossible to quantify the effect of the above complexation and relate such to the removal and transport of heavy metals observed in the experiment.

In a study by Al-Hamdan and Reddy (2008), redox potential throughout the sample during electrokinetic treatment was below 258 mV and 22 mV, for kaolin and glacial till, respectively. The contaminated sludge sample in this study contains high amounts of organic matter and is submerged during the experiment. This indicates that such a low redox state inside the contaminated sample likely have occurred. It would provide a sufficiently low redox state for Cr to be present in the reduced Cr(III) form. Trivalent chromium will form stable Cr-(hydr)oxides and organic complexes. The organic complexes are very stable and difficult to break and are present over a broad range of pH (van der Perk, 2006). So although Cr is present in major percentages in the organic fraction, it is considered to be very immobile at the redox potential present in the soil – resulting in low or no removal of chromium from the contaminated sludge despite significant presence of this contaminant.

An overall low redox state of the sludge may also have a great effect on the state of Mn. Mn is one of the metals that showed maximum removal. According to van der Perk (2006), at neutral to low pH, manganese is mainly present as  $Mn^{2+}$ . Only at very oxidizing conditions, Mn will be found in the solid Mn(IV)oxide form. The redox state occurring in the sample during treatment will be sufficiently low for Mn to be present in its reduced state Mn(II). So despite part of the initial Mn is in the Mn(IV)-oxide fraction of the sludge (figure 7), it will become more mobile under the influence of the applied electrical current due to reduction to Mn(II).

The redistribution pattern observed for the heavy metal contaminants was also found for Ca and Mn, and K and Mg, although the latter two did not show net removal. This trend in the redistribution for these constituents, however, was opposite to the heavy metal trend. Values were lowest in section 1 (closest to the anode) and rising towards section 4, with again a lower value for  $C/C_0$  in section 5 (figure 10). This may imply movement towards the cathode under influence of possible electromigration and diffusion into the electrolytes from the sections directly in contact with the electrolyte solution.

Increased concentrations were visible, mainly, in the cathode reservoir solution for the extracted, non-contaminant metals Ca and Mn. The calculated removal from the electrolyte concentrations coincided roughly with removal percentages generated by the analysis on the sludge after treatment (table 10).

A drop in voltage towards the end of the experiment can be seen for experiment II (figure 6). This implies that, using a constant current, the resistance of the sample decreased during the experiment ( $U = I \cdot R$ ). It may be due to the additional release of ions into the pore solution and electrode solutions, increasing the ionic strength of the fluid and the conductivity. Throughout the entire experiment, the difference in voltage between the output supply carbon electrodes and the double junction reference electrodes on either side of the sample (figure 4) remained the same (figure 6) – around 25% loss of voltage was observed, possibly mainly due to the polarization occurring at the transfer of current between the carbon electrodes and the electrolyte solution.

### *Experiment III*

In this experiment the constant current was increased to 80mA, in order to be able to see more removal during the experiment. The carbon bar electrodes are replaced

by titanium grid electrodes with the aim of the efficiency of the electrode material. Table 3 contains more details on the experiment.

After experiment III, removal > 15% was shown for Zn, Cd and Cu (table 8). As in experiment II, a clear redistribution pattern was observed for these metals. The pattern, however, was opposite to the pattern observed in experiment II. In experiment III lowest relative concentrations of heavy metals in the sludge were found at the anode side, highest values at the cathode side, indicating movement towards the cathode. The concentration of heavy metals in the electrolyte solutions, as in experiment II, did not reflect the removal found by the sludge analysis.

In the comparison of removal with the distribution pattern (figure 7), no similarities between removal and distribution were found. Cd removal percentage corresponded with the carbonate phase, whereas all other heavy metals that were removed showed association with the organic fraction.

If the removal percentages are converted into the concentrations that should have been found in the electrode solutions (table 11) a discrepancy can be observed. No significant increase in metal content was observed in the electrode solutions. Although expected from the sludge removal results, none of the contaminant metals demonstrated concentrations > 1 ppm (figures B.5 and B.8). Zn showed concentrations > 1 ppm, however, still not comparable to expected values.

Table 11: Expected and measured electrolyte solution concentrations calculated from sludge analysis removal percentages.

constituent	expected [ppm]	measured [ppm]
Zn	106	40
Cd	3	1
Cu	28	1
Ni	3	1
Pb	11	0
Cr	11	1

A possible explanation is the occurrence of precipitation due to high pH, because of buffer exhaustion, in the cathode reservoir during the experiment. At those sampling points in time, whenever a high pH was observed, a drop in metal concentrations was visible (figure B.8). The heavy metal constituents, may have precipitated in the form of metal (hydro)oxides or carbonates. Inside the sludge compartment no precipitation has been observed. Precipitation was only present inside the cathode compartment, on the sides of the Perspex box, at the electrode, and the mesh between the solution and the

soil compartment. Since the amount of precipitation was not quantified and analyzed, it is impossible to make a mass balance for experiment III. In order to be able to create an accurate mass balance in future research, all precipitates should both be dissolved before sampling and analysis and fully sampled. This could prove difficult since undetectable precipitation may still be present, e.g. in the filter between sample and electrolyte, inside a porous electrode, or in the (first few millimeters of the) sample.

As was observed in experiment II, hardly any removal of Cr took place during experiment III. As explained above, this might be due to low redox potential throughout the sample and the concurring immobility of Cr(III).

Mn removal was again potentially enhanced by the low redox state of the sludge during the experiment. Similar to experiment II, and together with Ca, Mn showed maximum removal (table 8).

Similar to the removal and redistribution patterns of the heavy metals, removal from and redistribution in the sludge was observed for the non-contaminant metals Ca,

Mn: maximum removal at the anode side (section 1) increasing towards section 5, indicating possible transport in the direction of cathode. In this experiment, however, it is more difficult to see such a pattern for K and Mg (figure 13).

The precipitation found at the cathode at high pH at the surface included Mn, as was observed by quick scan micro XRF. This was confirmed by additional ICP-OES analysis on the solution that included the precipitation of the cathode at the end of experiment IV. The combination of a high pH and oxygen availability at the surface of the solution, that was in direct contact with air, may have caused dissolved Mn(II) to oxidize to Mn(IV), forming precipitation. Other metals that showed a drop in concentration during sampling when high pH occurred, such as Fe, Ca and Mg, may have precipitated at the cathode in the possible form of (hydr)oxides or carbonates.

Voltages during experiment III demonstrated a general decrease (figure 6). The observed increase at the end of the experiment might be due to the formation of precipitates in the cathode reservoir. Precipitates will increase the electrical resistance of the soil system when they lead to pore clogging inside the porous medium. This increase in resistance is resulting in a higher potential gradient output in order to keep the current constant ( $U = I \cdot R$ ). As stated above, no precipitation was observed by eye inside the sample, only inside the cathode compartment.

#### *Experiment IV*

In experiment IV, the current was kept constant at 80mA, similar to experiment III. The titanium grid electrodes have been replaced by the carbon bar electrodes as used in experiment II. In this experiment, accidentally, no NaCl has been added to the electrode solutions. Refer to table 3 for more details.

In contrast to experiment III, in which the same current was applied, only Zn and Cd showed a net removal from the sludge. Roughly the same redistribution pattern in the sludge removal data was found in experiment IV for Zn, Cd and Ni (figure 14), indicating movement towards the cathode. Pb and Cr did not show consistent distribution. Also, both are having negative removal percentages  $< -10\%$ , possibly due to heterogeneities in the sludge or redistribution from residual fraction to the other fractions that are included by the *aqua regia* method (see above for explanation).

In the above experiments, no heavy metals, with the exception of Zn, were found in solution, concentrations were  $< 1$  ppm. According to the sludge analysis, however heavy metals did show removal. In experiment IV this was observed as well. Although the slightly decreasing concentrations in time of Zn in the anode reservoir are consistent with the idea of transport from anode towards the cathode, the catholyte reservoir does not show increasing concentrations (figure C.8). As in experiment III, pH in the cathode reservoir increased during this experiment, resulting in precipitation. The precipitation may have contained Zn, explaining the lack of Zn in solution. No precipitation was found inside the sludge. Again, the precipitation was not quantified and analyzed, leading to the inability of constructing a mass balance for the elements removed from the sludge.

Consistent with experiments II and III, Mn and Ca were the metals that were removed most ( $> 25\%$ , table 8). For Mn, the same redistribution pattern can be found once more: lowest values in section 1, highest in section 5 closest to the cathode, indicating movement from anode to cathode (figure 14). For Ca, however,



this pattern is absent. Also for the non-removed metals K and Mg, no consistent distribution pattern as found (figure 15). Possibly heterogeneous distribution of the metals inside the sludge may have resulted in non consistent distribution pattern.

Aside from the change of electrode material, a major difference between experiments III and IV is the absence of NaCl in the 4<sup>th</sup> experiment (IV). The lack of NaCl might have affected the removal of all metal species (table 8). When compared to experiment III, smaller overall removal percentages were observed in experiment IV, despite similar applied electrical current. This might be explained by the fact that Cl<sup>-</sup> is capable of complexing metals such as Cu and Zn, which can enhance the release of metals from solid phase into solution, as is explained above. Major absence of Cl<sup>-</sup> may thus lead to less complexation of metals and possibly less extraction from the solid phase, and inhibiting transport of the metals present in the sludge.

It would be expected that without addition of NaCl, the transference number of all other constituents in solution, i.e. the relative contribution of the ionic species to the total transport of ions in the pores of the sample, will become larger (Acar & Alshawabkeh, 1993). Or, if the metal in solution has a relatively higher concentration in the total pore fluid, that the particular ion will have a higher transference number and thus will be more effectively removed by the electrical current. On the other hand, the lack of NaCl in the fluid may lead to a lower conductivity of the solution and an increase of current passing through the solid particles rather than through the pore fluid.

Another possible explanation on the differences in removal of metals after treatment might be the variation in pH of the sludge after the experiment. Experiment III demonstrated lower pH values (figure 11) of the sludge after treatment, however, only observed in the section closest to the anode (section 1). The overall removal of all metals from this section is larger in experiment III than in experiment IV. Most likely, the difference in pH between both experiments might have been partly responsible for the difference in removal, rather than direct effects of the lack of NaCl.

Another major difference between experiments II and III, and experiment IV is the change in voltage loss at the electrodes during the experiment (figure 6). Initially the voltage loss between the output and the reference electrodes was > 50% and increasing in time. Also, the voltages over the double junction reference electrodes were as low as during experiment II, in which only 40mA constant current was applied versus 80mA in experiment IV. A lower potential gradient over the contaminated sludge indicates less movement of ions by electromigration and therefore less net transport of metal from or within the sludge, most likely resulting in less observed net removal at the end of the experiment.

The effect of the lack of NaCl on the removal of metals from the contaminated sludge cannot be isolated since multiple parameters were changed among experiments II and III, and IV.

A general note is valid for all experiments on the anion concentration data of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> that were analyzed using IC. Any observed increase in nitrate in the catholyte reservoir, e.g. in experiment III (figures B.9 and B.11), is contra intuitive, since nitrate will be available in the system as nitrate anions only and do not form any positively charged complexes. A potential explanation for this can be that nitrate was transported in the low redox state of N, i.e. transported in the form of NH<sub>4</sub><sup>+</sup>

instead of  $\text{NO}_3^-$ . The same may hold for  $\text{SO}_4^{2-}$  that might have been transported in the reduced state of S,  $\text{HS}^-$ . This is supported by the expected low redox state of the contaminated sludge during treatment, as explained above. The samples taken from the electrolyte solutions probably containing the reduced species, were not immediately analyzed, but were stored in 50 mL Greiner tubes for a few weeks before analysis. With sampling and during storage, possible reduced species from the reduced cathode reservoir, such as  $\text{NH}_4^+$  and  $\text{HS}^-$  may have oxidized. It is unclear whether the redox state of the cathode reservoir fluid really was reduced all over, since the reservoirs were always in direct contact with the atmosphere.

### *Experiments S1 and S2*

The side experiments S1 and S2 were conducted in a different setup from experiments II – IV (figure 5). It was designed to compare results of removal by electromigration of a contaminated sample with and without addition of organic polymers. These polymers were added during the pretreatment of the contaminated sludge in order to extrude water from and compact the sludge. As can be read in the *Materials, methods and experimental* section above, unfortunately all aged contaminated sludge available for this study was pretreated by addition the organic polymers. Therefore a sample of soil originating from the river banks of the river Kromme Rijn were spiked using a heavy metal cocktail containing the same heavy metal contaminants, however, in different concentrations.

No analyses were done on the sample of the side experiments after treatment. Removal percentages are therefore calculated from the concentrations that were found in the electrode solutions. No precipitation occurred during experiment S1 or S2 – the pH of the electrolyte solutions remained within precipitation limits. In contrast to experiment II – IV electroosmosis was observed during both side experiments, most likely due to the firm compaction of the side experiment samples, causing overlap of diffuse double layers, contrary to the loosely fitted sample in experiments II – IV. The electroosmosis caused different fluid levels in the electrode compartments. These levels were not closely monitored during the experiments. This may have affected calculations on the removal via electrode solution concentrations.

The observed electroosmosis was towards the cathode, in case of experiment S1, whereas experiment S2 showed movement of water towards the anode. This implies that the foremost movement of ions and the associated drag on the surrounding water molecules within the sample was opposite: for S1, movement of cations in the double layer towards the negatively charged cathode was most important, while the anionic movement to the anode in S2 was most significant. The addition of charged polymers to the sample may have induced this observed opposite water transport. By creating an excess of positively charged surfaces from the addition of polymers, the negatively charged surfaces present in the sample may have changed to positively charged, favoring anionic movement and associated draft of water, resulting in electroosmosis towards the anode. Despite the observed electroosmosis, no differences in behavior of metal concentrations in the solution in time were found (figures D.1, D.2 and E.1, E.2). The movement of water by means of electroosmosis, as stated above, was not quantified. Thus the effect of electroosmosis on the net transport of the metals during experiments S1 and S2 cannot be quantified.

In contrast to experiment II to IV, both side experiments showed significant removal percentages for all heavy metals (table 9). As the sequential extraction demonstrated, the distribution of metals in the spiked sample proved very different

from the aged contaminated sludge. The spiked soil, therefore, provided more easily extractable heavy metals, which is very likely to be, responsible for the higher removal percentages. Removal percentages as found by spiked laboratory samples may only be representative for recently contaminated soils, rather than for historically and aged contaminated soils.

S2 showed higher removal percentages than experiment S1, for all metals, including the contaminant metals, with the exception of Cr. The addition of polymers to S2 may have possibly lead to the increased removal by providing an additional source for the complexation of metals from the solid phase onto organic molecules, thereby increasing their mobility. As explained above, complexation, however, may alter the valence and mobility of the heavy metal in solution. For S1 and S2, the same pattern of heavy metal concentrations during the experiment in the electrode fluids were found for both experiments (figures D.1, D.2 and E.1, E.2). Removal percentage calculated from these concentrations showed higher removal percentages for S2, indicating a possible positive influence of the addition of the polymers on the extraction of metals from the spiked sample.

As stated above, the spiked soil showed different metal distribution than the contaminated sludge. The effects of the addition of polymers may therefore be different for the sludge than has been observed in this study for the spiked soil. No tests were conducted varying the amounts of polymer added, whereas differences in polymer concentration might play a role in the removal of heavy metals from the sludge. Further research can be done on the effects of polymer addition to the removal of heavy metals from an aged sludge, to see whether this might enhance extraction of these metals from the contaminated sludge.

## Conclusion

In a laboratory setup the potential of electroremediation in a heavy metal and mineral oil contaminated aged sludge was investigated.

A sequential extraction procedure of both the aged contaminated sludge and spiked soil provided insight in the distribution of the metals over the various binding mechanisms. Although all metals appeared to be mainly situated in the organic matter/sulfide phase, transport and removal proved to be very diverse. For example, both Cu and Cr were mainly present in the organic fraction, however, Cu showed substantial removal, whereas no removal at all was observed for Cr. Therefore, the pattern of distribution of the various heavy metals present in the contaminated sludge cannot be directly related to their removal rates by electroremediation. When exploring the mobility of heavy metals in a contaminated sludge during electroremediation by means of sequential extraction, the results should be carefully interpreted.

Sequential extraction demonstrated that a spiked soil sample is not suitable for extrapolation to real contaminated field soils and sludge. The ageing of contaminants in field soils is of great importance for their distribution and therefore for the mobility of metal contaminants. In general, mobility and transport by electroremediation will most likely decrease with increasing ageing time.

In this study, the application of a constant electrical current of  $0.5 \text{ mA/cm}^2$  for 167 hours, with a corresponding potential gradient of around  $0.25 \text{ V/cm}$  passing through a contaminated aged sludge sample, proved to be insufficient for removal of heavy metals (Cu, Cd, Cr, Ni, Pb, Zn). Increasing the current constant current to  $1 \text{ mA/cm}^2$  over  $\sim 180$  hours with a corresponding  $0.5 \text{ V/cm}$  potential gradient, resulted in observed removal for Cd, Cu, Zn  $> 15 \%$ , whereas Ni and Pb showed removal percentages  $< 10\%$  and Cr demonstrating no removal at all. While Cr is the most abundant heavy metal contaminant with initially almost 1300 ppm present in the sludge, no removal of this contaminant was observed. The low redox conditions and a pH 4 - 5 in the sludge during treatment is likely the main cause for the immobility of Cr.

Despite the addition of an acetate buffer pH conditions in both electrode reservoirs changed during the experiments due to the production of  $\text{OH}^-$  and  $\text{H}^+$  at the cathode and anode, respectively. pH in the cathode reservoir increased regularly during the experiments, resulting in precipitation of the various metals present in the solution. It occurred inside the porous electrode, at the sides of the Perspex setup, on the electrolyte surface and onto the mesh. In order to construct a correct mass balance on the removal of heavy metals, the precipitation should be dissolved before sampling the electrode fluid in future research.

No matter whether partly or no removal was observed, redistribution inside the sludge of both heavy metals and non-contaminant metals occurred during all experiments. Lateral movement was observed from one section to another section inside the sample. For Cd, Cu, Zn, and Mn and Ca, a clear, general movement towards the negatively charged cathode was observed in all experiments. Patterns for Ni, Pb, Cr and other non-contaminant metal were less apparent. It is unknown whether redistribution of metals over the various binding mechanisms (speciation) took place within the soil fractions. A sequential extraction after treatment might give insight in possible fraction redistribution.

Removal of non-contaminants Ca and Mn exceeded the removal of the heavy metals during all experiments. No major acid weathering of the soil was observed in this research since only minor amounts of Al, Fe and Si were released into solution.

Varying the electrode material in this study did not prove to be of influence for the transfer of current from the power supply into the system. The NaCl concentration in the electrode reservoirs, however, did have a large influence on the efficiency of the transfer of current from the electrodes into the electrolyte fluid. A lack of NaCl showed a major increase in the difference between the output voltages and the actual potential gradient that was present in the contaminated sample.

The addition of cationic and anionic polymers to the contaminated sludge during pretreatment may alter the behavior of the pore fluid. Opposite electroosmosis was observed in the compacted spiked soil samples with and without addition of polymers. In turn, this can have an influence on the net transport of heavy metals during electrokinetic remediation. From this study, however, it was not possible to quantify the effect of the observed opposing electroosmotic movement on the removal of heavy metals.

It appeared not possible to extrapolate the electrical current and potential gradient due to multiple parameter changes per experiment. A set of experiments that solely varies the current applied to the contaminated sample might provide insight in the effect of further increasing the applied current on the removal rates of the various heavy metals. It is expected that this effect will vary between different contaminated materials and contaminants. Higher current application may very well lead to additional removal, maximum removal limits will apply when unwanted side effects take place such as soil heating, acid weathering, low efficiencies, electrode weathering. Longer runtimes may also result in additional removal. Efficiency versus total electrical output, however, should be investigated further. This may also apply for the addition of any enhancement fluid to the process, such as salts, pH buffers, organic solvents, complexing agents.

### *Recommendations*

For efficient removal of heavy metals from an aged contaminated sludge, the implementation of electroremediation favors a controlled setting, with respect to the electrolyte fluids and the electrodes. The environment of the system in which the electroremediation takes place, with emphasis on pH and selection of additives in the electrode reservoirs, eventually determines the removal achievements of the contaminant heavy metals.

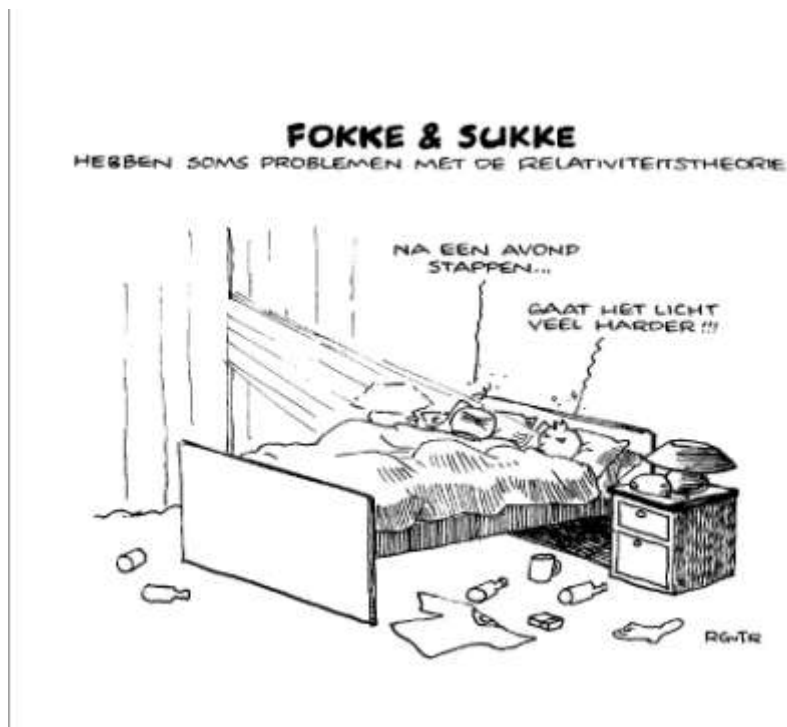
The control of the pH of the solution in the electrode reservoirs, possible addition of enhancement fluids, close regulation of the applied potential gradient and current are more easily achievable in an on-site batch reactor than during direct in-situ field implementation – the sludge or soil in between the electrodes in a field setup will generally be a very inhomogeneous black box. Unwanted side effects of high potential gradients (e.g. 1 V/m or even higher) such as soil heating, soil cracking or instability can be avoided or minimized in a batch reactor. Any of these effects can be monitored closely and possibly avoided early on. With a batch reactor unwanted reactions outside an in-situ treatment area are avoided.

Homogenization by pretreatment sorting, where only the highly contaminated fraction is preserved and the sludge is homogenized in terms of density and particle size, will be favorable for electroremediation.

An exploratory laboratory bench-scale experiment before possible on-site electroremediation will provide insight in the removal of the various contaminant metals present with the projected applied current and possible addition of enhancement or pH controlling fluids.

## Acknowledgements

Some people were really needed in order to get this thesis done. First of all I would like to thank Guus Loch and Ana Lima at the university for their supervision on the subject. Whenever I had a question that was related to the subject of electroremediation or soils in general, Guus would turn enthusiastic the moment he could start telling "things" about soil, whether it was about the principles or about the location where I could get my soil sample for use in the lab. Initially, I found conversations with Ana about my subject very hard. She was always asking tough questions, such as what do *you* want to investigate, what does make *you* tick, and what do *you* think will happen. I think I still do not know fully the answers to her questions, but she made me think a step further than just doing my master research and write some thesis about it. A huge thanks to John Dijk, Han de Kreuk and Maurice Coremans at BioSoil R&D, B.V. for providing the principle subject for this study, together with some of the funding and the laboratory setup. Without them I would not have had an immense heap of contaminated sludge at my disposal to make the lab dirty with. Pieter Kleingeld has been an enormous help in getting my head round the electrical and practical aspects of this thesis. He came up with great practical ideas and helped me a million by improving the setup with his great DIY solutions - he is just a great engineer. I appreciated the help I got from all the laboratory staff for getting the analyses done. My roomies in N102 provided me with plenty feedback and discussion, as well as an abundance of lame jokes, coffee breaks, lunch breaks, last-minute or not so last-minute holiday destinations, etc... Unfortunately, there were never enough cookies around to get through the day. Thanks to my parents for their "home base" support on all sides of life on getting to the point of this master thesis. I think I will be able to manage now...! Last but not least, a great hug for my girlfriend, who probably adsorbed too much of both my enthusiasm and frustrations during this thesis.



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### **List of appendices**

In the appendices the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during the experiments are presented.

Appendix A: experiment II

Appendix B: experiment III

Appendix C: experiment IV

Appendix D: experiment S1

Appendix E: experiment S2

## Appendix A

In this appendix the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during experiment II are presented.

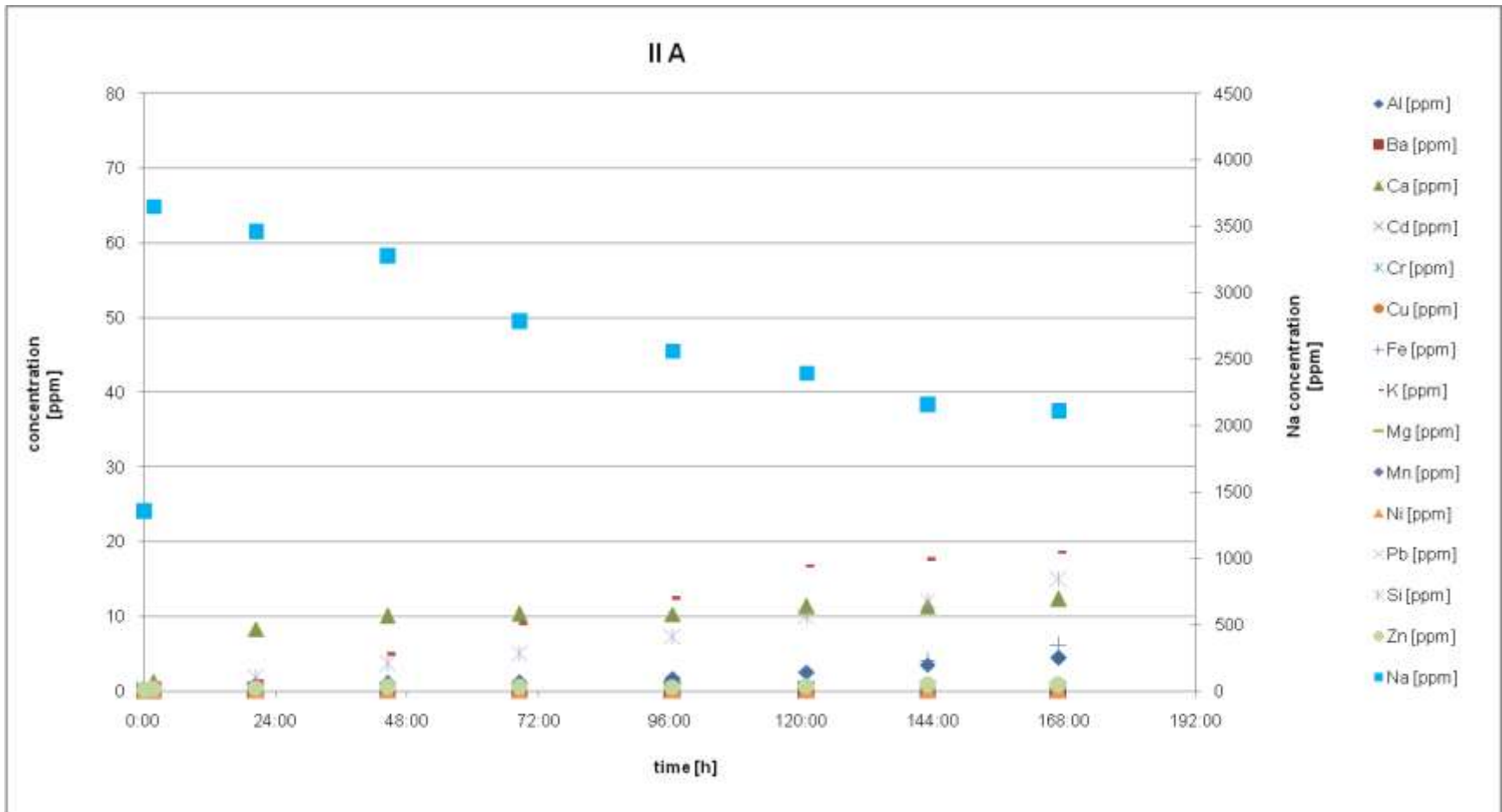


Figure A.1: Concentrations of all metals in anode reservoir solution during experiment II.

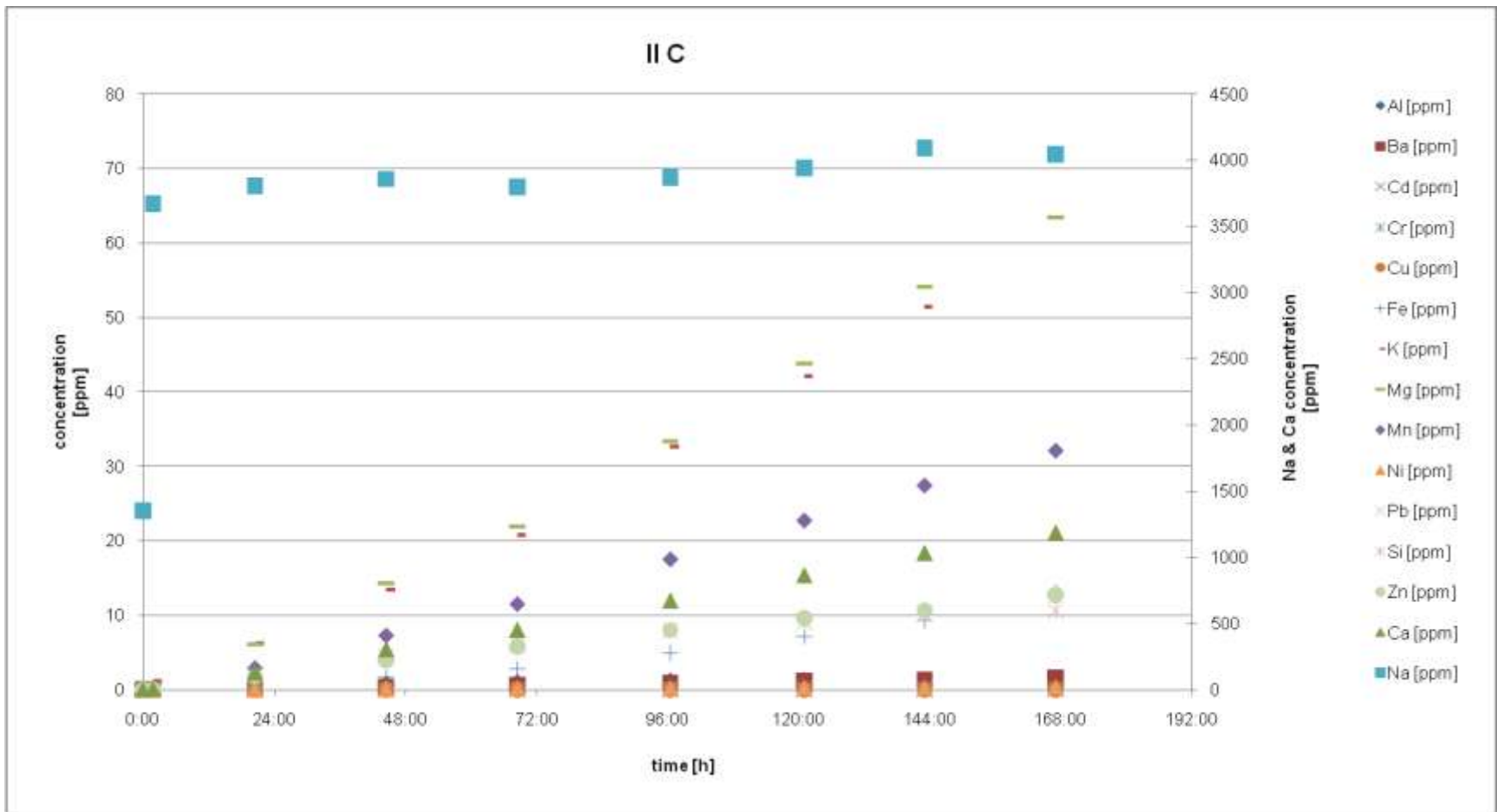


Figure A.2: Concentrations of all metals in cathode reservoir solution during experiment II.

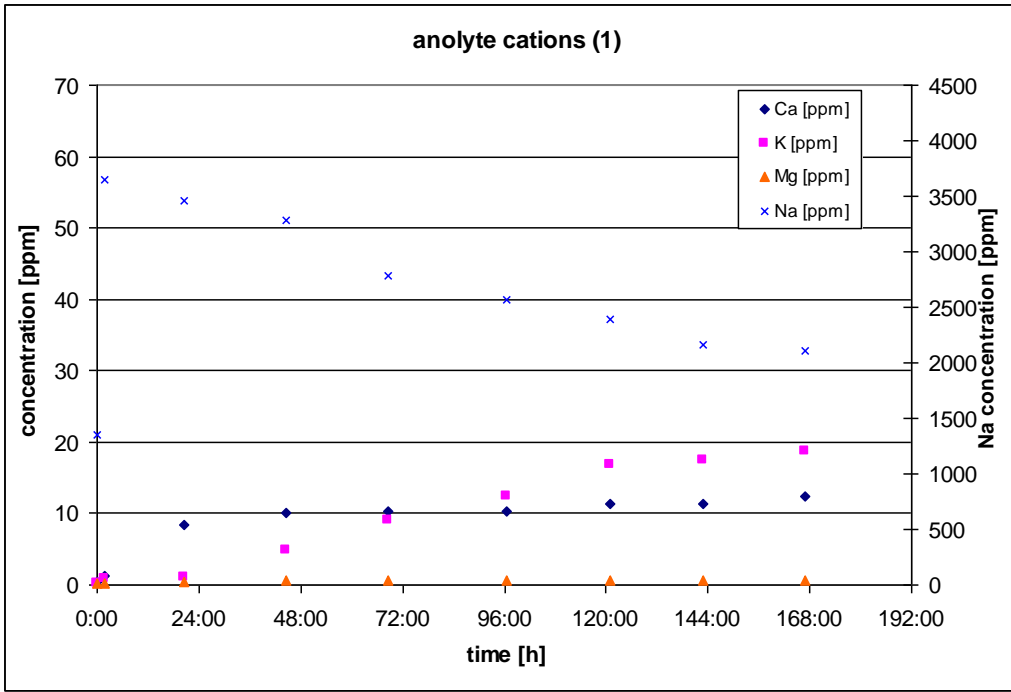


Figure A.3: Concentrations of non-contaminant metals in anode reservoir solution during experiment II.

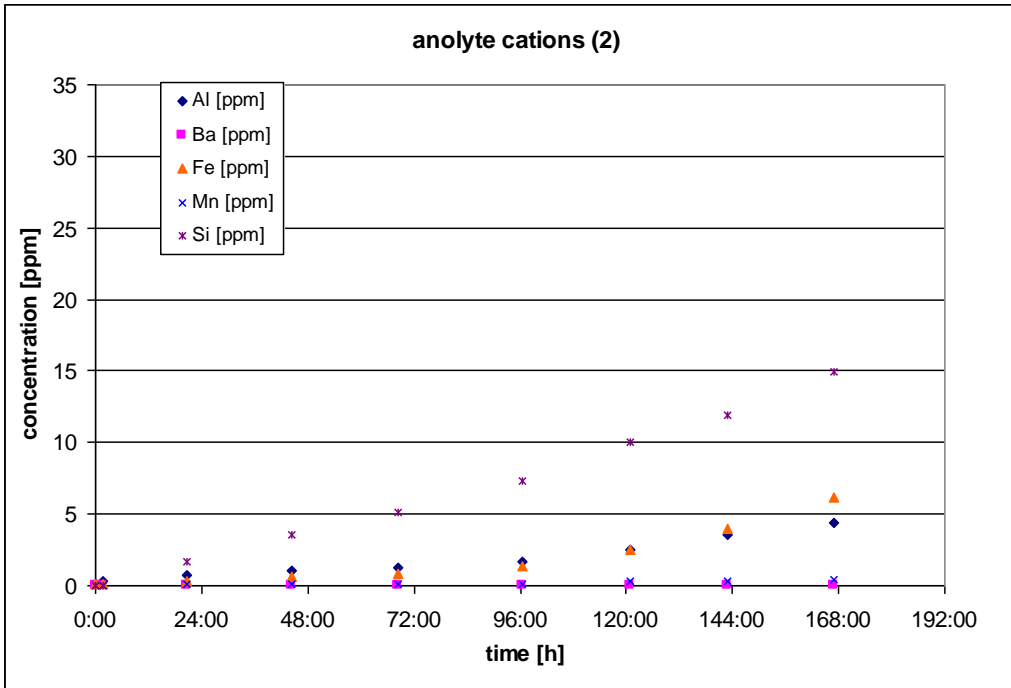


Figure A.4: Concentrations of non-contaminant metals in anode reservoir solution during experiment II.

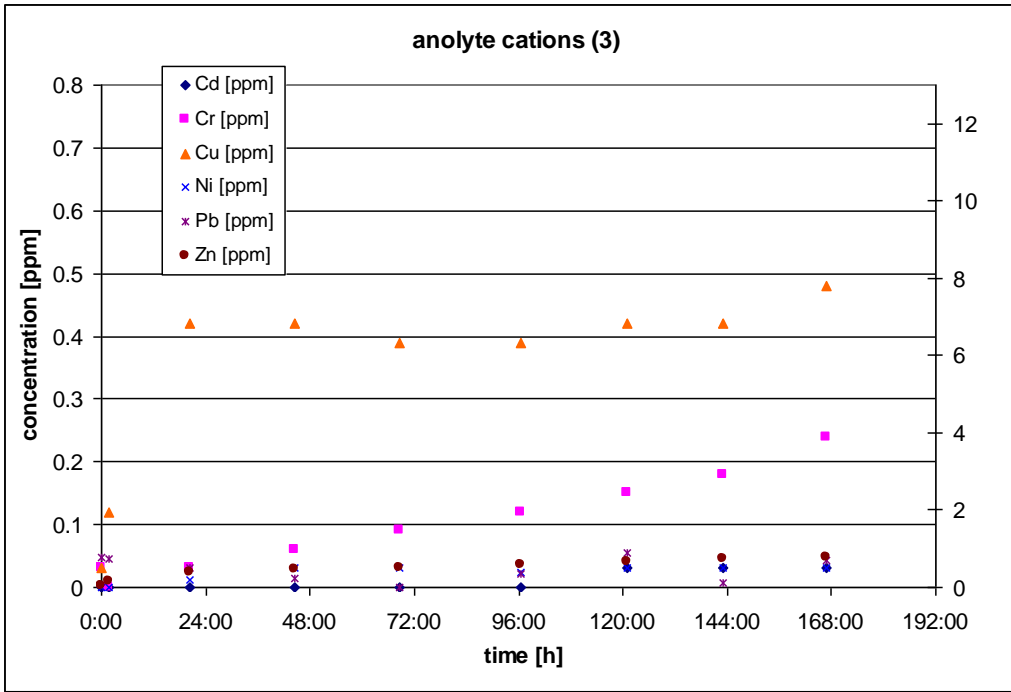


Figure A.5: Concentrations of contaminant metals in anode reservoir solution during experiment II.

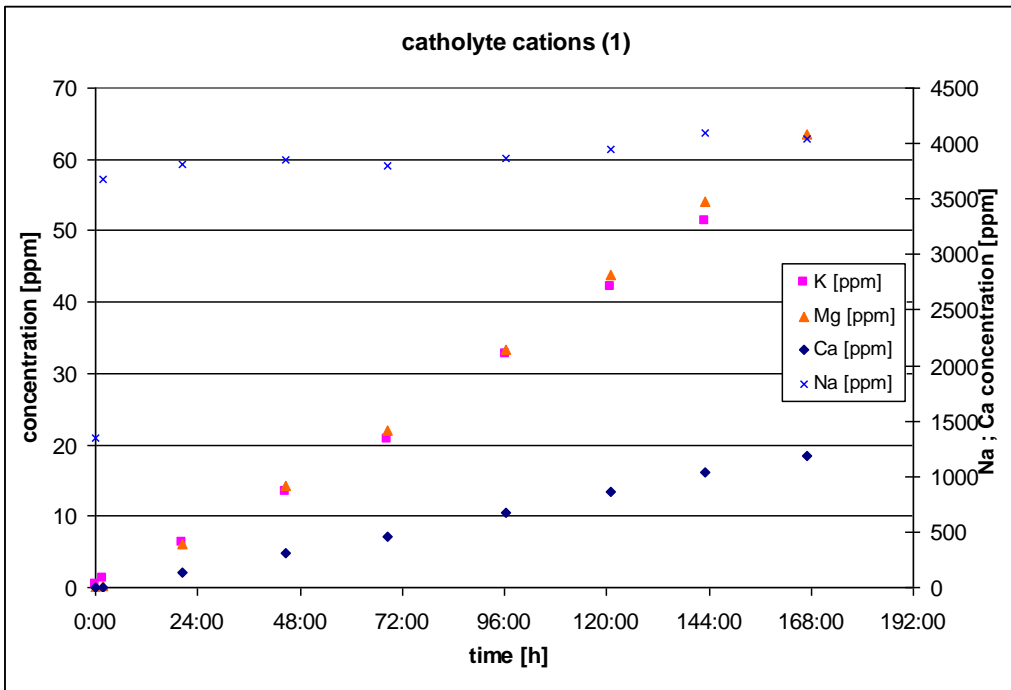


Figure A.6: Concentrations of non-contaminant metals in cathode reservoir solution during experiment II.

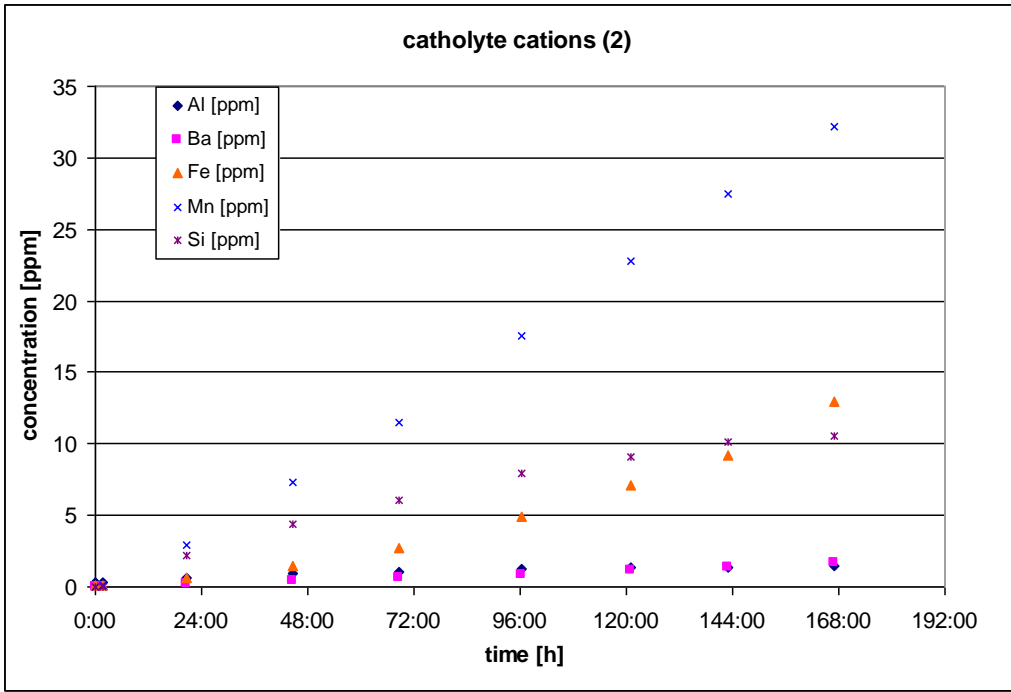


Figure A.7: Concentrations of non-contaminant metals in cathode reservoir solution during experiment II.

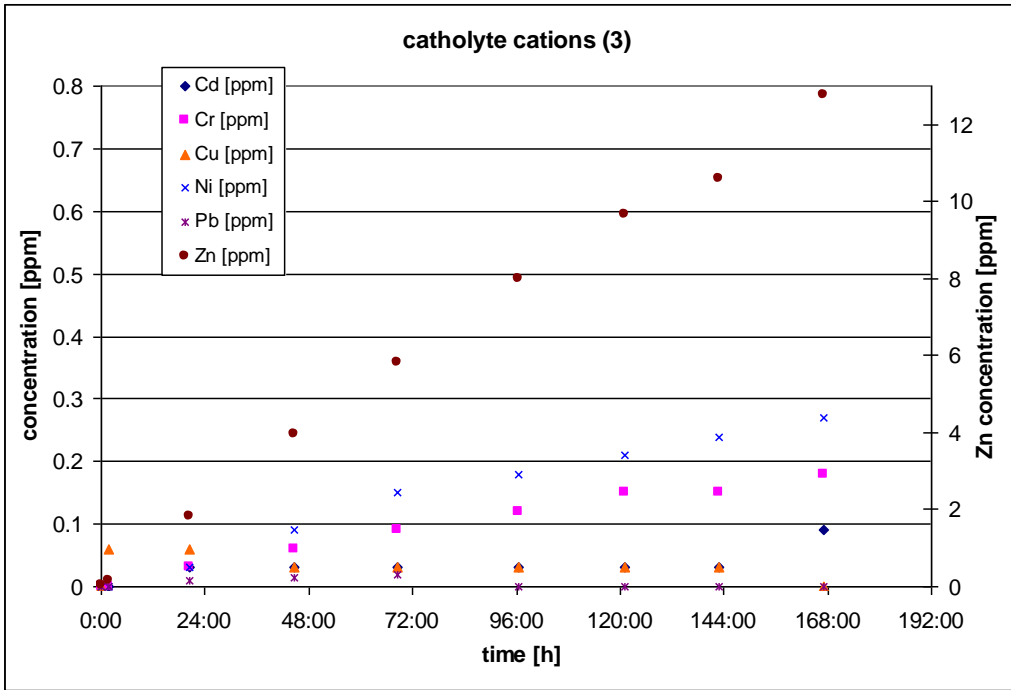


Figure A.8: Concentrations of contaminant metals in cathode reservoir solution during experiment II.



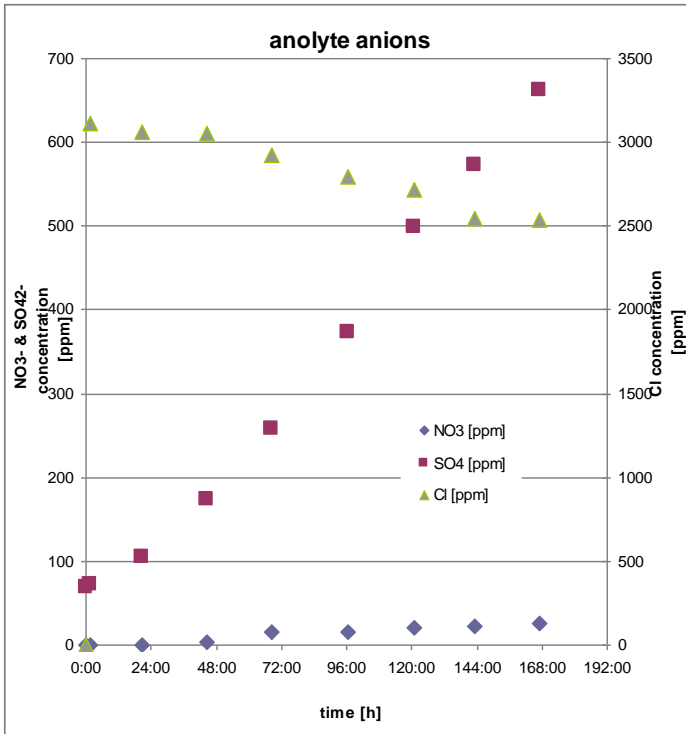


Figure A.9: Concentrations of anions in anode reservoir solution during experiment II.

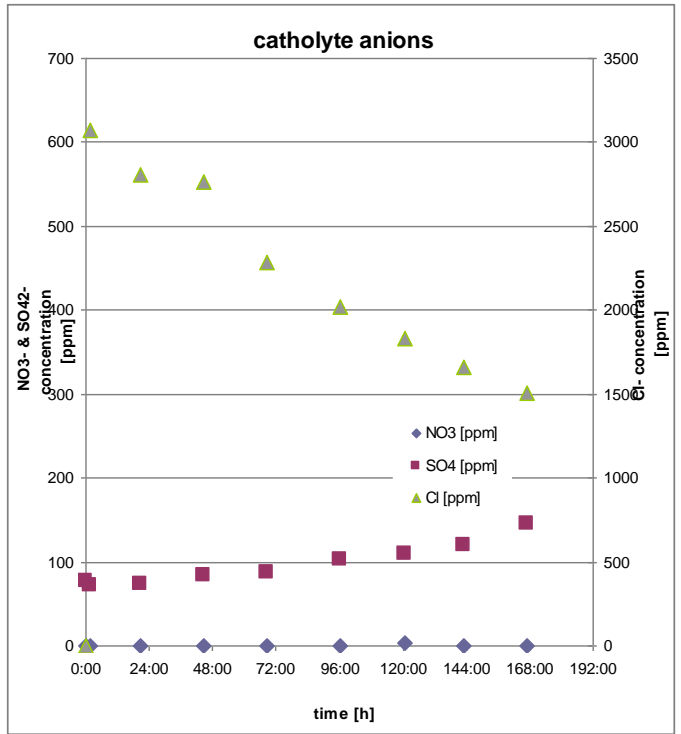


Figure A.11: Concentrations of anions in cathode reservoir solution during experiment II.

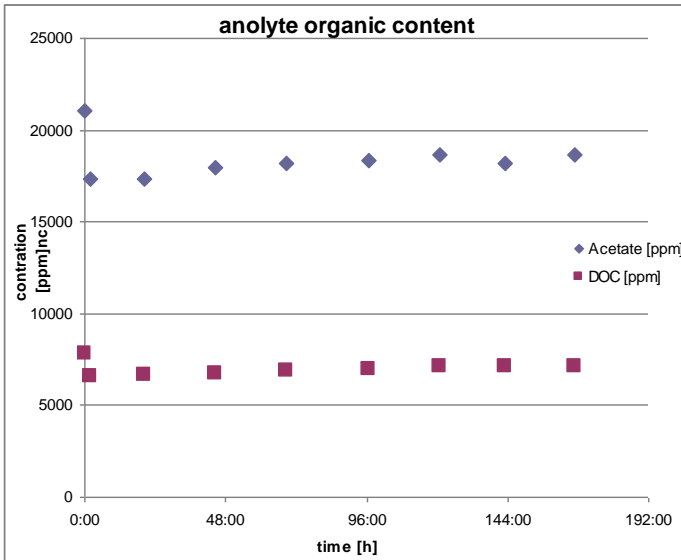


Figure A.10: Concentrations of acetate and DOC in anode reservoir solution during experiment II.

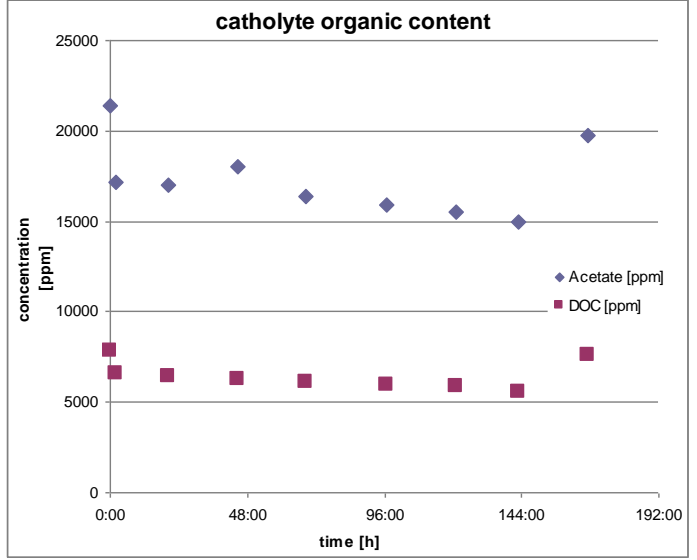


Figure A.12: Concentrations of acetate and DOC in cathode reservoir solution during experiment II.

## Appendix B

In this appendix the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during experiment III are presented.

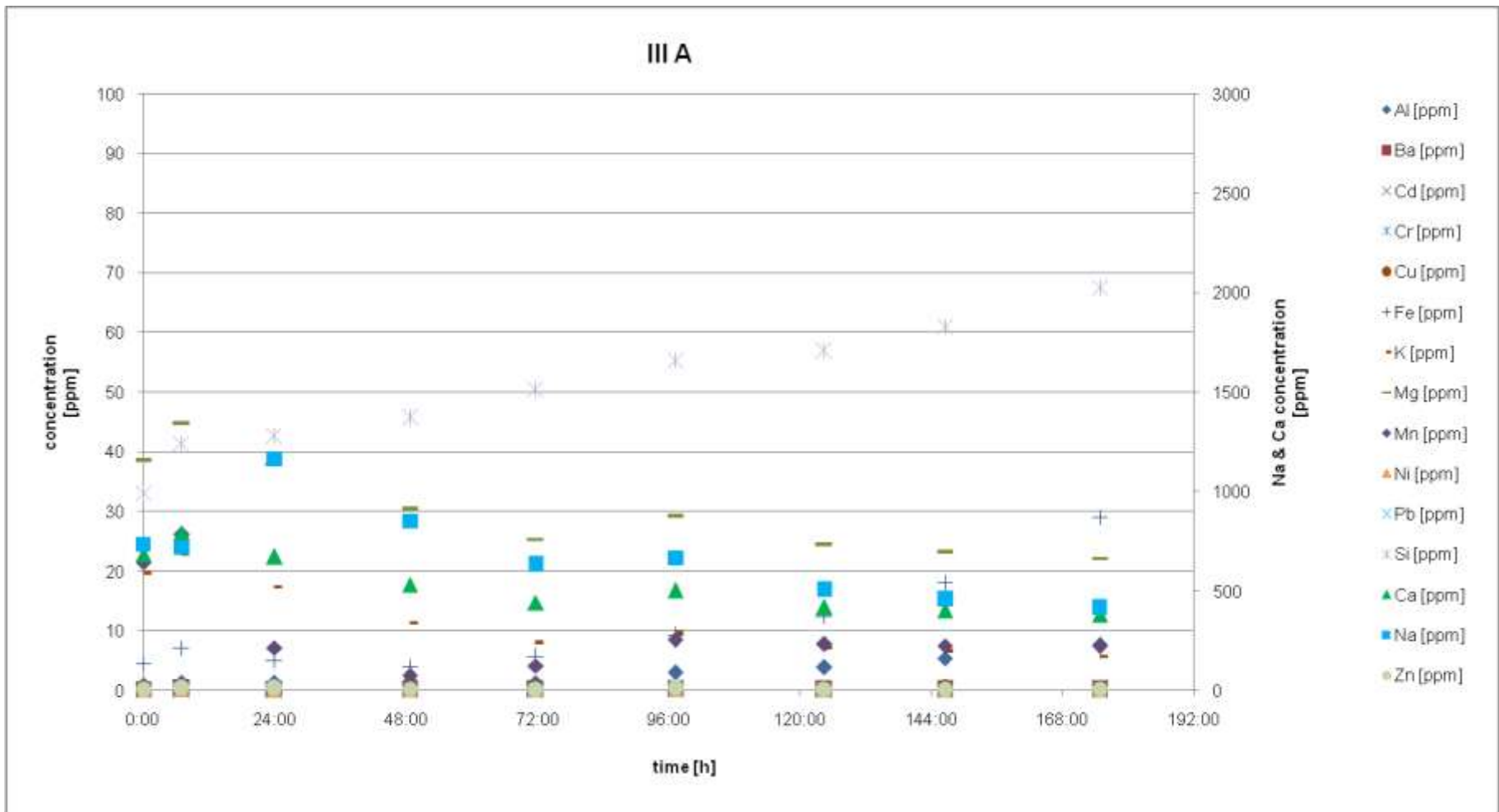


Figure B.1: Concentrations of all metals in anode reservoir solution during experiment III.

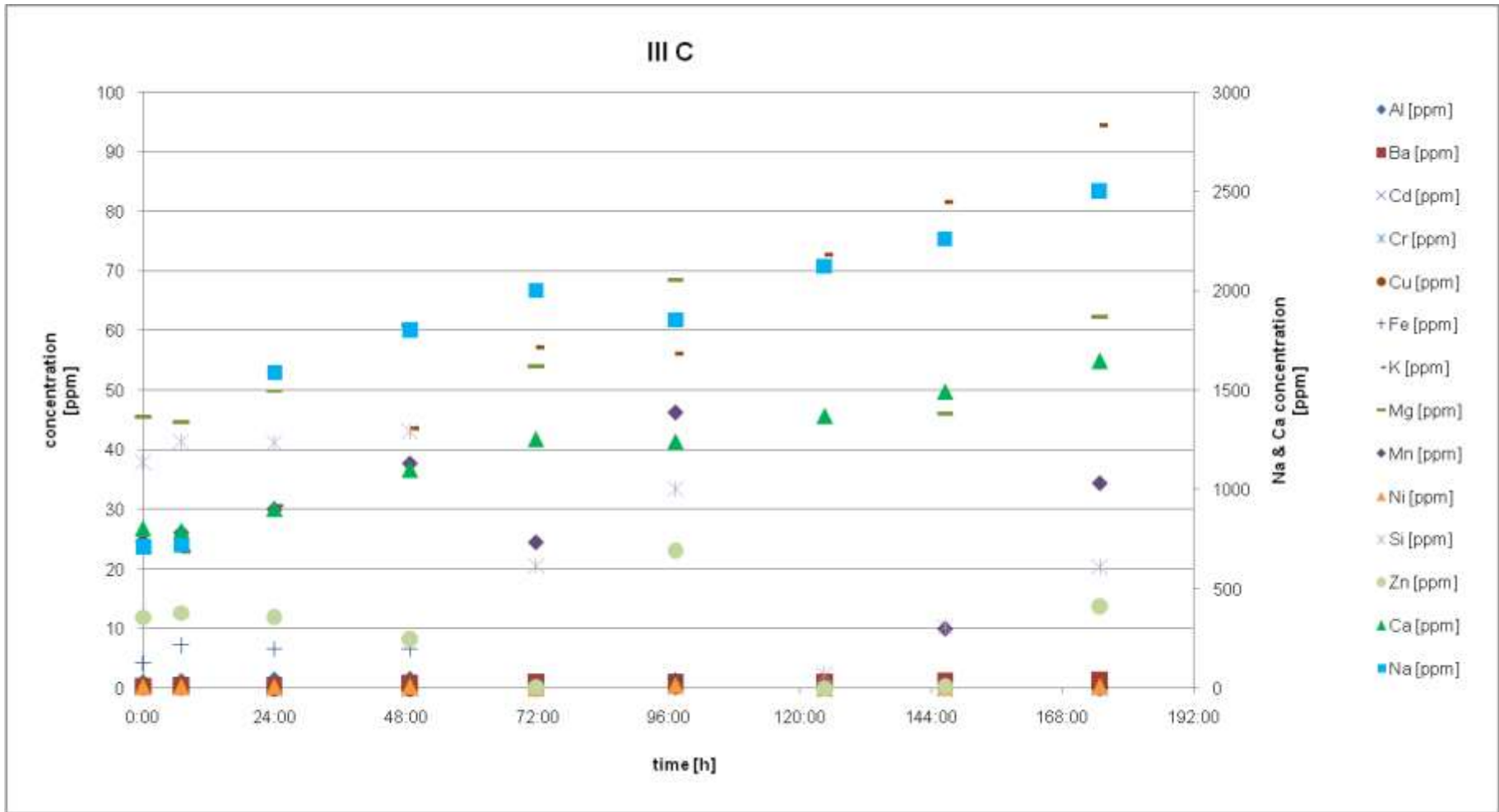


Figure B.2: Concentrations of all metals in cathode reservoir solution during experiment III.

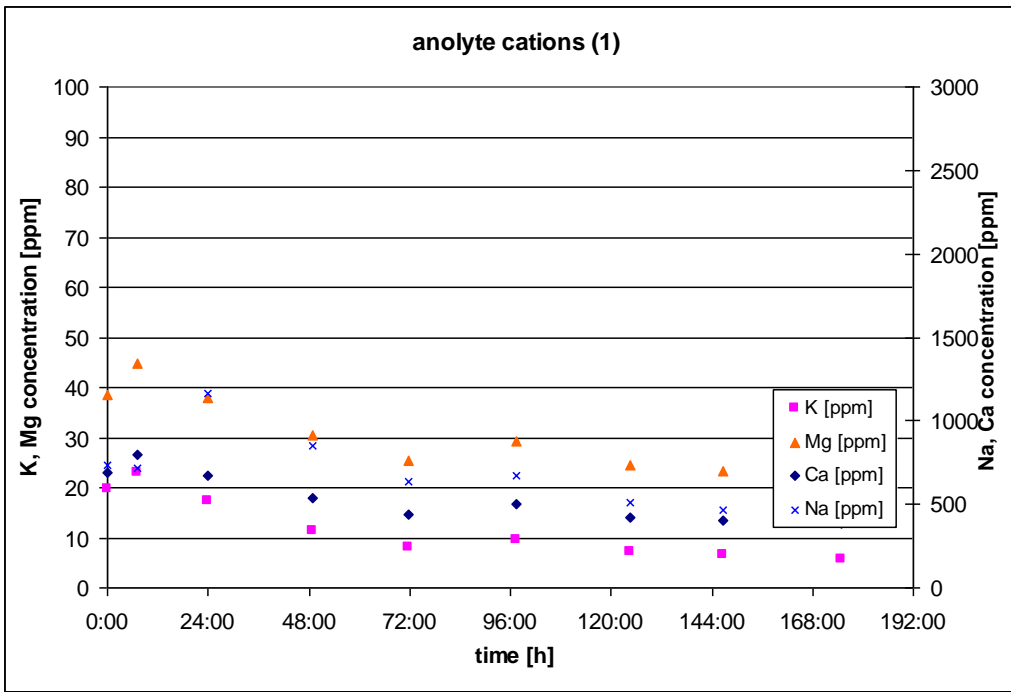


Figure B.3: Concentrations of non-contaminant metals in anode reservoir solution during experiment III.

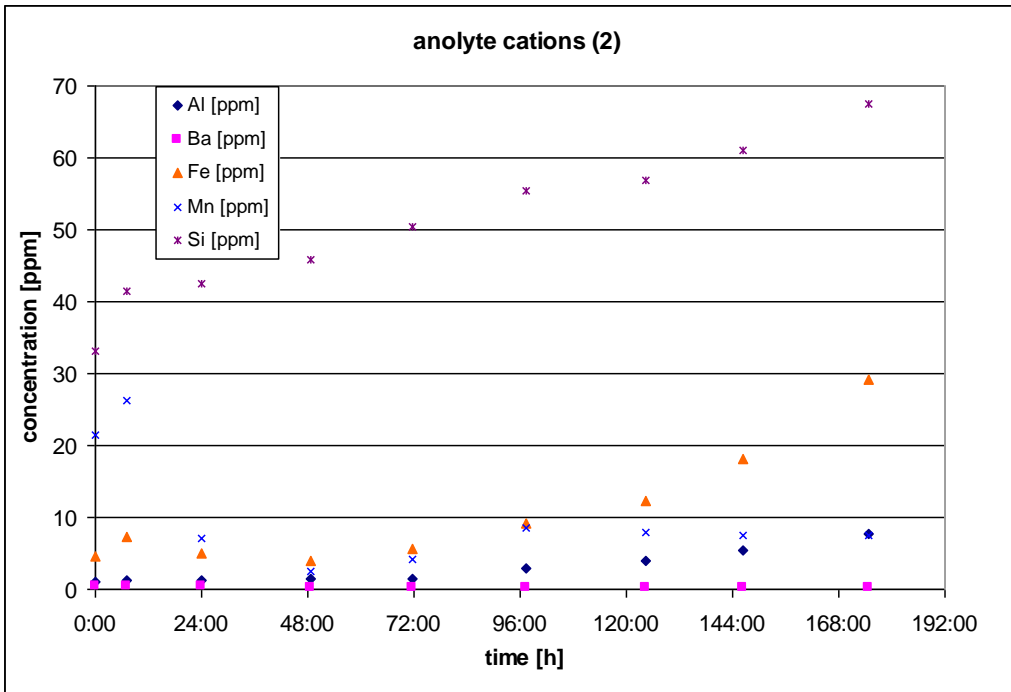


Figure B.4: Concentrations of non-contaminant metals in anode reservoir solution during experiment III.

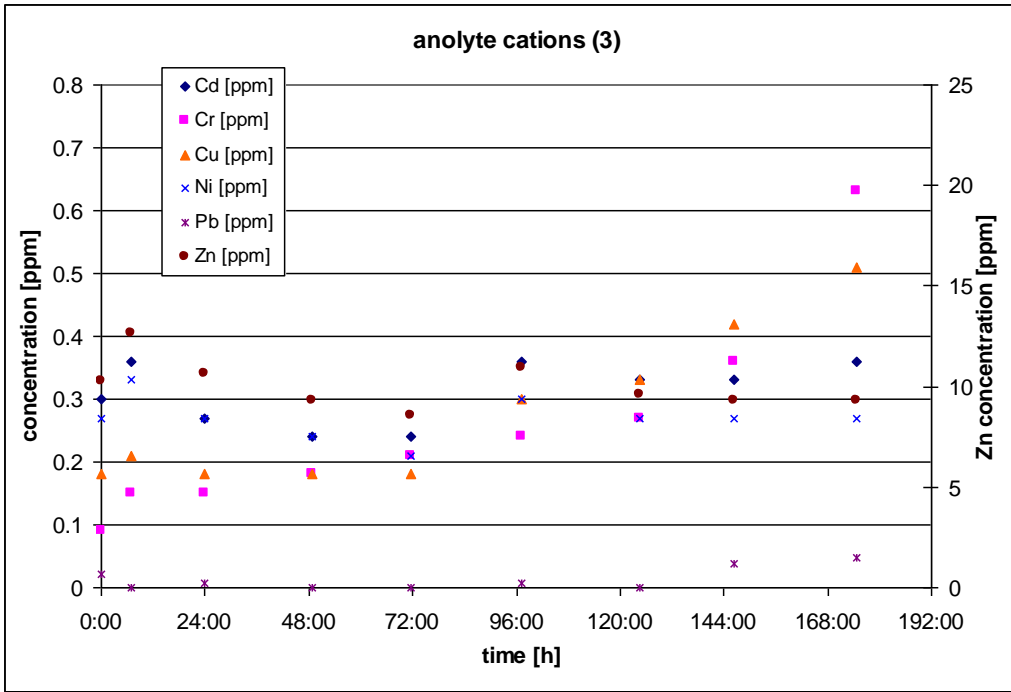


Figure B.5: Concentrations of contaminant metals in anode reservoir solution during experiment III.

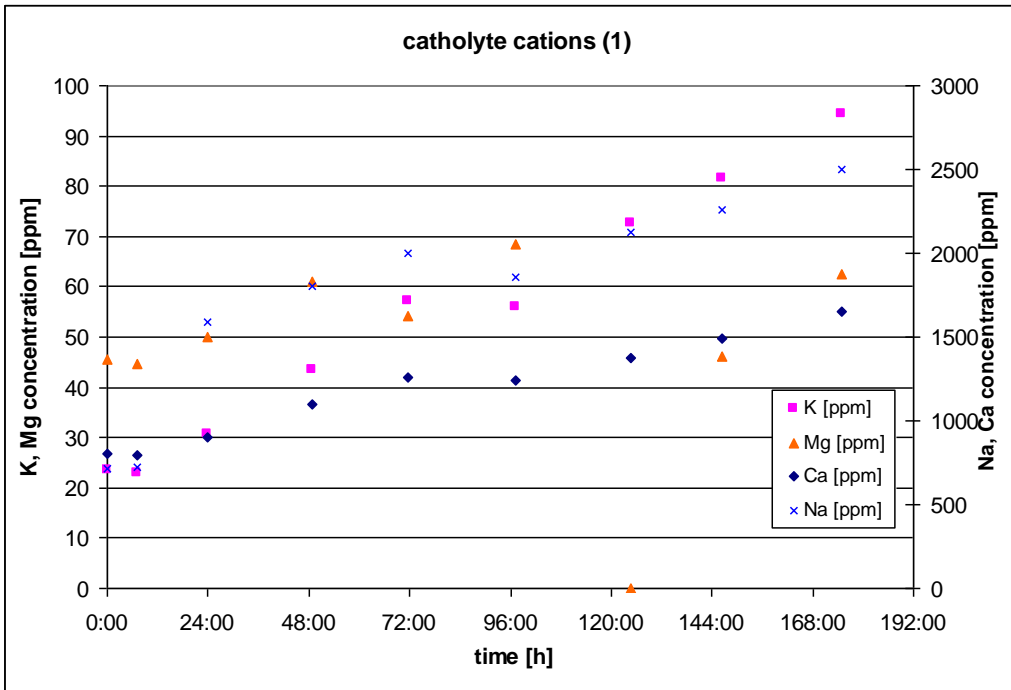


Figure B.6: Concentrations of non-contaminant metals in cathode reservoir solution during experiment III.

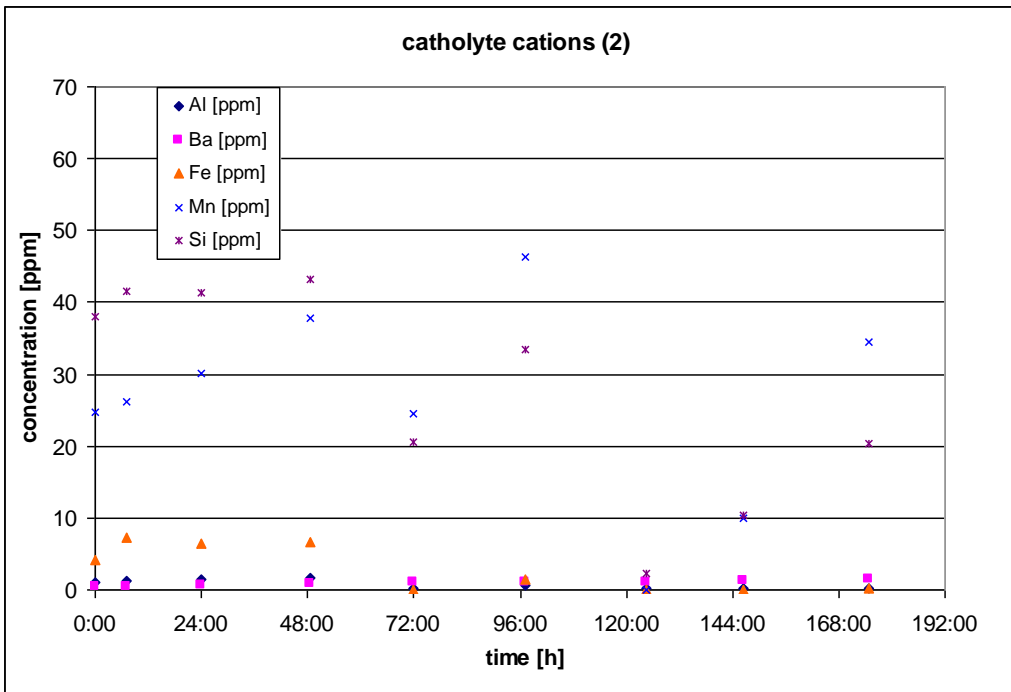


Figure B.7: Concentrations of non-contaminant metals in cathode reservoir solution during experiment III.

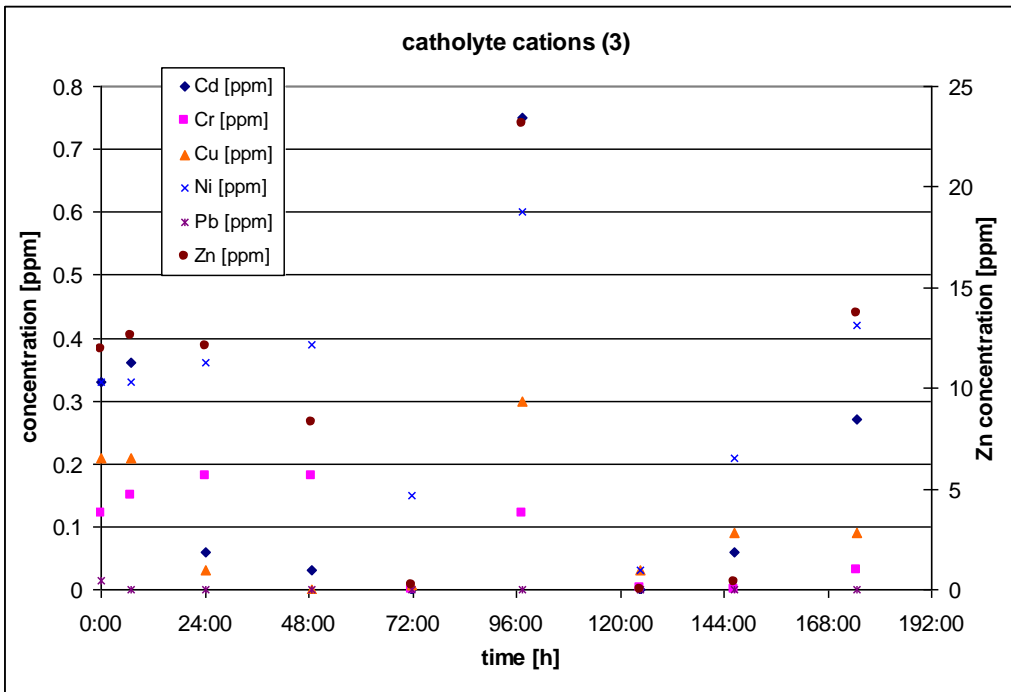


Figure B.8: Concentrations of contaminant metals in cathode reservoir solution during experiment III.

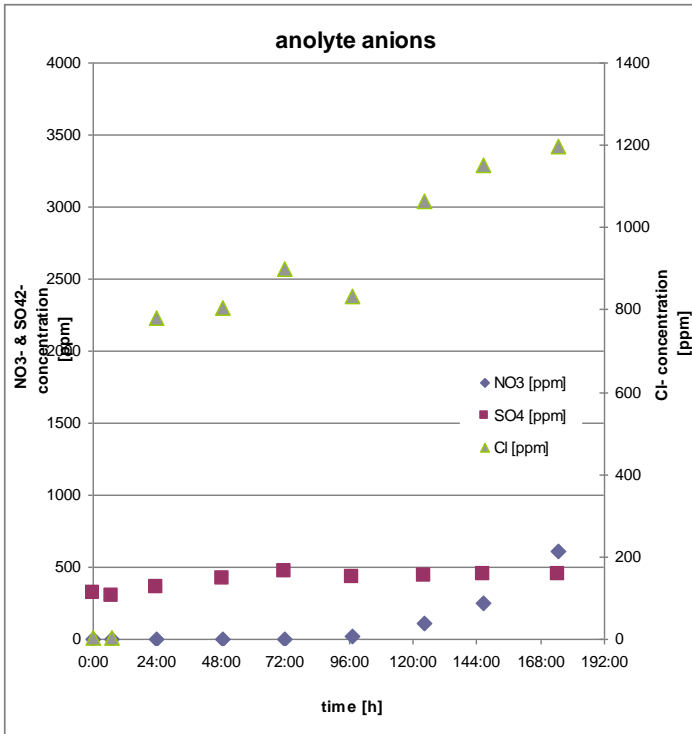


Figure B.9: Concentrations of anions in anode reservoir solution during experiment III.

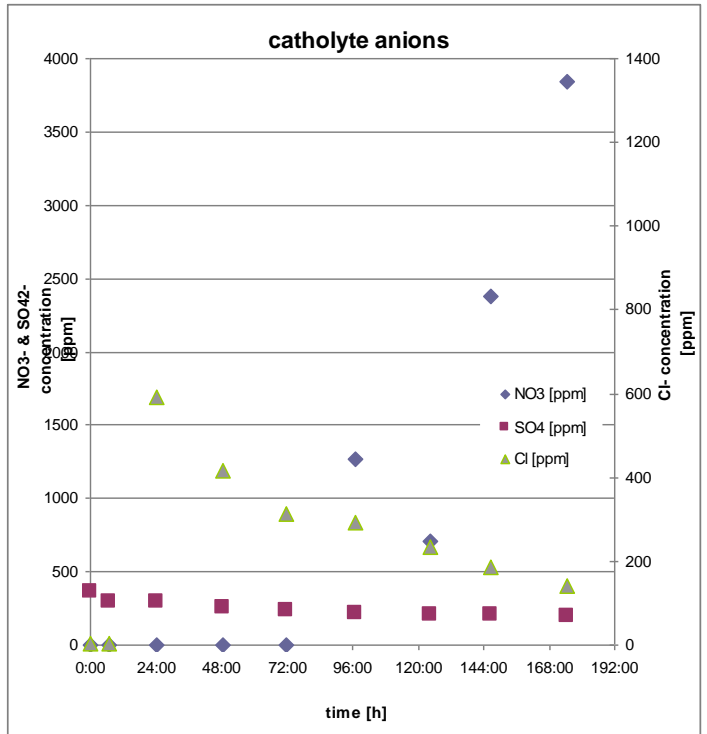


Figure B.11: Concentrations of anions in cathode reservoir solution during experiment III.

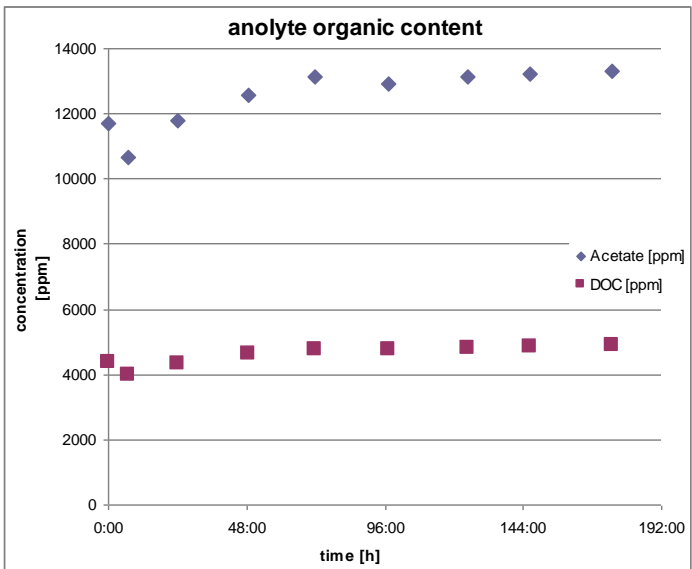


Figure B.10: Concentrations of acetate and DOC in anode reservoir solution during experiment III.

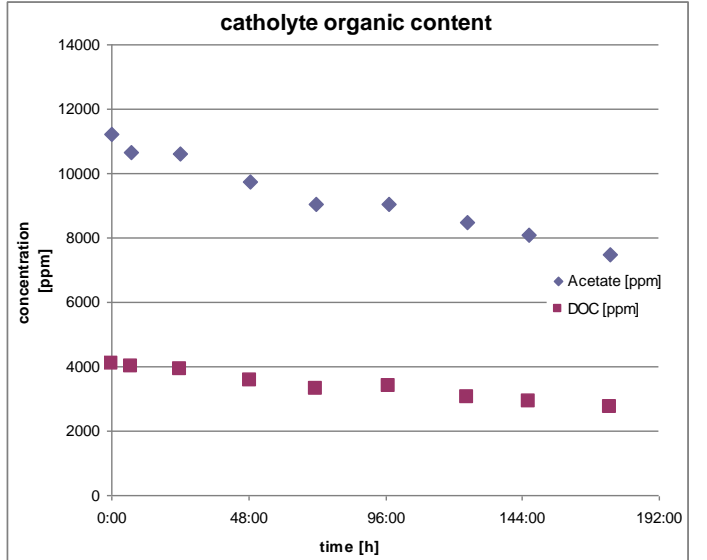


Figure B.12: Concentrations of acetate and DOC in cathode reservoir solution during experiment III.

## Appendix C

In this appendix the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during experiment IV are presented.

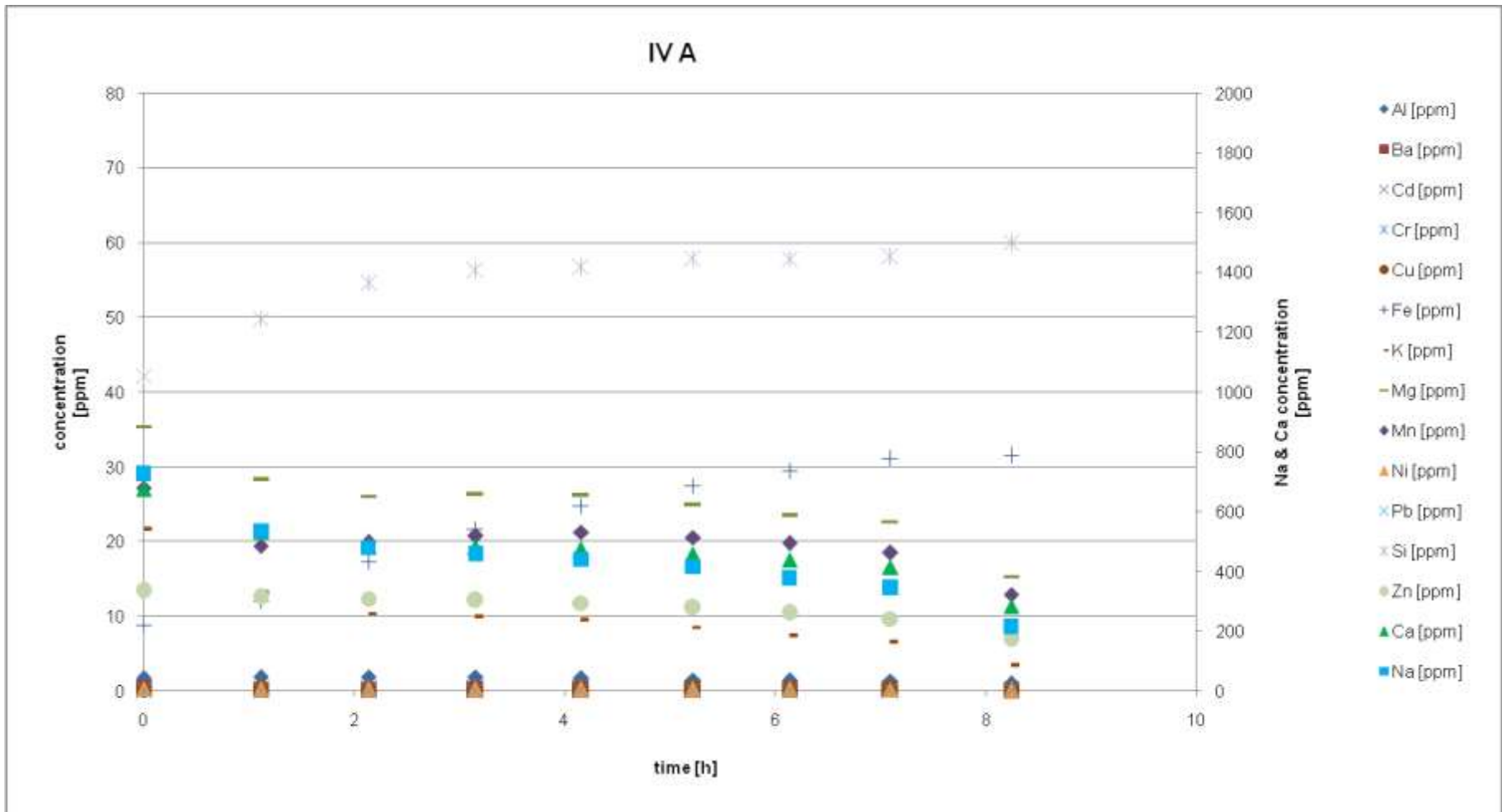


Figure C.1: Concentrations of all metals in anode reservoir solution during experiment IV.



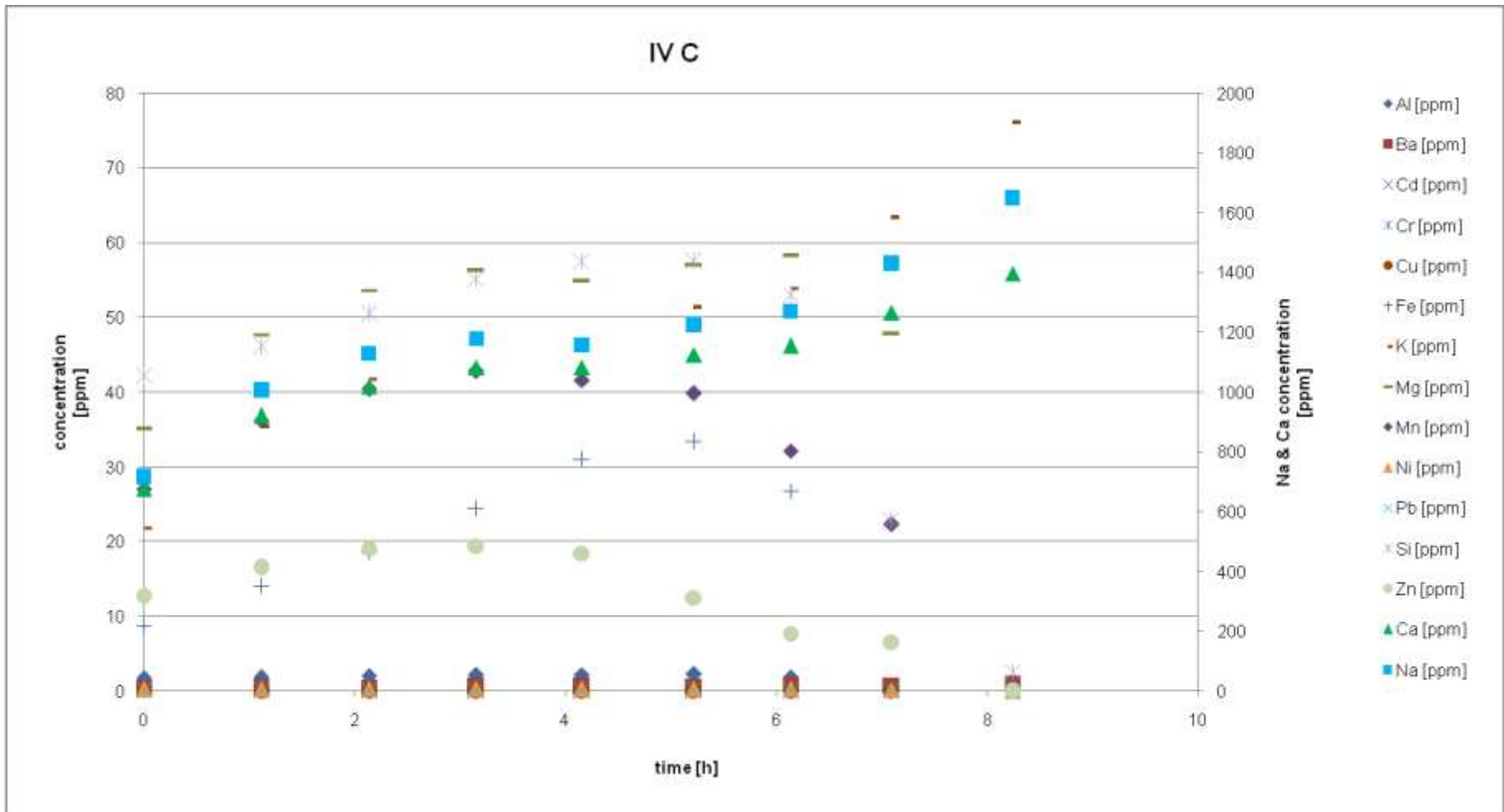


Figure C.2: Concentrations of all metals in cathode reservoir solution during experiment IV.

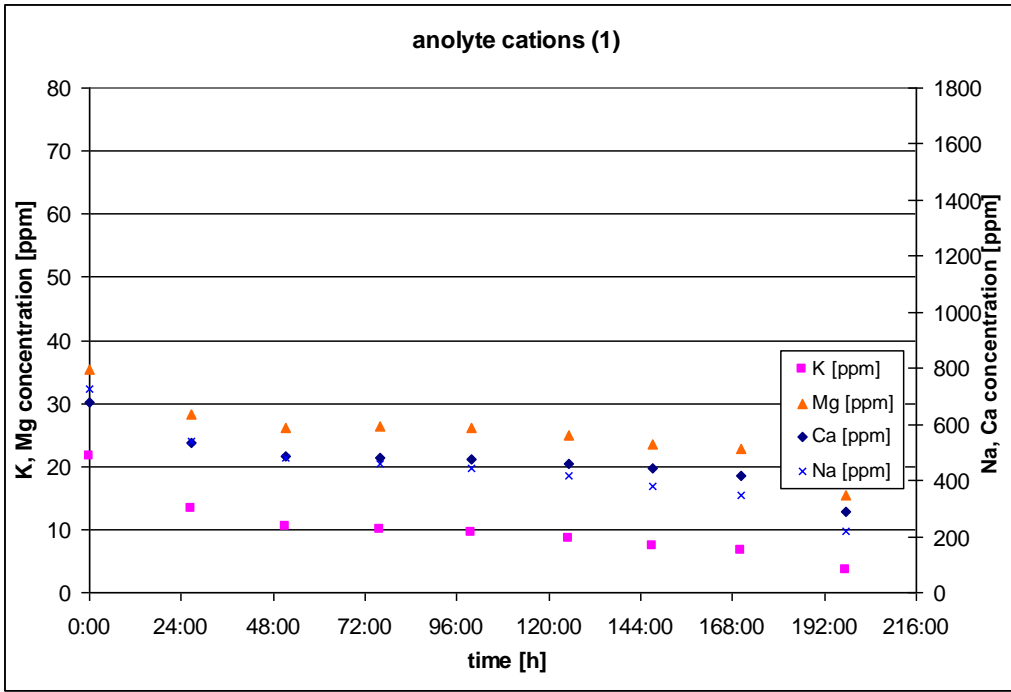


Figure C.3: Concentrations of non-contaminant metals in anode reservoir solution during experiment IV.

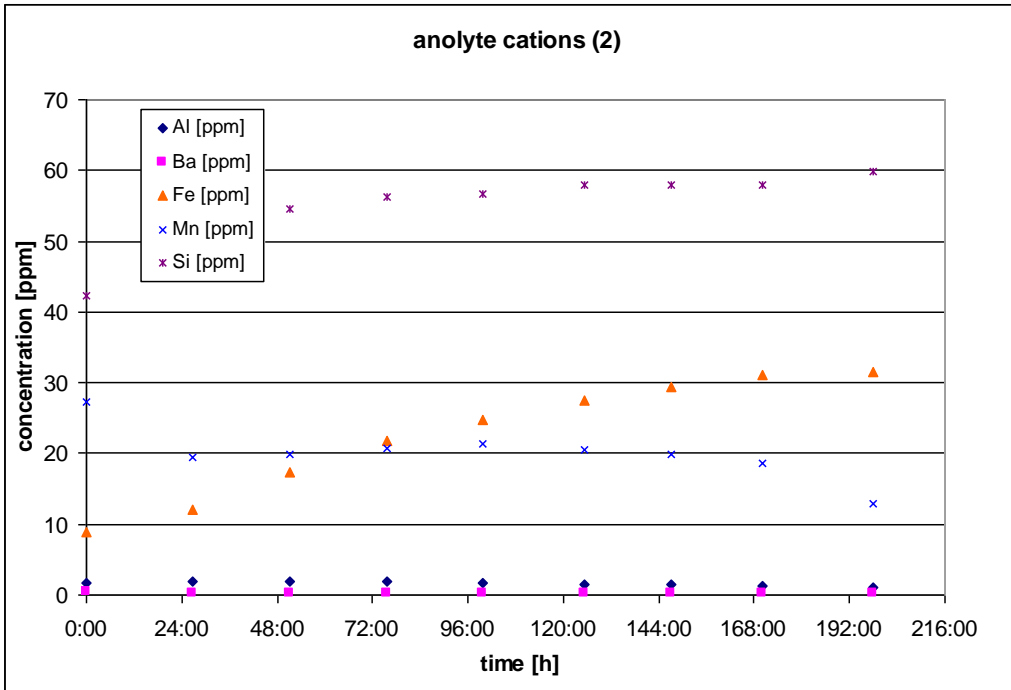


Figure C.4: Concentrations of non-contaminant metals in anode reservoir solution during experiment IV.

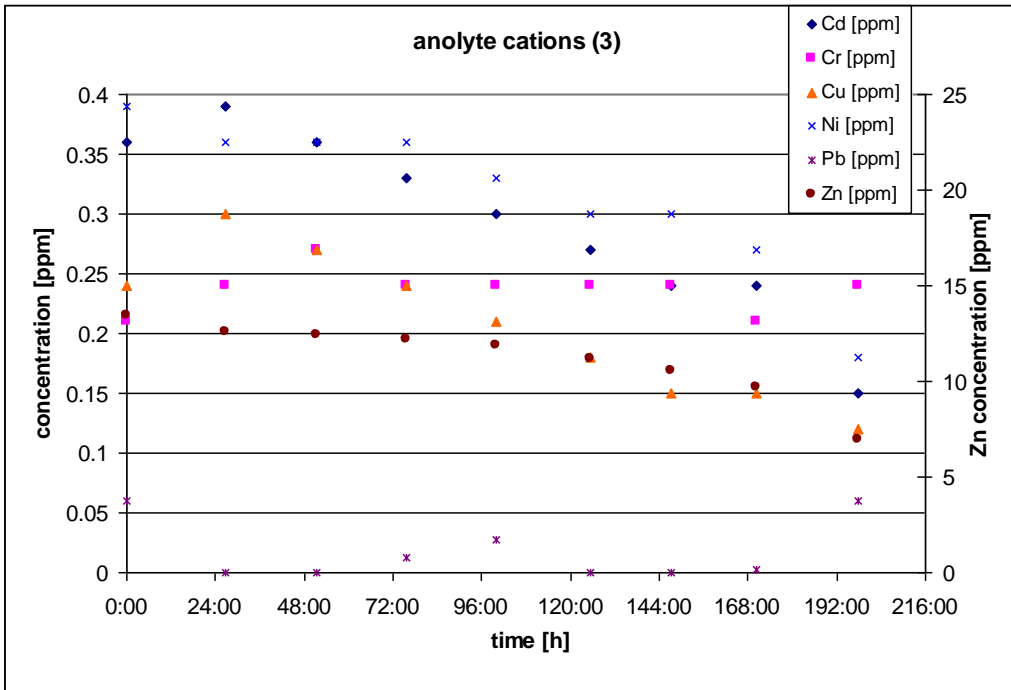


Figure C.5: Concentrations of contaminant metals in anode reservoir solution during experiment IV.

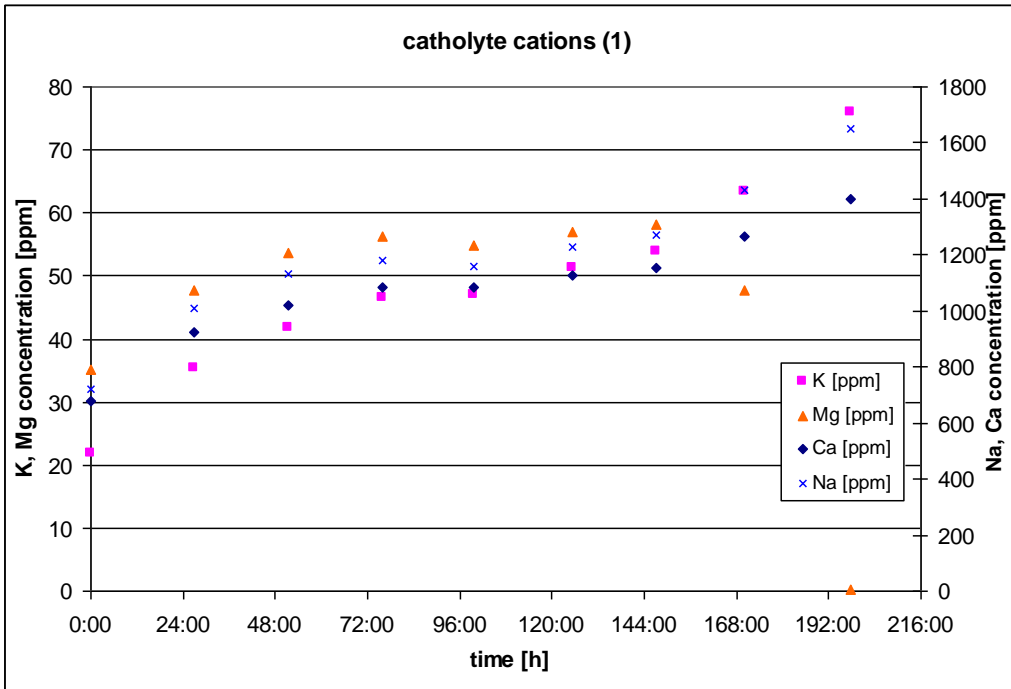


Figure C.6: Concentrations of non-contaminant metals in cathode reservoir solution during experiment IV.

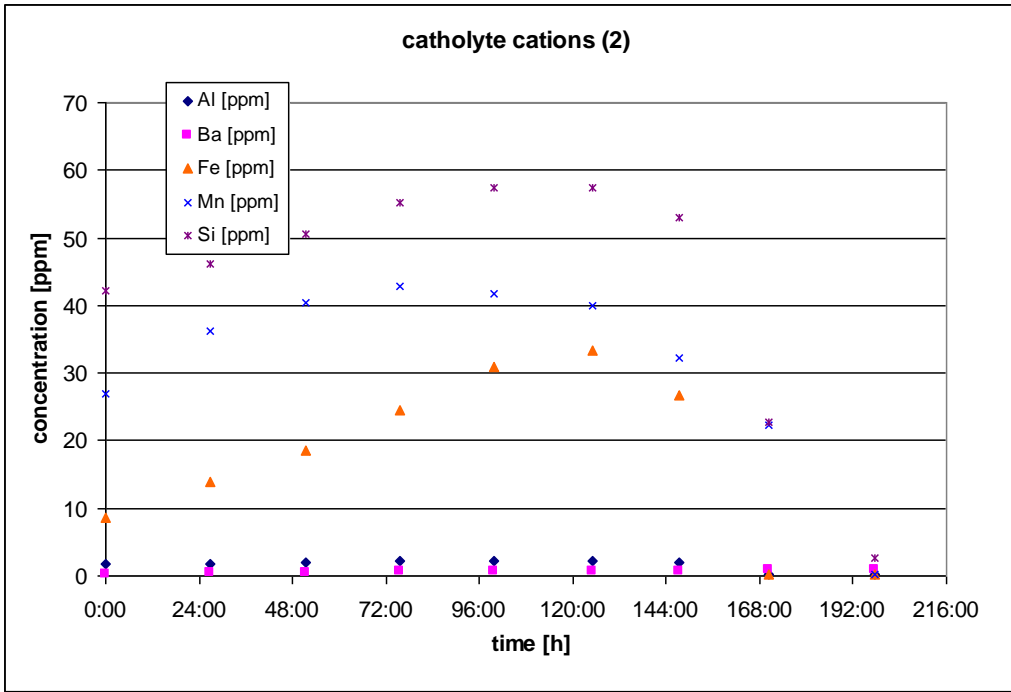


Figure C.7: Concentrations of non-contaminant metals in cathode reservoir solution during experiment IV.

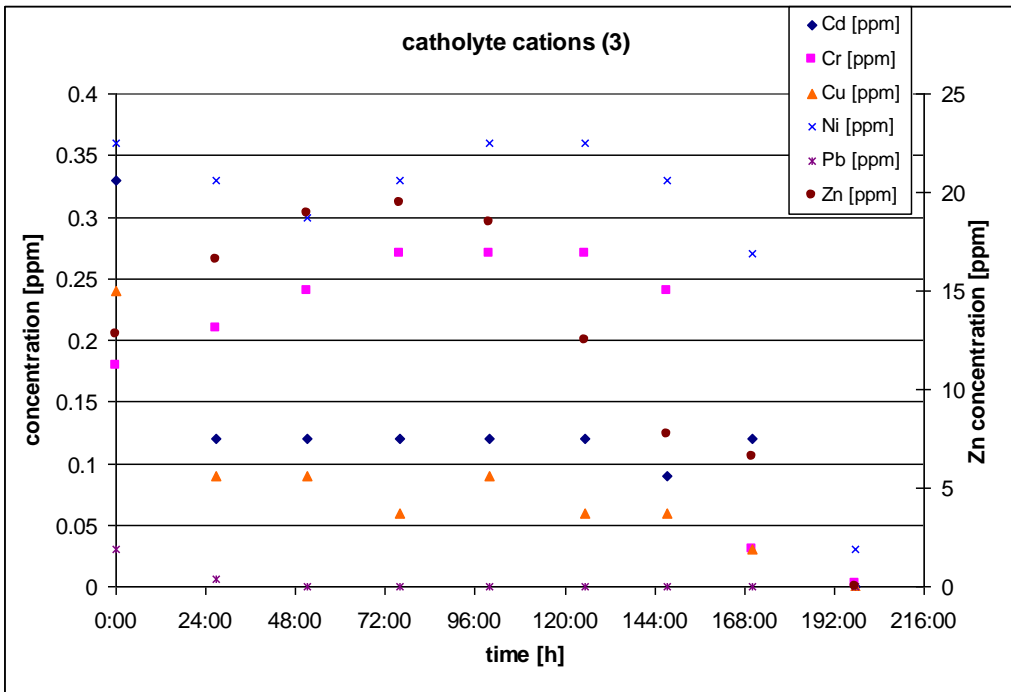


Figure C.8: Concentrations of contaminant metals in cathode reservoir solution during experiment IV.

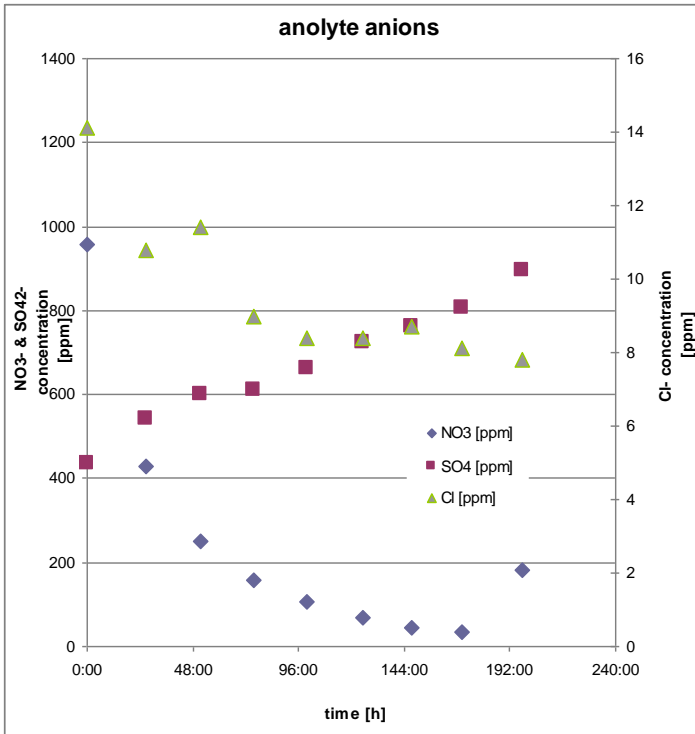


Figure C.9: Concentrations of anions in anode reservoir solution during experiment IV.

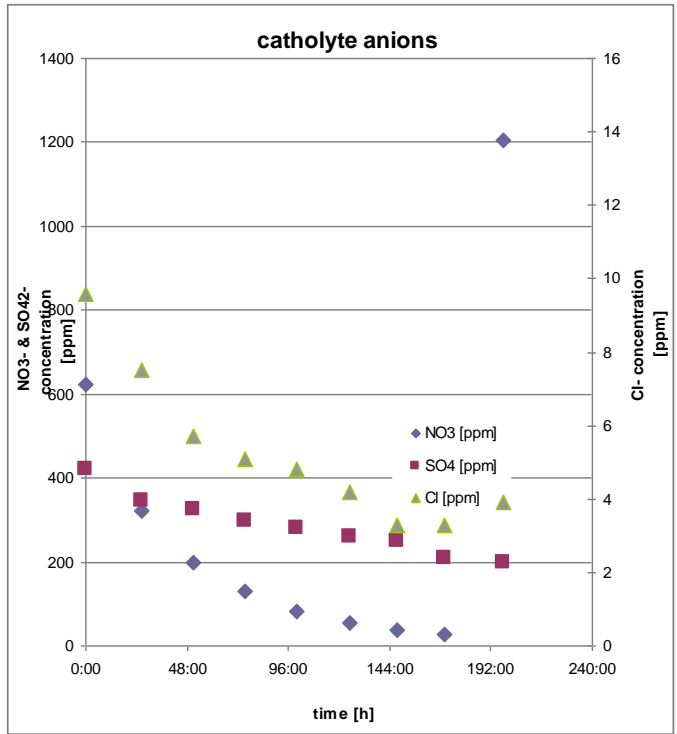


Figure C.11: Concentrations of anions in cathode reservoir solution during experiment IV.

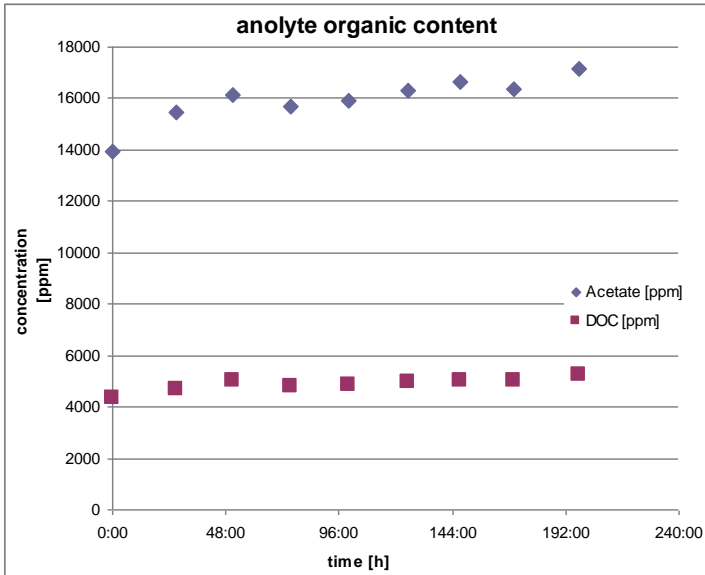


Figure C.10: Concentrations of acetate and DOC in anode reservoir solution during experiment IV.

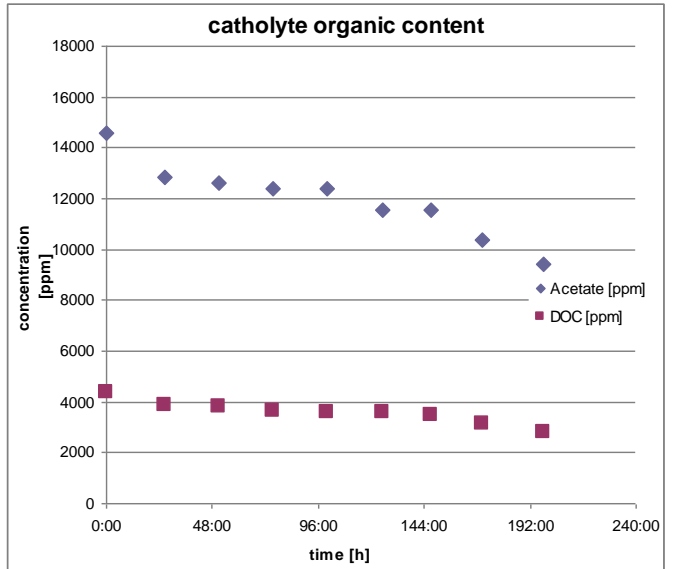


Figure C.12: Concentrations of acetate and DOC in cathode reservoir solution during experiment IV.

## Appendix D

In this appendix the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during experiment S1 are presented.

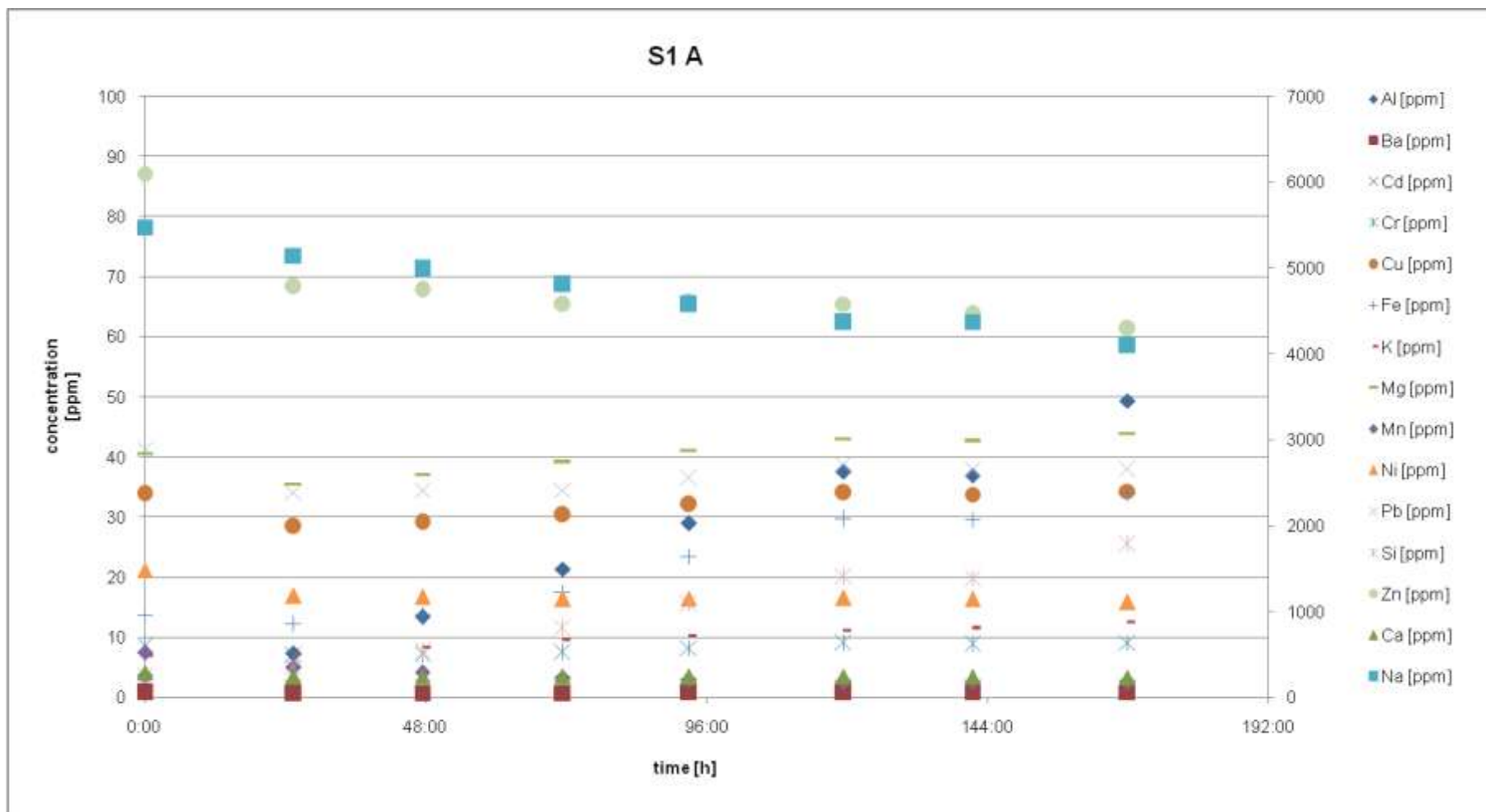


Figure D.1: Concentrations of all metals in anode reservoir solution during experiment S1.

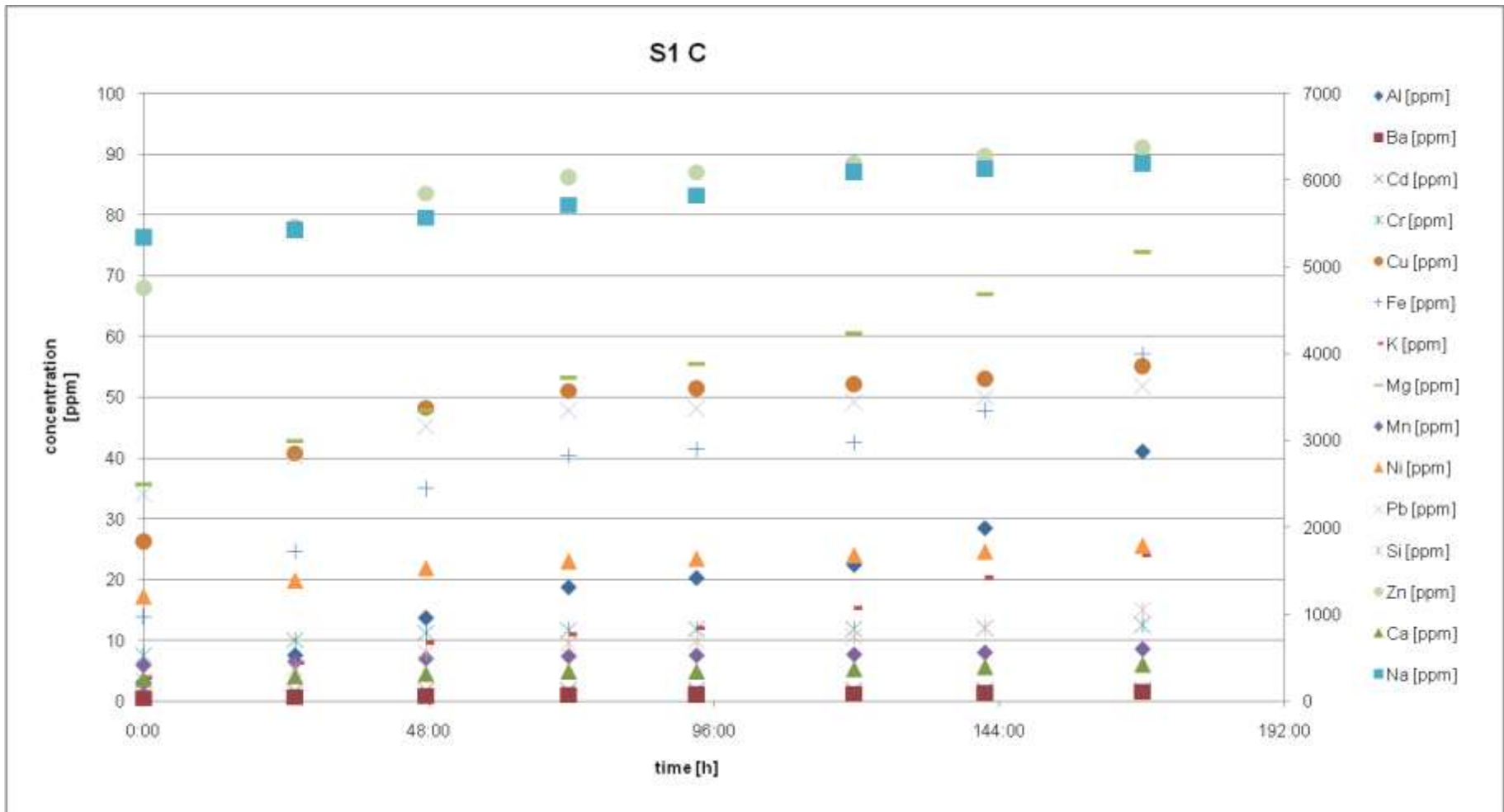


Figure D.2: Concentrations of all metals in cathode reservoir solution during experiment S1.

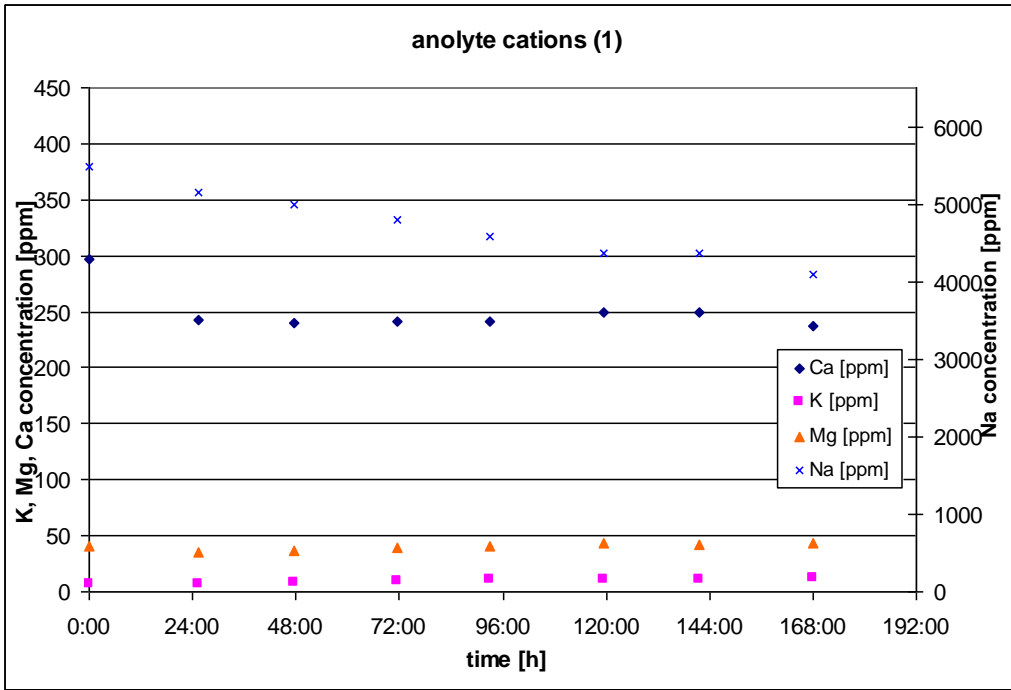


Figure D.3: Concentrations of non-contaminant metals in anode reservoir solution during experiment S1.

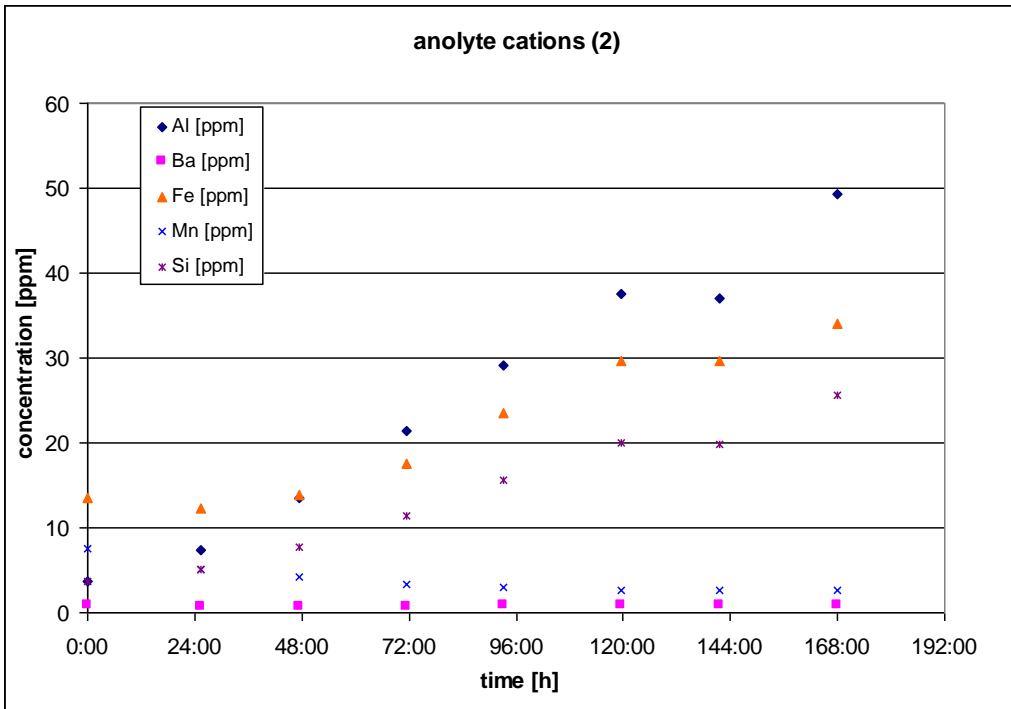


Figure D.4: Concentrations of non-contaminant metals in anode reservoir solution during experiment S1.



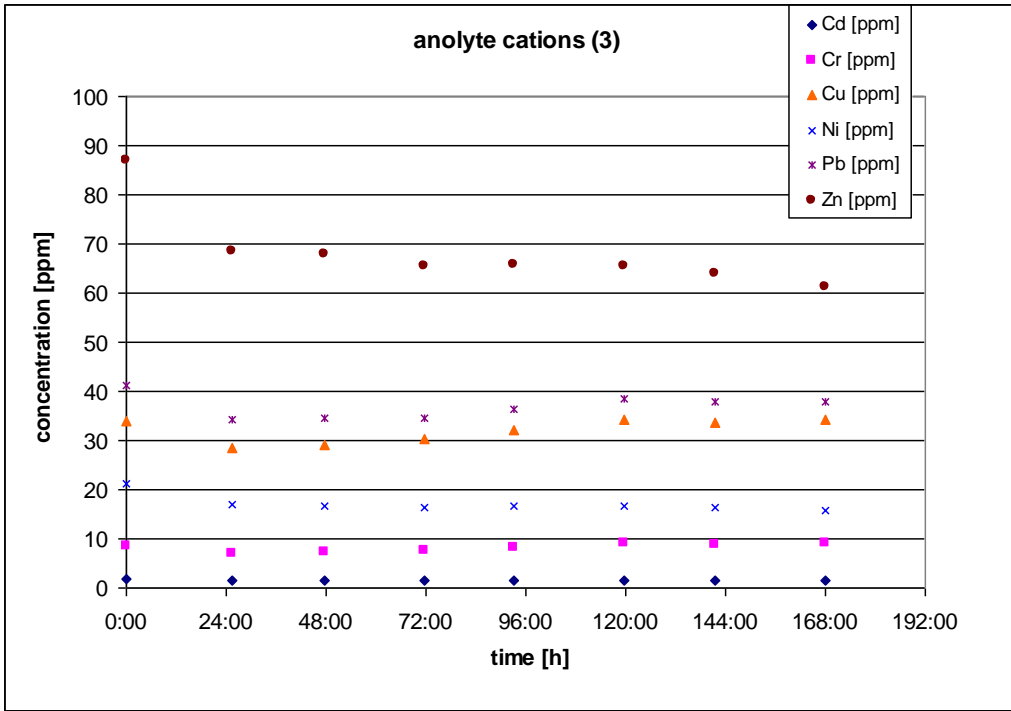


Figure D.5: Concentrations of contaminant metals in anode reservoir solution during experiment S1.

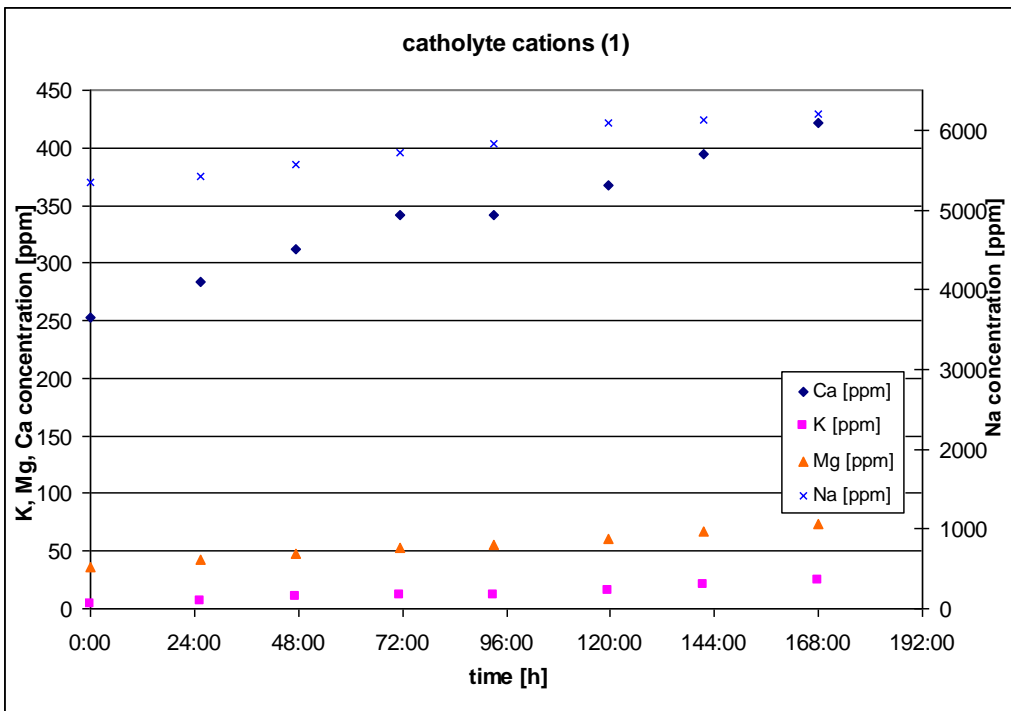


Figure D.6: Concentrations of non-contaminant metals in cathode reservoir solution during experiment S1.

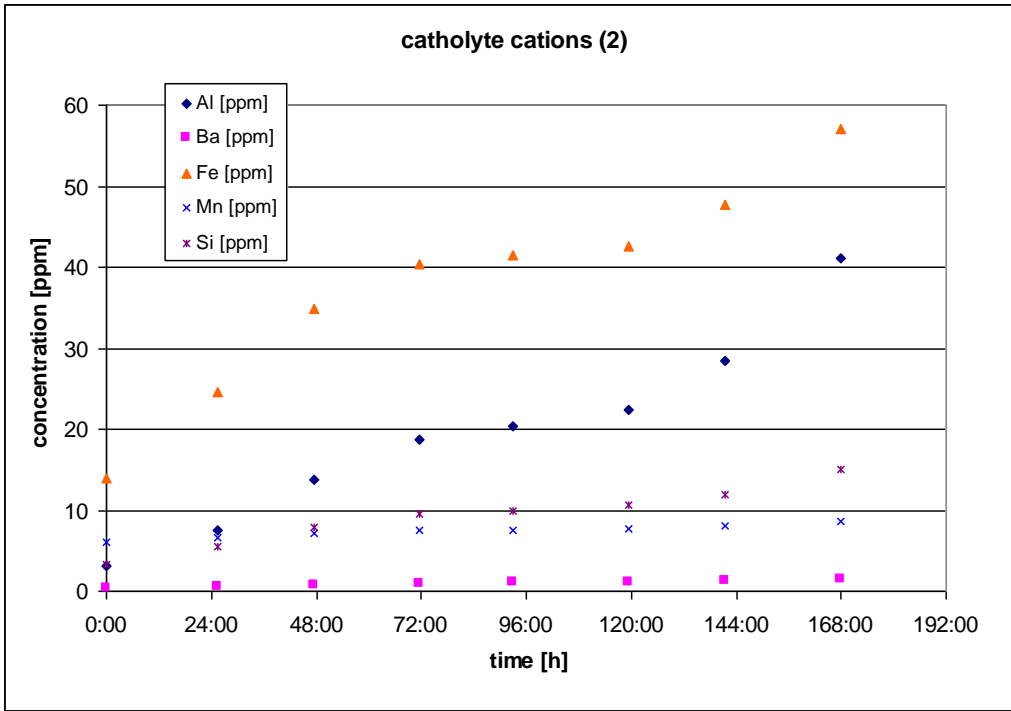


Figure D.7: Concentrations of non-contaminant metals in cathode reservoir solution during experiment S1.

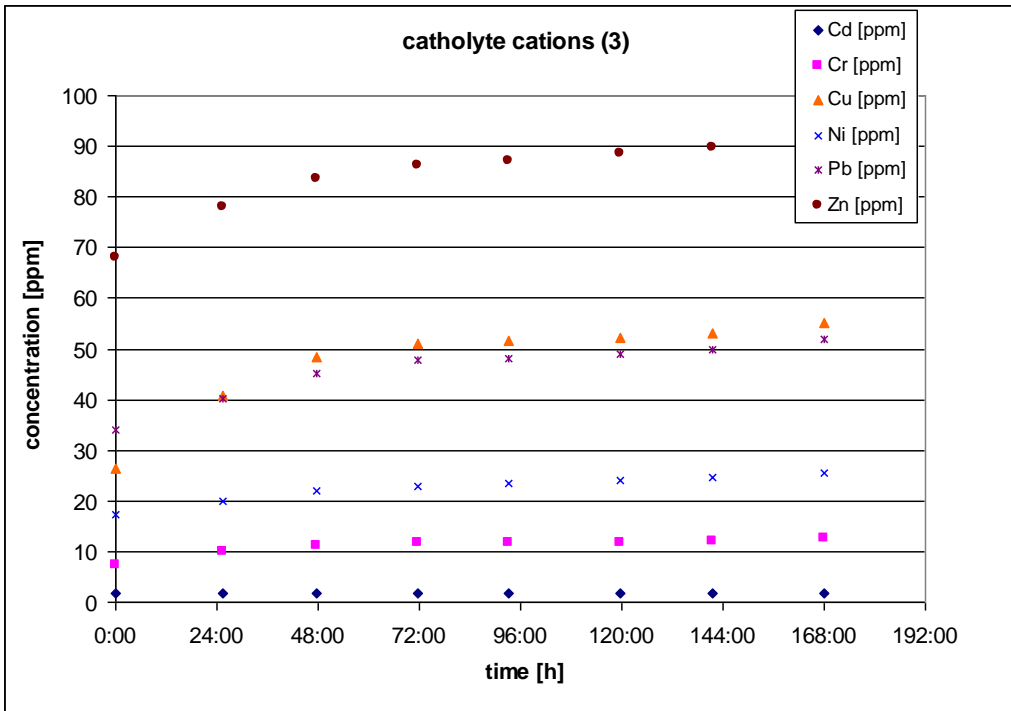


Figure D.8: Concentrations of contaminant metals in cathode reservoir solution during experiment S1.

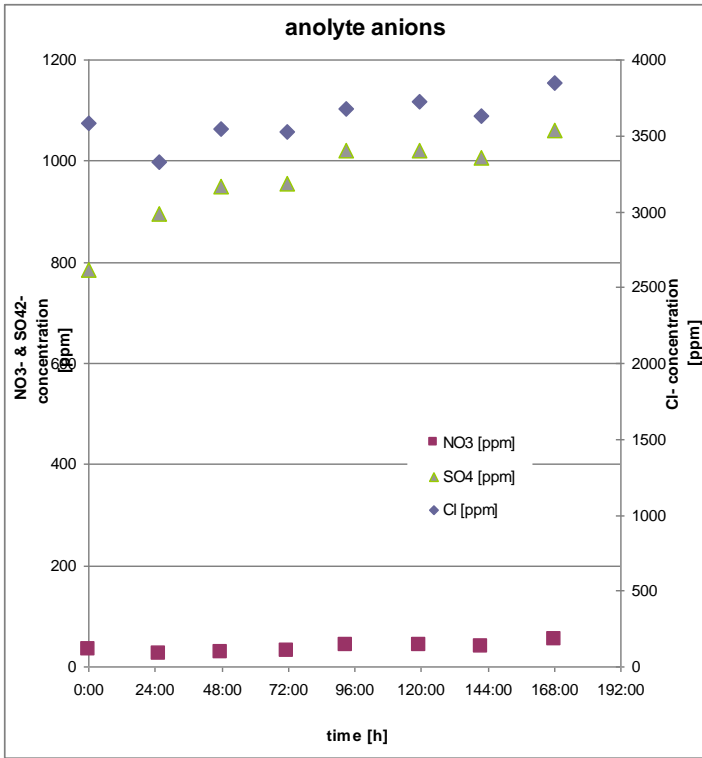


Figure D.9: Concentrations of anions in anode reservoir solution during experiment S1.

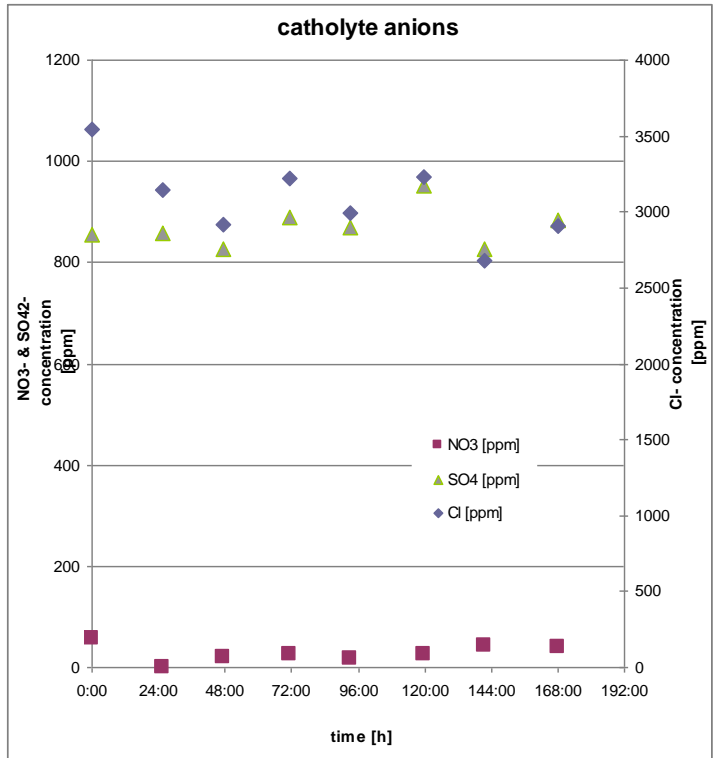


Figure D.11: Concentrations of anions in cathode reservoir solution during experiment S1.

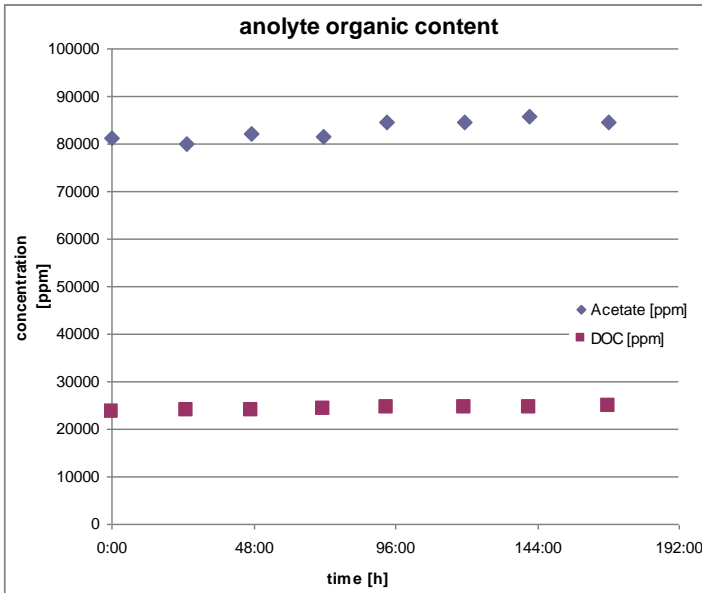


Figure D.10: Concentrations of acetate and DOC in anode reservoir solution during experiment S1.

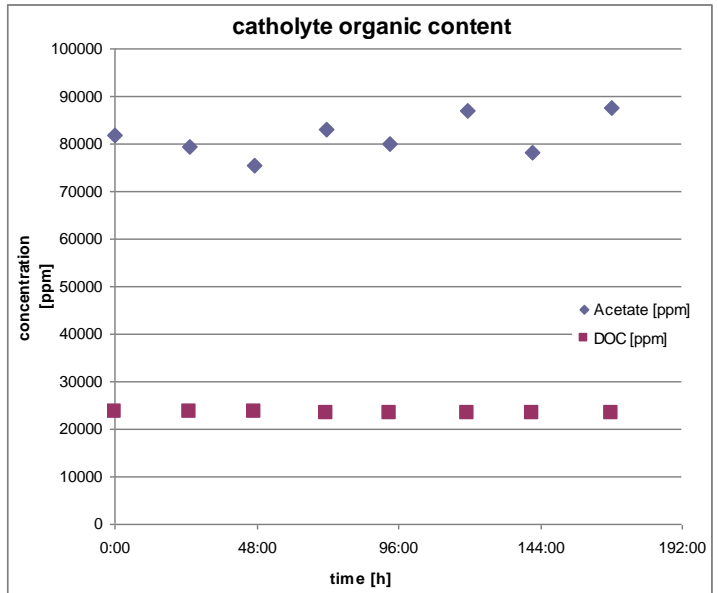


Figure D.12: Concentrations of acetate and DOC in cathode reservoir solution during experiment S1.

## Appendix E

In this appendix the concentrations of all metals, anions and organic content in both the anode and cathode reservoir during experiment S2 are presented.

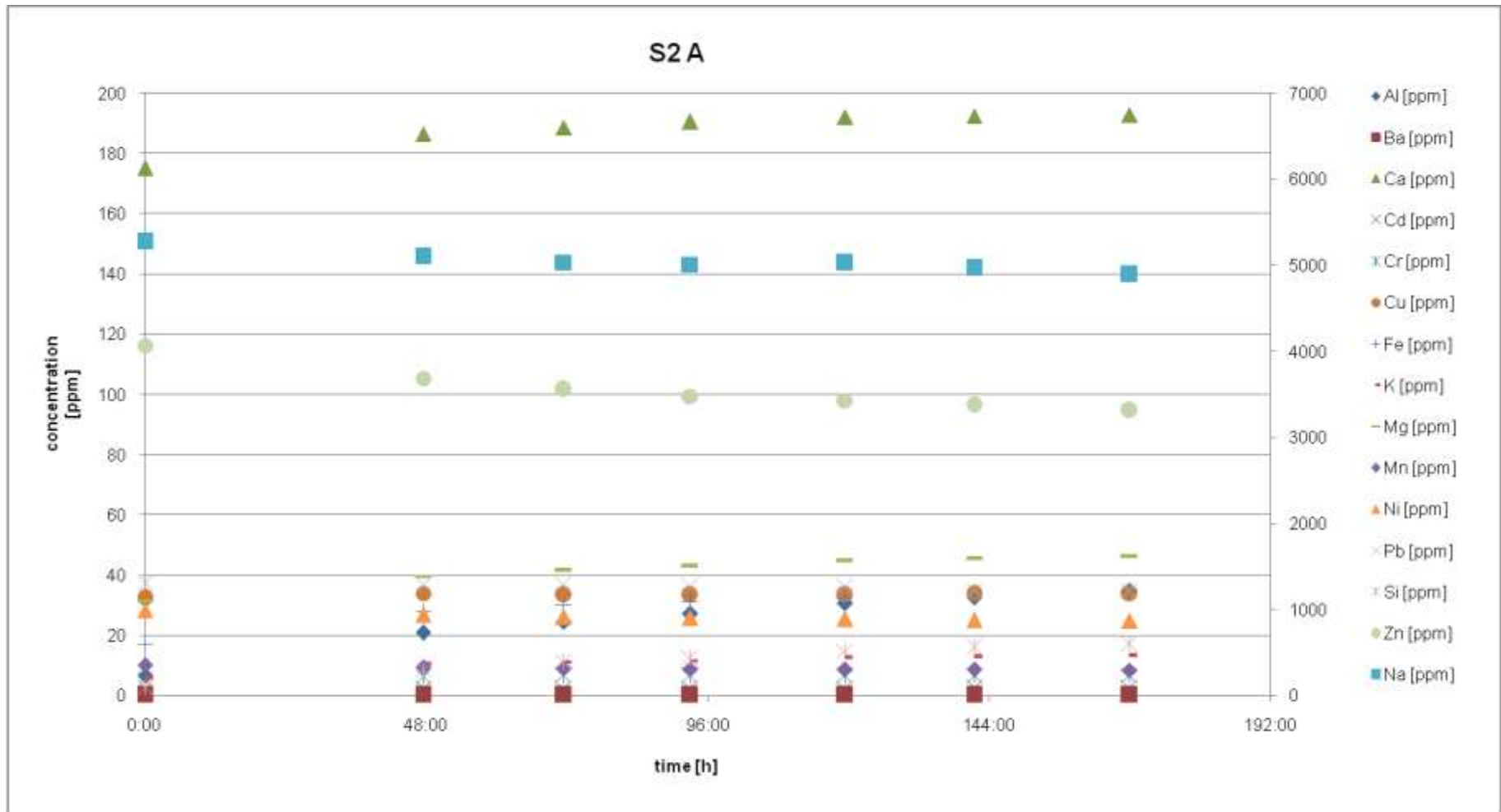


Figure E.1: Concentrations of all metals in anode reservoir solution during experiment S2.

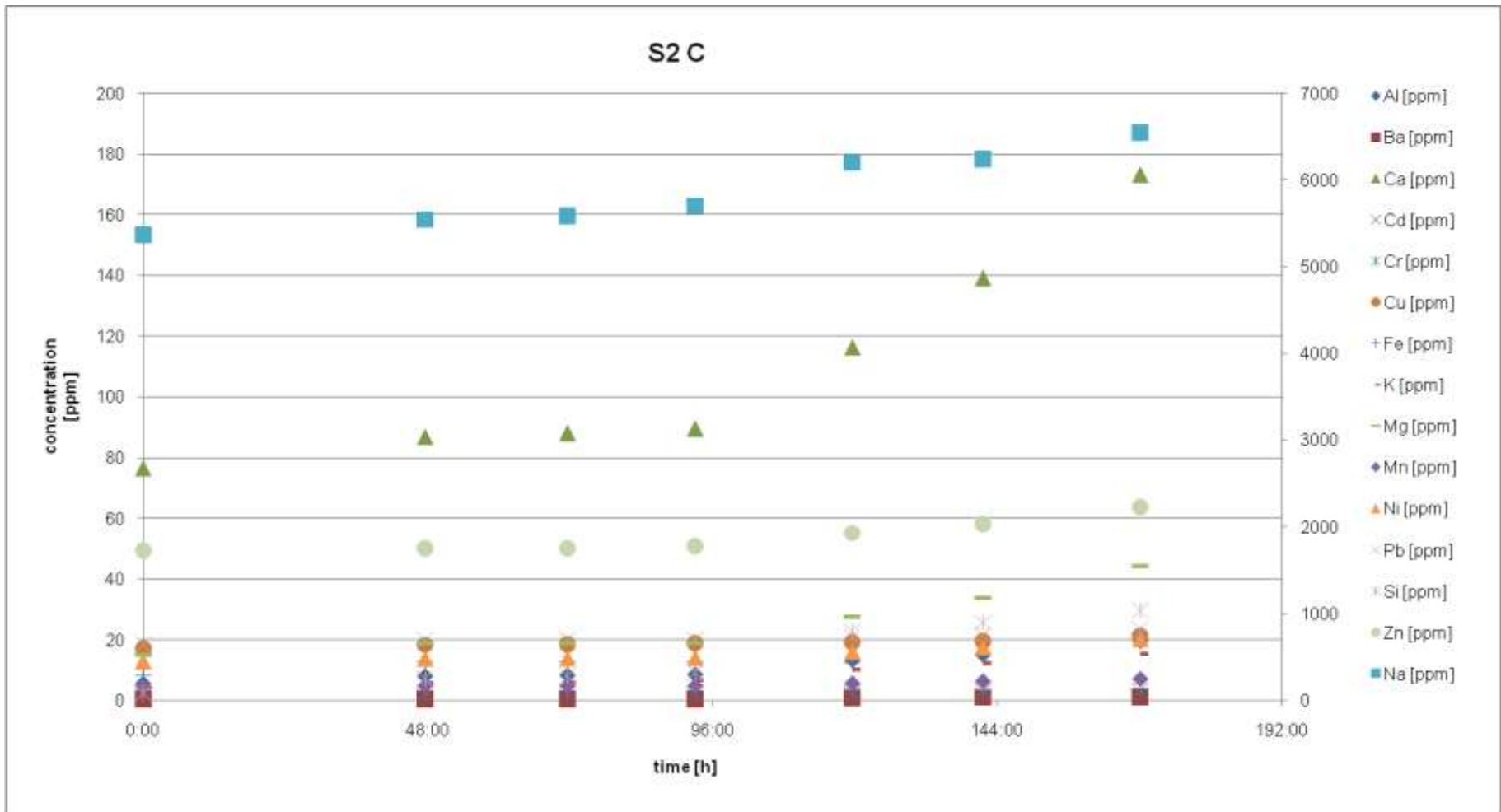


Figure E.2: Concentrations of all metals in cathode reservoir solution during experiment S2.

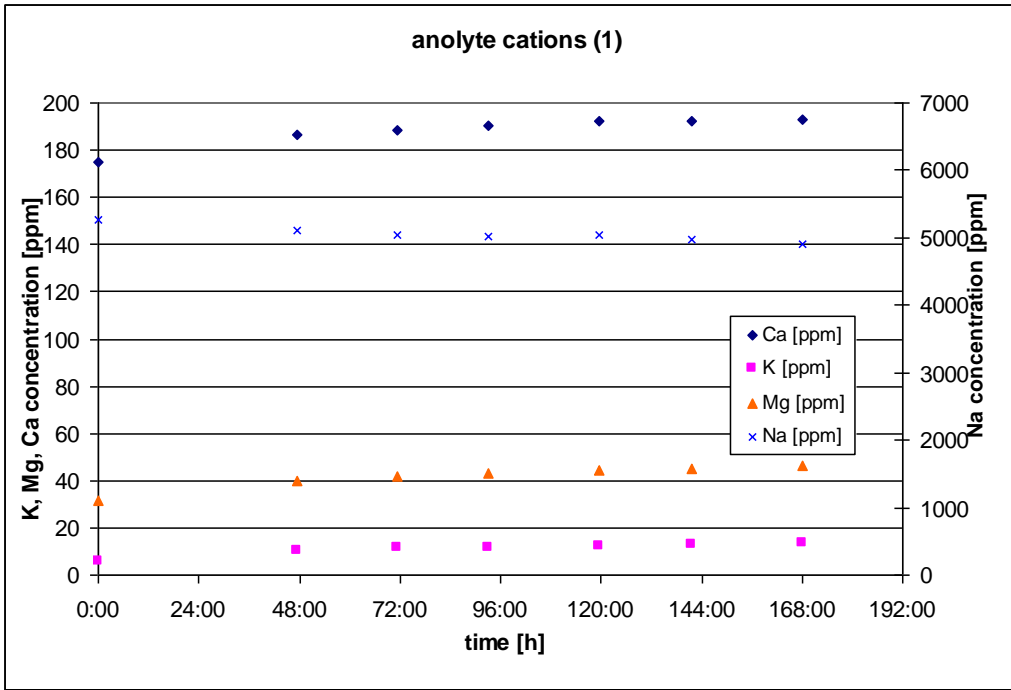


Figure E.3: Concentrations of non-contaminant metals in anode reservoir solution during experiment S2.

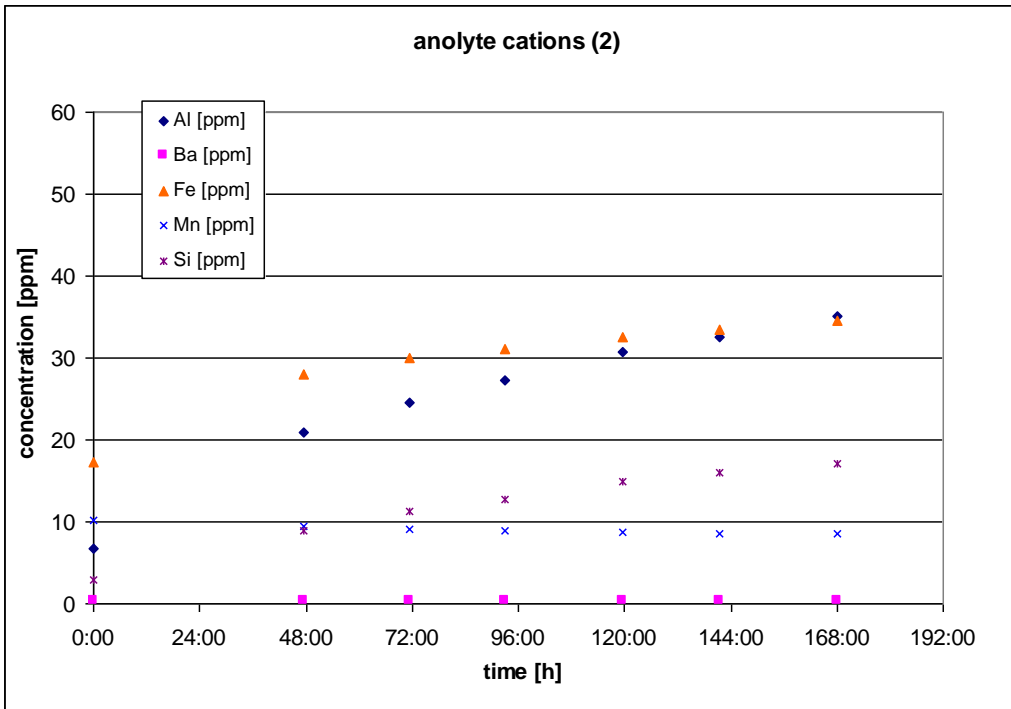


Figure E.4: Concentrations of non-contaminant metals in anode reservoir solution during experiment S2.

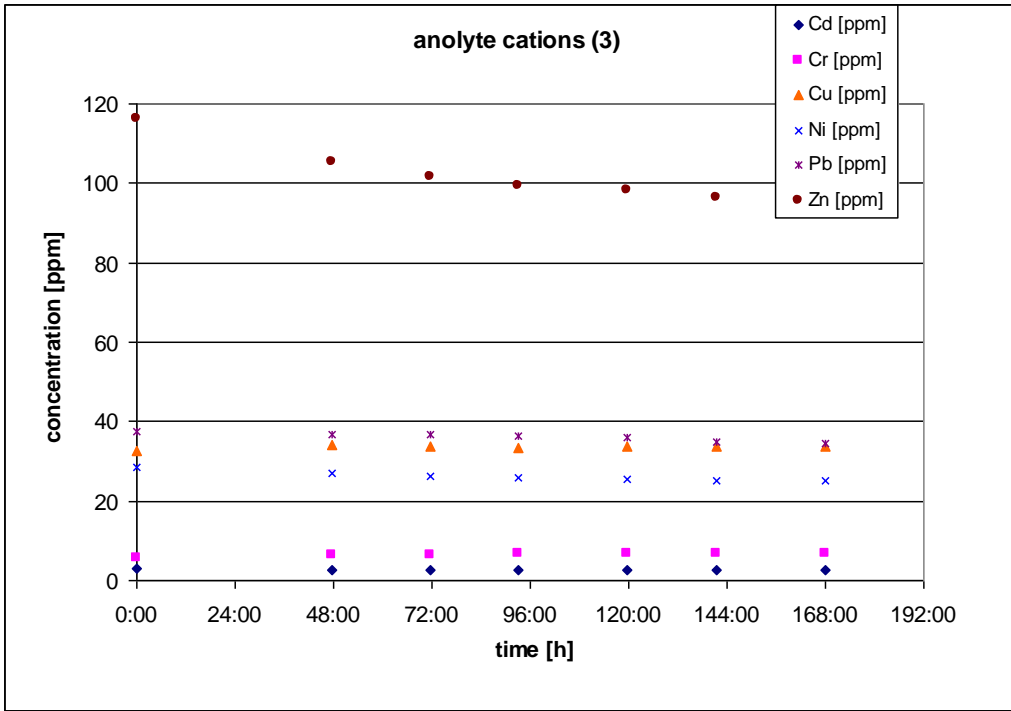


Figure E.5: Concentrations of contaminant metals in anode reservoir solution during experiment S2.

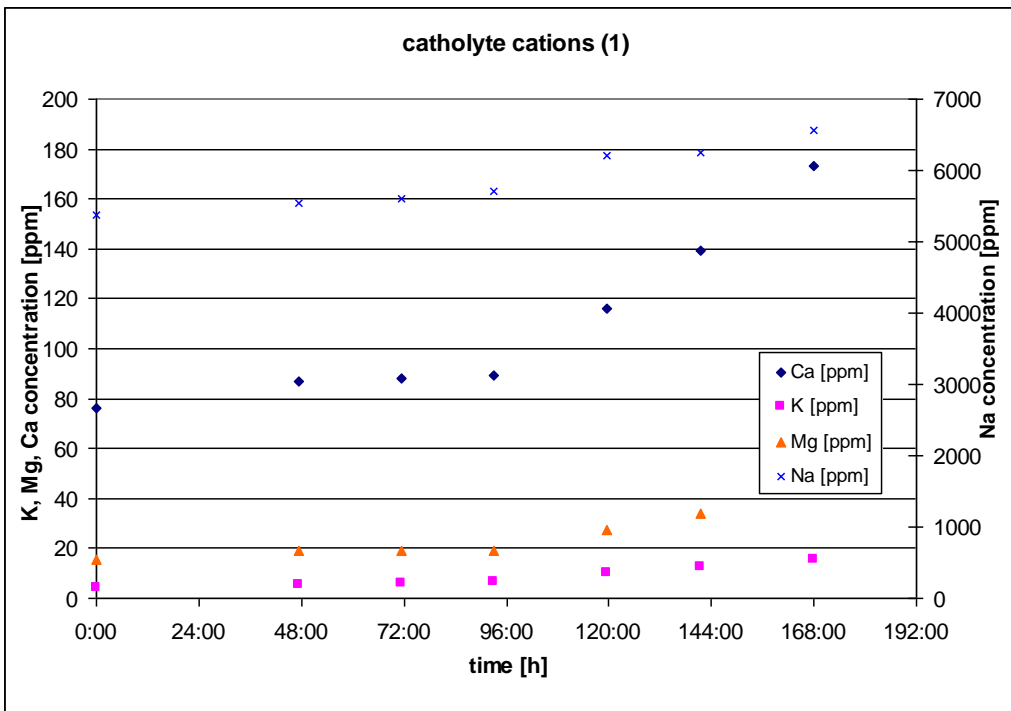


Figure E.6: Concentrations of non-contaminant metals in cathode reservoir solution during experiment S2.

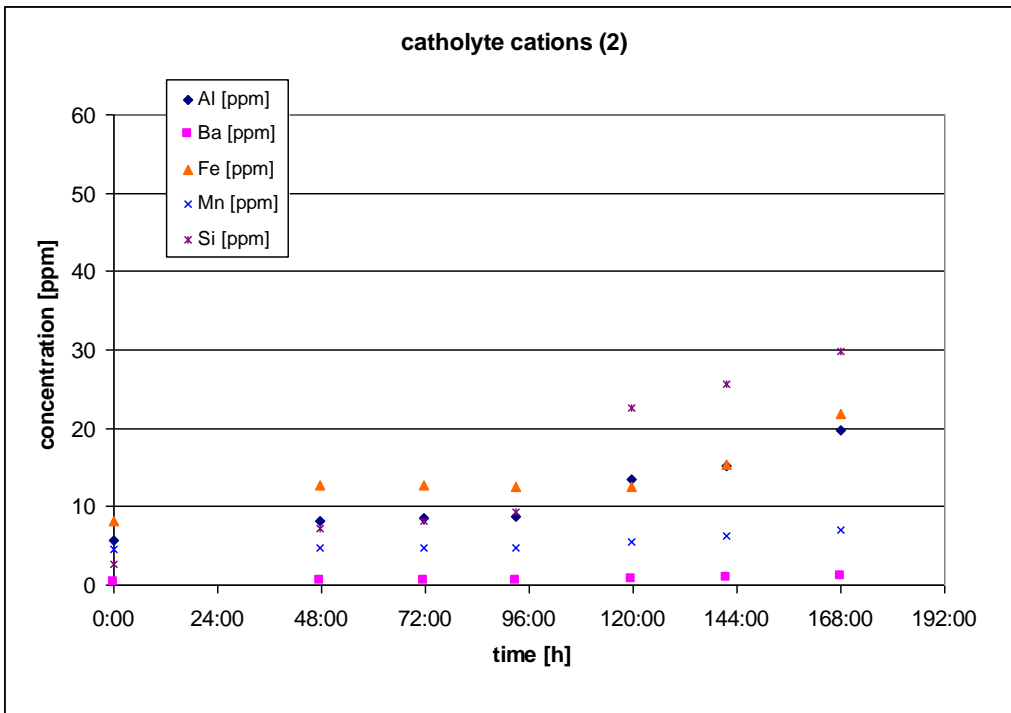


Figure E.7: Concentrations of non-contaminant metals in cathode reservoir solution during experiment S2.

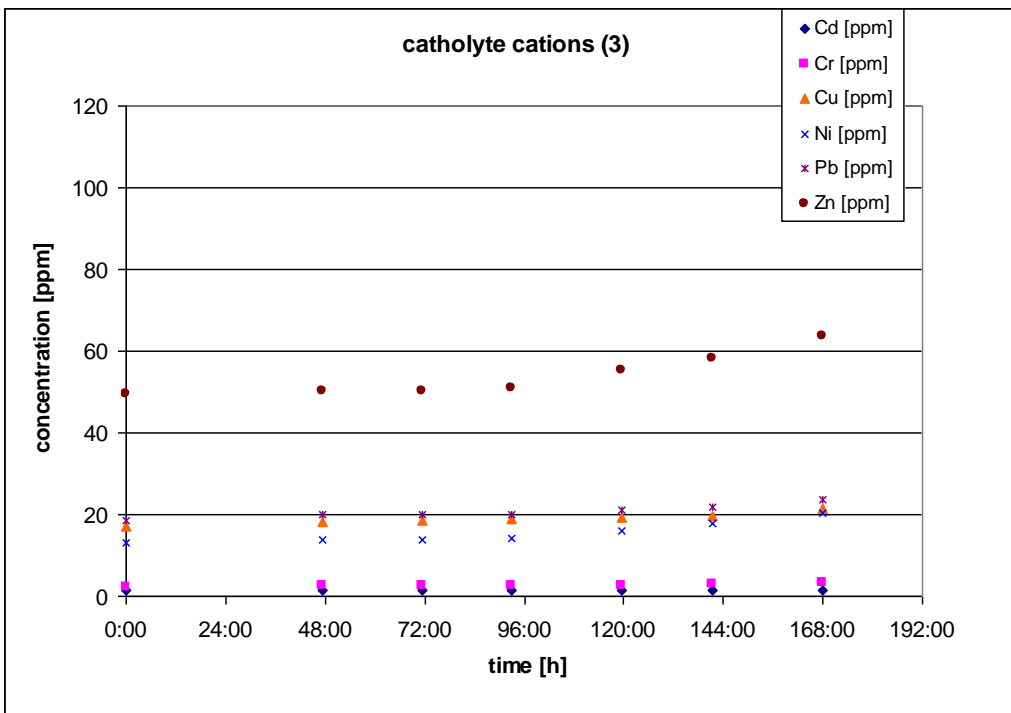


Figure E.8: Concentrations of contaminant metals in cathode reservoir solution during experiment S2.



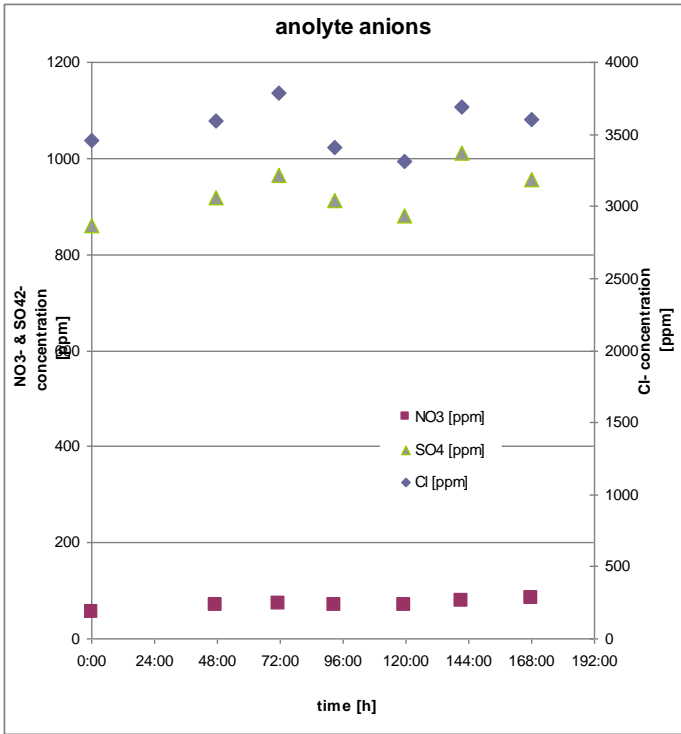


Figure E.9: Concentrations of anions in anode reservoir solution during experiment S2.

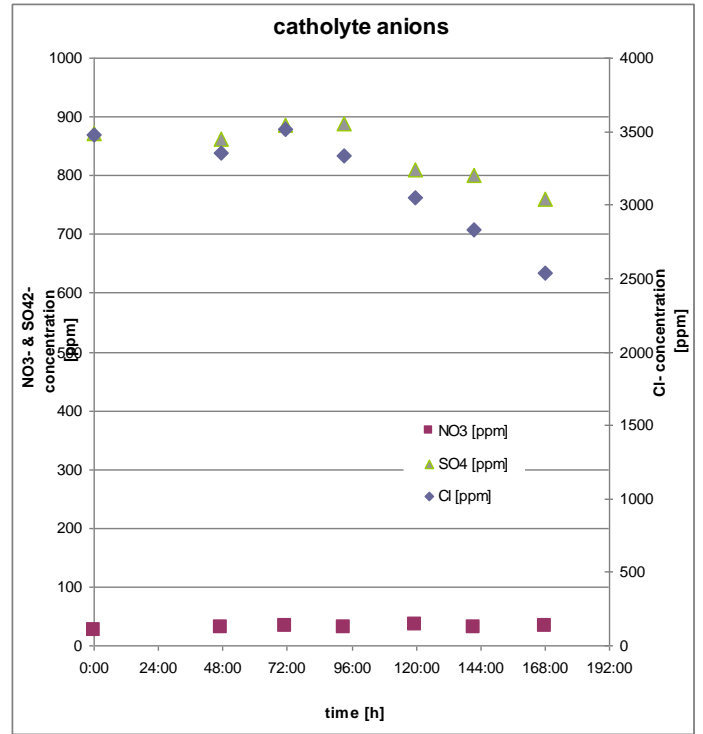


Figure E.11: Concentrations of anions in cathode reservoir solution during experiment S2.

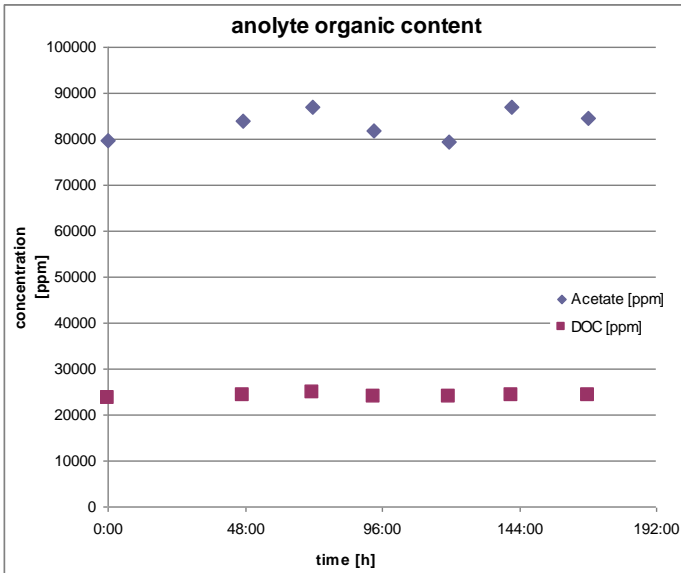


Figure E.10: Concentrations of acetate and DOC in anode reservoir solution during experiment S2.

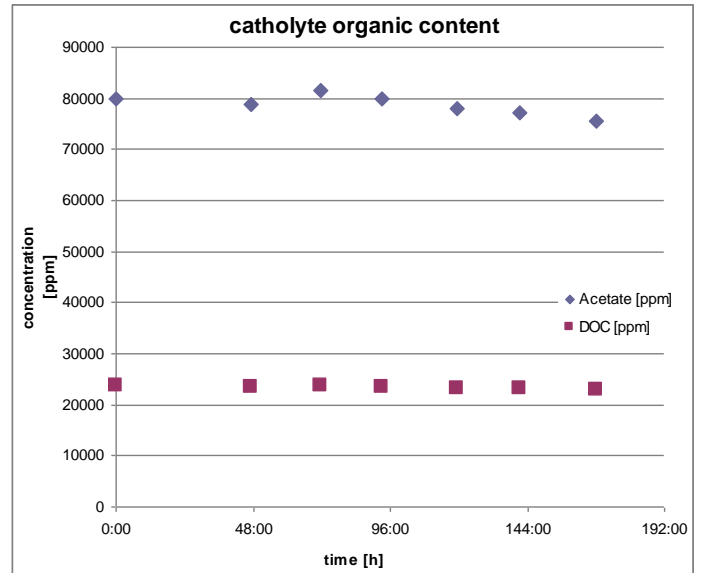


Figure E.12: Concentrations of acetate and DOC in cathode reservoir solution during experiment S2.