

Electrodialytic extraction of Cd and Cu from sediment from Sisimiut Harbour, Greenland

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Abstract

A previous study showed that the sediment of Sisimiut Harbour, Greenland is polluted with Cu and Cd to an extent where toxicological effects must be expected. This study was aimed at evaluating the possibility for removing Cu and Cd from this sediment by an electrodialytic method and also to evaluate the removal rate of the two heavy metals. The sediment was suspended in distilled water during application of current. Both heavy metals were removed successfully. The Cu concentration was reduced from 97 to 16 mg/kg and the Cd concentration was reduced from 0.55 to 0.03 mg/kg after 28 days with an applied current density of 1.2 mA cm⁻². However, it was seen that the removal rate decreased considerably after 3 days with an applied current density of 0.5 mA cm⁻² and the major part of the two heavy metals was removed during the first 3 days (the Cu concentration was reduced with 74% and the Cd concentration with 80%). Thus a large reduction in concentrations can be obtained relatively fast. During the process of electrodialytic treatment the sediment suspension is acidified and reaches pH 2 after about 3 days (with 0.5 mA cm⁻²), where it stabilizes. A comparison with chemical extraction in HNO₃ at about the same pH showed that 50–70% more Cu and 11% more Cd was removed during the electrodialytic treatment.

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1. Introduction

Increased heavy metal concentrations are found in harbour sediments worldwide. A great concern for increased heavy metal concentrations in the aquatic environment of the Arctic region exists because this environment is so vulnerable to toxic compounds. In a previous investigation of the heavy metal pollution of the sediment in Sisimiut Harbour [1] it was found that the harbour sediment had concentrations of Cu and Cd that were in the range where toxicological effects can be expected according to the OSPAR limiting concentrations (Oslo Paris Commission for protection of the aquatic environment in the North-Eastern Atlantic Sea). It was also found that Pb, Zn, Cr and Ni did not reach such problematic concentrations [1].

Greenland is an autonomous part of Denmark with its own legislation, however, there is not yet Greenlandic limiting values for pollutants in harbour sediments in Greenland and therefore

the Danish limiting values are used in this paper together with the OSPAR limiting concentrations for evaluating concentrations of Cd and Cu.

In many Danish harbours, sediment is dredged in order to maintain navigational depth. Traditionally the dredged sediment was dumped at sea, but an increased awareness of the pollution level and the danger of relocating the pollution have influenced this practice, so the most polluted sediment is now disposed off at land at high costs. Sediment from Sisimiut harbour is not dredged since the navigational depth constitutes no problem. This means that only if it is found necessary to avoid spreading of contamination from the harbour to the surroundings, the sediment should be dredged and treated.

Heavy metals tend to be associated to organic matter in the sediment, e.g. [2] and that was also the case in the Sisimiut sediment [1]. Furthermore, there seemed to be a relation between fine fraction and heavy metal concentration in the Sisimiut sediment [1], which is not always seen, e.g. not in sediment from Göteborg Harbour, Sweden [2]. Relocation of sediment with increased heavy metal concentrations from the harbour into the surroundings may occur by sediment transport and sedimen-

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tation resulting in spreading of the pollution. Relatively high concentrations of both Cu and Cd were found in sediment samples taken in the waterway to the harbour in Sisimiut underlining potential for spreading to the surroundings [1].

The present investigation deals with an electro-dialytic method that has shown potential for removal of heavy metals (Cu, Zn, Pb, Cd) from Danish and Norwegian harbour sediments [3]. In the present work it is investigated whether Cu and Cd, the two problematic heavy metals, can be removed from the Sisimiut harbour sediment with electro-dialytic remediation. Next to the possible reduction in heavy metal concentration during treatment, focus is laid on the removal rate and the influence of pH on the process.

2. Electro-dialytic remediation of harbour sediment

Electro-dialytic remediation was first developed for removal of heavy metals from soils, but the method has also shown promising results for removal of different heavy metals from other porous heavy metal polluted waste products [4] such as harbour sediments [3]. The method is based on application of an electric dc field to the polluted medium. By the use of ion exchange membranes the main direction for the electromigration within the polluted medium is determined to be out of the medium.

Originally, in soil remediation experiments, the polluted medium was placed in the desalination compartment as stationary and water saturated, e.g. [5]. Later it has been shown that for treatment fine-grained materials such as fly ash [6] and harbour sediment [7] it is beneficial to treat the material in a stirred suspension instead of as a stationary matrix. In the stirred system the removal of heavy metals was better and the voltage was more stable (the experiments were conducted with constant current).

The principle of electro-dialytic treatment of a stirred suspension is shown in Fig. 1. When the ion exchange membranes are placed as shown, compartment (III) with the suspended medium is a desalination compartment. Compartments (I) and (V) are electrode compartments whereas compartments (II) and (IV) are concentration compartments. The outer set of membranes

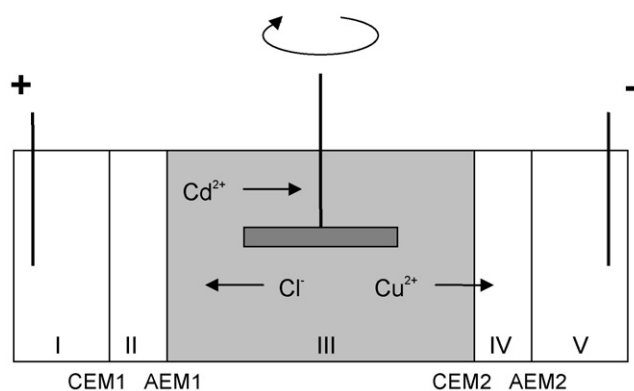


Fig. 1. Principle of electro-dialytic remediation of a stirred suspension of fine-grained material (AEM=anion exchange membrane and CEM=cation exchange membrane).

ensures that the elements from the central compartment will not reach the electrodes and take part in the electrode processes by, e.g. electro-precipitation at the cathode where the size of cathode may increase or formation of toxic gases at the anode (e.g. Cl_2 when chloride ions are present in the polluted medium).

Nystrøm et al. [8] conducted electro-dialytic remediation experiments in cells as shown in Fig. 1 with Norwegian sediment and found that the best removal of heavy metals generally was obtained when the sediment was suspended in distilled water as opposed to various extracting reagents as HCl, NaCl, lactic acid, citric acid and ammonium citrate. During the application of the electric dc field the sediment suspension was acidified which was aiding heavy metals mobilization and this acidification was more efficient in mobilization than the extraction reagents. The order electro-dialytic removal of heavy metals (in percentage) in a suspension of distilled water was $\text{Cd} > \text{Zn} > \text{Pb} > \text{Cu}$, which is also the order found for other harbour sediments [3]. Thus the two heavy metals in the present investigation, Cd and Cu, represent the more and less mobile of these four heavy metals in these previous experiments.

3. Experimental

Experiments were conducted with two sediment samples from Sisimiut Harbour, Greenland. The two samples are named batch (I) and batch (II). The experimental series with batch (I) includes Cu, whereas the experiments with batch (II) includes both Cu and Cd.

3.1. Characterization

The concentrations of Cd and Cu were measured after pre-treatment as described in Danish Standard 259 “Determination of metals in water, sludge and sediments – General guidelines for determination by atomic absorption spectrophotometry” in which 1.0 g of dry sediment and 20.0 cm^3 7.3 M HNO_3 were heated at 200 kPa (120°C) for 30 min. The liquid was separated from the solid particles by vacuum through a $45 \mu\text{m}$ filter and diluted to 100 cm^3 . The heavy metal concentrations were measured by AAS (atomic absorption spectrometry) equipped with graphite furnace for Cd measurements. The units used in this paper are mg/kg dry matter. The initial concentrations of each of the two sediment batches were found on basis of five independent measurements.

The concentrations of Cu and Cd in the fraction less than $63 \mu\text{m}$ were measured after wet sieving of the sediment for particle separation (the same procedure from Danish Standard 259 was used to measure the Cu and Cd concentration). Five independent measurements were made.

The content of organic matter was found as a loss of ignition after 30 min at 550°C . Sediment pH was measured by mixing 10.0 g dry sediment and 25 cm^3 1.0 M KCl. After 1 h of contact time pH was measured using a pH electrode. The carbonate content was determined by the volumetric calcimeter method. Water content of the sediment was measured as weight loss after 24 h in an oven at 105°C . The conductivity was measured in after 1 h in a suspension of sediment in distilled water (liquid to solid

ratio of 4), corresponding to the liquid to solid ratio that was used in the electrodiolytic experiments. A triple determination was made on the conductivity measurements. For organic content, pH and carbonate content five measurements were made for each sediment batch. Determination of organic content, pH and carbonate content were made with dry samples.

3.2. Release of heavy metals as a function of pH

To examine the pH-dependent extraction of the heavy metals from the sediment, the following procedure was used: 2.5 g dry sediment and 25 cm³ HNO₃ in various concentrations (from 0.01 to 0.25 M) were suspended for 48 h. The suspensions were filtered (0.45 μm), and the heavy metal concentrations measured in the liquid phase with AAS. Extraction in distilled water was made as reference. Each extraction was made in duplicate.

3.3. Electrodialytic remediation experiments

A total of six remediation experiments were made in cells as shown in Fig. 1. The cell is a horizontal cylinder made from Plexiglas with an internal diameter of 8 cm. The length of the electrode compartments were 5 cm, the length of compartments II and IV were 1.5 cm and the central compartment was 10 cm long. The membranes used were obtained from Ionics (anion exchange membrane 204 SZRA B02249C and cation exchange membrane CR67HUYN12116B). Platinum coated electrodes from Permascand (bar electrodes 3–4 cm long and 2 mm in diameter) were used.

A power supply (Hewlett Packard E3612A) was used to maintain a constant current. Through a hole in the top of the central compartment with the sediment suspension, a stirrer was placed approximately in middle height of this compartment. The stirrer was a flexible plastic flab (length 5 cm and width 6 mm) fastened to an insulated wire. A HETO motor, with a rotation velocity of 1300 rpm was used to stir the sediment suspension. During the experiments, all sediment particles were kept in solution and no sedimentation was observed.

In each of compartments I, II, IV and V 500 cm³ 0.01 M NaNO₃ with pH adjusted to about 2 with HNO₃ was circulated (each compartment with own circulation system). During the experiment pH in compartments IV and V were manually adjusted to between 2 and 3.

In the central compartment (III) 87.5 g air-dried sediment was suspended in 350 cm³ distilled water (distilled water chosen from the experience with an other harbour sediment [8]) where suspension in distilled water showed the best heavy metal removal result in comparison with different desorbing agents. The liquid to solid ratio was 4 (air-dried sediment).

The current was kept constant during the experiments and the current density can be calculated from the current and the active membrane area, i.e. the area covered by suspension in the central compartment. The suspension reached to about 2 cm below the hole where the stirrer was placed, but the height differed slightly during the experiments. The active surface area of the membranes was about 41 cm². The current was 50 mA (1.2 mA cm⁻²) in experiments A and B and 20 mA (0.5 mA cm⁻²) in the last

Table 1

Experimental parameters of the six electrodiolytic experiments

	A	B	C	D	E	F
Batch	I	I	II	II	II	II
Liquid:solid	4	4	4	4	4	4
Solution in compartment III	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O	H ₂ O
Duration (days)	14	28	1	3	7	14
Current density (mA cm ⁻²)	1.2	1.2	0.5	0.5	0.5	0.5

four experiments (C–F). In Table 1 the duration, current density and sediment batch are shown for the experiments.

By the end of the electrodiolytic experiments the suspension from the central compartment was filtered. The sediment was dried and crushed in a mortar by hand before the heavy metal concentrations (three samples) and pH (three samples) were measured. The contents of Cd and Cu in membranes, electrolyte solutions and on the electrodes were measured (after extraction in 1 M HNO₃ for the membranes and rinsing the electrodes in 5 M HNO₃).

4. Results and discussion

4.1. Characterization of the sediment

For evaluation of the measured heavy metal concentrations in the sediment samples the values of the OSPAR Commission can be used. Denmark participates in the OSPAR commission (Oslo Paris Commission) for protection of the aquatic environment in the North-Eastern Atlantic Sea, which started in 1998. In OSPAR a set of guiding ecotoxicological assessment criteria (EAC) for the different heavy metals have been made. The EAC values can be used for evaluation of water and sediment quality but it must be stressed that the values are only guidelines. The EAC values consist of two concentrations. If the concentration is above the highest value, it can be considered highly polluted, and toxicological effects can be expected. Between the two values further investigations must be made to evaluate the risk, and finally, below the lowest value, no risk is considered for toxicological effects.

For practically handling of sediment, Denmark has introduced limiting concentrations [11] which also consist of two values. If all the concentrations are below the lowest value the sediment can be dumped at sea. If some analysis shows concentrations between the two values, specific evaluation will be needed, but the sediment can probably be dumped at sea at specific places. If the sediment contains pollutants at concentrations exceeding the highest value, the sediment must (most likely) be deposited at land.

The OSPAR EAC concentrations for Cd and Cu are:

- 0.1–1.0 mg Cd/kg;
- 5.0–50 mg Cu/kg.

The Danish Limiting values for Cd and Cu are:

- 0.4–2.5 mg Cd/kg;
- 20–90 mg Cu/kg.

Table 2
Characteristics of the two sediment batches (n.a. = not analysed)

	Batch I	Batch II
Cu (mg/kg)	97 ± 24	129 ± 26
Cd (mg/kg)	n.a.	0.55 ± 0.02
pH	7.7 ± 0.1	8.0 ± 0.1
Organic content (%)	4.0 ± 0.2	3.7 ± 0.2
Carbonate content (%)	2.4 ± 0.2	1.3 ± 0.1
Conductivity (mS cm ⁻¹)	n.a.	4.6 ± 0.3
Fraction <63 μm (%)	8.9	17.0
Cu (fine fraction) (mg/kg)	320 ± 17	530 ± 22
Cd (fine fraction) (mg/kg)	n.a.	7.8 ± 0.3

As seen, the Danish legislative limiting values are higher than the OSPAR limiting values, but the OSPAR limiting values are considered highly relevant when working with sediment from the Greenlandic environment, because this arctic environment is so vulnerable to pollution. The measured concentrations of Cu and Cd in the two batches of sediment are shown in Table 2. Compared to the OSPAR toxicological assessment criteria the Cu concentration is in a range that can be considered highly polluted and toxicological effects can be expected (more than 50 mg/kg). The Cu concentrations also exceeded the highest Danish limiting value and cannot be dumped at sea. The concentration of Cd is in a level where the OSPAR limiting values advises further investigation to evaluate the risk and is in the lower end of the concentration interval where further investigation is needed to consider the possibility for dumping at sea regarding the Danish limiting values.

It is seen that the Cu concentration was higher in batch (II) than in batch (I). The variation within the five measurements made with each sediment batch is considerable (20–24% of the mean value) showing the inhomogeneous nature of the sediment. The variation in Cd concentration is less, about 4% of the mean concentration.

In Table 2 also the sediment characteristics: pH, carbonate content, organic content and fine fraction are given. In general, the characteristics differ only little between the two batches except from the percentage of particles in the fine fraction (<63 μm). It is seen that 17% and 8.9% per weight is below this fraction in batch (I) and batch (II), respectively. The conductivity of the air-dried sample was measured in distilled water and is relatively high probably mainly due to a high Cl concentration. The sediment was filtered at first and then left to air dry and the chloride that was present in the water after filtration was left after evaporation. In [1] a relation between fine fraction and heavy metal concentration in sediment samples in the Sisimiut area was found, and this fits well with the differences in the two present sediments, where batch (II) is the sediment with the most fine particles and the highest Cu concentration. The Cd concentration was measured in batch (II) only.

It is seen from Table 2 that both Cu and Cd are concentrated in the fine fraction, since the concentrations in this fraction is much higher than in the sediment as total. It may be possible to concentrate the heavy metals by size fractionation of the sediment (washing), where the coarse fraction may be considered unproblematic in relation to heavy metal concentration. Electrolytic

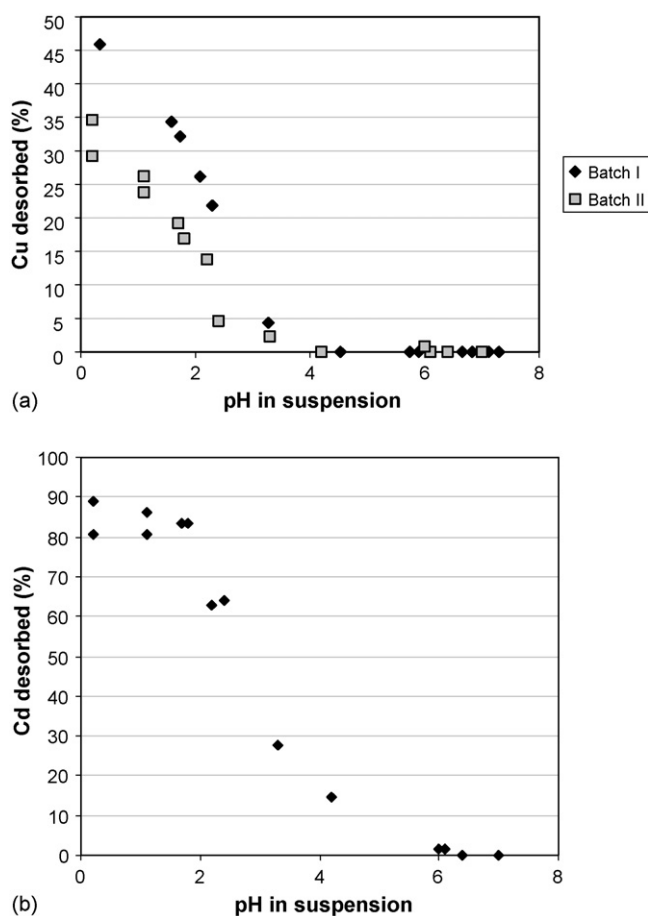


Fig. 2. Extraction of (a) Cu as a function of pH in sediment from batches I and II and (b) Cd extraction as a function of pH in batch II.

remediation of the fine fraction of a soil after particle separation has shown great potential [12] and the method is considered useful for the treatment of fine fraction of harbour sediment, as well.

4.2. Release of heavy metals as a function of pH

Fig. 2(a) and (b) shows the percentages of Cu and Cd that are extracted from the sediment at different pH values. The extracted percentage is calculated on basis of the mean initial concentration of each batch. At the natural pH of the sediments (7.7–8.0) it is seen that extraction is limited. As pH decreases, the extraction of both Cu and Cd increases. This is in accordance with what was reported in [13] for sediment from Bremen Seehausen, Germany.

At pH values below about 4, Cu extraction starts. However, the percentage of Cu extracted from the sediment did not exceed 50% even at pH of 0.3 in either of the batches. The difference in extracted percentages between the two batches of sediment at the different pH values can be due to both sediment characteristics and variation in concentration within each batch as shown in Table 2. From Fig. 2(b) it is seen that Cd is extracted to a higher percentage (from sediment batch II) than Cu, and an extraction percentage of about 80–90% Cd is obtained at pH values below 2. Furthermore, Cd extraction starts at a higher pH than Cu: at

pH 4.1 about 15% Cd is extracted while at this pH no Cu is extracted.

Compared to similar extraction curves for a Norwegian harbour sediment (Haakonsvern, Bergen) given in [3], Cu extraction starts at a higher pH in the Sisimiut sediment (in the Norwegian sediment extraction starts around pH 1). In both sediments though, the maximum Cu extraction did not exceed 50%. In sediment samples from four different Danish harbours the Cu extraction reaches 70–95% at pH around 0.2 [3].

Cd can be extracted at a higher pH in the Norwegian sediment from [3], at pH around 7, than in the Sisimiut sediment. In the Norwegian sediment the extraction reaches about 100% at pH less than 2 (Cd extraction was not investigated in the Danish sediments in [3]).

The differences in extraction pattern in the different sediments must be linked to the nature of the metal bonding with the sediment matrix, however, the different bonding mechanisms have not been investigated yet. In summary it can be said, that the mobility of Cu in the Sisimiut harbour sediment at acidic pH is less than in the Danish sediments and similar to the Norwegian sediment. The Cd extraction pattern in the Sisimiut harbour sediment differs from the pattern in the Norwegian sediment in the fact that extraction starts at a higher (neutral) pH in the Norwegian sediment. In both sediments Cd extraction reaches 90–100% at highly acidic environments.

4.3. Electrodialytic remediation experiments

Effect of process parameters as liquid to solid ratio, current density and remediation of air-dried sediment versus wet sediment was investigated in [10] for other harbour sediments. When choosing the process parameters for the present investigation, the earlier experiences were used. The liquid to solid ratio of 4 was chosen on basis the findings in [10] where it was found that by increasing the liquid to solid ratio from 4 to 8 it was possible to reach only slightly lower concentrations after 14 days of remediation. Thus a liquid to solid ratio of 4 was used here, since the thinner the sediment suspension is the larger plant is necessary and with that increased costs. It was chosen to use air-dried sediment instead of wet sediment as it was sampled. In [19] it was shown that there was no significant difference on the final concentration in the sediment after 14 days of remediation whether the remediation was conducted with wet or air-dried sediment. Since it is easier to ensure the same weight of sediment is used in each of the experiments, air-dried sediment was used.

The current was chosen from earlier experiences with sediment from Haakonsvern, Norway [10] to 50 mA (1.2 mA cm^{-2}). For the Haakonsvern sediment it was found that increasing the current to 70 mA or 90 mA did not result in lower final concentrations after 14 days of applied current. However, the current of 50 mA was from the first two experiments (A and B) found too high for the sediment from Sisimiut (discussed below) and the current was decreased to 20 mA (0.5 mA cm^{-2}) in the last four experiments (C–F). The variation in voltage is shown in Fig. 3. Since the experiments were conducted with a constant current, the voltage is directly linked to the resistivity of the cell, thus when the voltage increases, this shows an increase in resistiv-

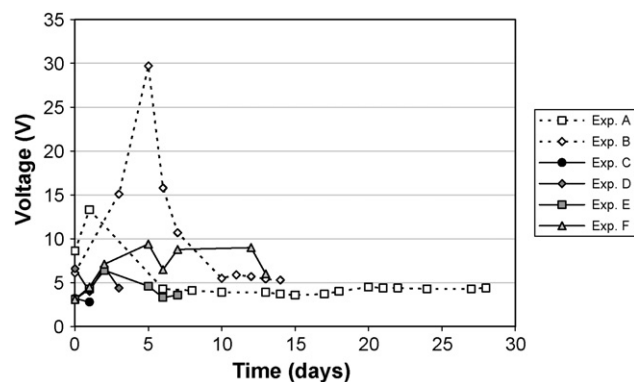


Fig. 3. Cell voltage during electrodiolytic experiments vs. time.

ity, i.e. a decrease in electric conductivity. Previously [9] it was found in electrodiolytic soil remediation (soil stationary) that the Cu removal was almost equal over the surface area of soil when using bar electrodes placed in separate electrolyte solutions, and thus the electric field is regarded equally distributed over the cross area of the cell in the present experiments.

During the first 5 days the voltage increased in experiment (B), while a decrease was seen in the next 5 days. Then the voltage stabilized at a level of about 6 V. The increase in the beginning may be an indication of the ions initially present in the sediment being removed without being replaced by new ions in the central compartment. The decrease in voltage after 5 days shows that at this point an increasing conductivity (decreasing resistivity) is found in the cell, probably in the central compartment. This may very well be linked to the acidification of the sediment partly due to water splitting at the anion exchange membrane as described in [5] and [14] and/or diffusion of H^+ ions from compartment (IV) through the cation exchange membrane into the sediment suspension. It is not possible from Fig. 3 to predict what is the highest value of the voltage and when it starts to decrease again in experiment (A) since data-points are missing between days 1 and 6, but it is seen that the decrease in voltage to the level of about 5–6 V happened earlier in experiment (A) than in (B).

It was chosen to reduce the current density to 0.5 mA cm^{-2} in the next four experiments (C–F) to avoid the relatively high voltage in the beginning of the experiments and this was successfully obtained since the voltage was lower and relatively more stable in these four experiments, as seen from Fig. 3. It is important to keep the voltage low in order to keep the cost for energy consumption to the process low.

The pH was measured during experiments C, D, E and F in the sediment suspension in compartment (III). Fig. 4 shows pH in this compartment at different times.

The sediment was acidified during the remediation process as described above. The pH of the sediments at the end of the experiments is shown in Table 3. In all experiments pH was decreased from the initial neutral range to acidic. The total charge passed through the electrodes was highest in experiment (B) (highest current density and longest duration) and the pH of the sediment in this experiment was also found slightly lower than in the remainder experiments. In experiment (C) the total charge

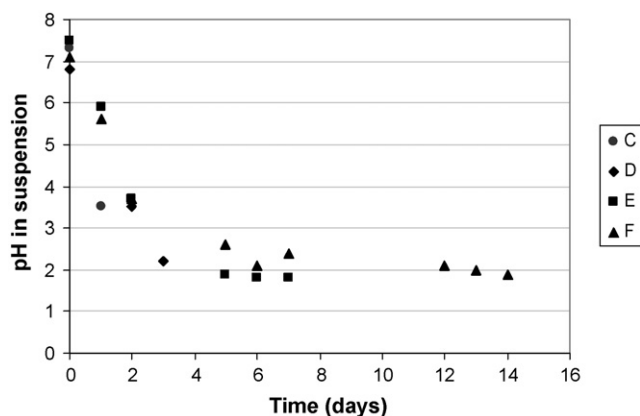


Fig. 4. pH in the sediment suspension during the electrodiolytic experiments C, D, E and F.

passed through the cell was the lowest and the final pH after treatment was slightly higher than in the others.

The total mass of the sediment was also reduced during the experiments (see Table 3) and this is due to dissolution of carbonates (about 1.3–2.4% in the actual sediments) and other particles that are dissolved in the acidic environment and partly due to oxidation of organic matter during the electrodiolytic process as it is known from electrodiolytic treatment of wastewater sludge [15].

Mass balances for the heavy metals in the five experiments were calculated on basis of initial sediment concentrations and the concentrations of heavy metals found in the different parts of the cell at the end of the experiment. The percentage of recovery expresses the percentage of the initial amount of the heavy metal that is found at the end of the experiment (sum of different parts of cell). The percentage of recovery was between 90% and 101% for Cd and between 92% and 105% for Cu. Since there are variations in the initial heavy metal concentrations within each batch of sediment used for the experiments (see Table 2) the recovery cannot be expected to be exact 100%, and the recovery was found in the acceptable range in these experiments.

The Cu and Cd concentrations in the sediment were decreased during all experiments, see Table 3. The Cu removal from sediment batch (I) showed that the concentration had decreased significantly after 14 days and was only slightly lower after 28 days of remediation compared to the first 14 days. The removed percentage of Cu was 82% and 84% in experiments A and B, respectively.

At the end of experiments A and B the Cu concentration was decreased from 97 mg Cu/kg to less than 17 mg Cu/kg, see

Table 3
Final (after electrodiolytic experiments) pH, dry mass of the sediment, Cu and Cd concentration

	Experiment A (1.2 mA cm ⁻² , 14 days)	Experiment B (1.2 mA cm ⁻² , 28 days)	Experiment C (0.5 mA cm ⁻² , 1 day)	Experiment D (0.5 mA cm ⁻² , 3 days)	Experiment E (0.5 mA cm ⁻² , 7 days)	Experiment F (0.5 mA cm ⁻² , 14 days)
pH	2.7	2.6	3.2	3.1	2.7	2.7
Dry mass (g)	78.4	76.6	85.9	76.2	76.5	73.7
Cu (mg/kg)	17 ± 1	16 ± 2	84 ± 7	46 ± 5	31 ± 6	23 ± 5
Cd (mg/kg)	n.a.	n.a.	0.4 ± 0.03	0.11 ± 0.01	0.04 ± 0.01	0.03 ± 0.004

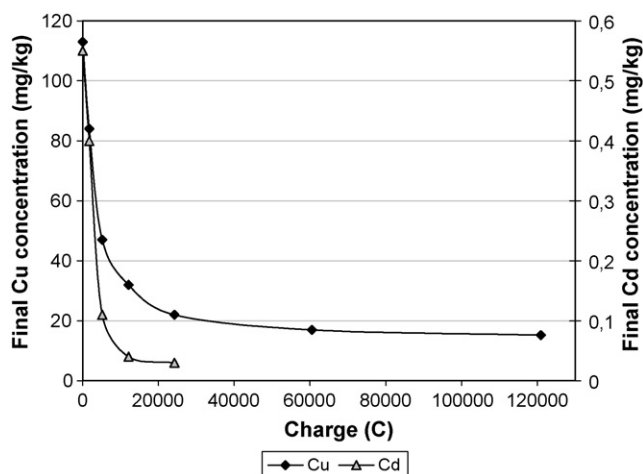


Fig. 5. Final Cu and Cd concentration in sediment after electrodiolytic treatment vs. total charge passed through the cell. With the current applied (20 mA) in the experiments until 24,192 C the charge transfer was 1728 C/day and for the two last points at the Cu graph the charge transfer was 4320 C/day (current 50 mA).

Table 3. Thus the final concentration reached was below the limit for classification as highly polluted sediment according to the OSPAR EAC criteria (>50 mg Cu/kg). However, the sediment cannot be considered without toxicological effect as the EAC limiting value for this is 5 mg Cu/kg. On the contrary to the lowest Danish limiting value of 20 mg/kg is met, and the sediment can be dumped at sea in relation to this legislation.

Since the major part of the remediation occurred within the first 14 days (comparing the result for Cu removal in experiments A and B), the duration of the next experiments, conducted with sediment from batch (II), was chosen to be equal to or less than 14 days. A 14 days experiment was made to compare results with the two different current densities (1.0 mA cm⁻² in experiment A and 0.5 mA cm⁻² in experiment F). The duration of the last three experiments was decreased to 7 days, 3 days and 1 day, respectively to investigate how early in the process the major removal of heavy metals occurred.

In all experiments less than 4% Cu and less than 2% Cd of the total mass was removed towards the anode, i.e. found in compartment (II) and in AEM1 + CEM1 (Fig. 1) at the end of the experiments. This small fraction may have been transported as negatively charged complexes, but which complexes has not been a part of the present study.

Fig. 5 shows the relation between the total charge (current × duration in seconds) passed through the cell in each experiment and the final concentrations obtained. In the fig-

ure the initial concentration shown is an average between the concentrations measured in the two batches.

The concentration that is decided to be the remediation criteria is determining the duration of the process. However it must be stressed that the lower the final concentration, the more energy and time consuming is the process (thus the more expensive) and there is probably also a limit in concentration below which remediation may not be possible or extremely time consuming. In the present investigation the lowest concentrations obtained were 17 mg Cu/kg and 0.03 mg Cd/kg.

The initial concentration of Cd was much lower in the sediment than the Cu concentration. This is expected to influence the transference number, i.e. the amount of current that is carried by the specific element. In percentage less Cd may be expected to be removed due to the lower expected transference number than Cu, but actually it showed that in percentage more Cd was removed. This shows that more Cd in percentage was mobilized during the process than in the case for Cu which is in accordance to what was found in [3] with sediment from Norway (Haakonvern, Bergen). This illustrates that the transference number depends on the mobile fraction rather than total concentrations and that the remediation success is highly dependent on the mobilization of the heavy metals.

After 7 days with applied voltage the remediation almost stopped for Cd. Between days 7 and 14 less than 0.01 mg Cd/kg was removed, but the concentration reached was also very low and thus the transference number decreases even more. The initial Cd concentration of 0.55 mg Cd/kg was less than the OSPAR concentration where toxicological effects are expected (>1.0 mg Cd/kg). The initial concentration was though too high to be in the range where no toxicological effect is expected (<0.1 mg Cd/kg). After a little more than 3 days of electro-dialytic treatment this lowest concentration was reached.

The part of the applied current that is transporting Cu and Cd out of the sediment is very small, i.e. most current is spend on carrying other ions out from the sediment. In another sediment from Haakonvern, Norway, a decrease in concentration of Ca, K, Na, Mg, Fe, Al was found after 14 days of electro-dialytic treatment [3]. Thus it is expected that a part of the current is carried by ions of these elements in the sediment from Sisimiut as well. An important charge carrier is also the proton ion, since this ion is highly mobile and the suspension was acidic. Of anions Cl^- is an important charge carrier in the system. A high percentage of current carried through the cell with harbour sediment suspension by other ions than the target ions (Cu and Cd) is in common with electrokinetic soil remediation. One example from literature is [16] who conducted electrokinetic experiments in a stationary-soil setup with an industrial polluted soil (Pb and Zn). After 23 days of applied electric field calcium had been a major current carrier whereas no significant amounts of heavy metals were removed.

The energy consumption for electro-dialytic extraction of Cd and Cu can be calculated from the present laboratory experiments, however, one must always be careful when evaluating the energy consumption, which may be very different to that in a full scale action. Calculating the energy consumption for a 3 days experiment with an applied current of 20 mA and an aver-

Table 4

Average removal rates at different time periods with a constant applied current of 20 mA

	Average Cu removal rate (mg/kg per day)	Average Cd removal rate (mg/kg per day)
1 day	45	0.15
2–3 days	19	0.15
3–7 days	3.8	0.02
7–14 days	1.4	0.001

age voltage of 6 V in the actual setup, the energy consumption is about 98 kWh t^{-1} dry sediment. For comparison, some values for energy consumption for laboratory electro-reclamation [17] of soils were found: peat (reduction in Cu concentration from 500 to 200 mg/kg) 56 kWh t^{-1} and fine argillaceous sand (reduction in Cd concentration from 275 to 40 mg/kg) 110 kWh t^{-1} . The energy consumption for the remediation of sediment in suspension is thus in the same range as electro-remediation of soil.

The average removal rates of Cu and Cd in different time periods with application of 0.5 mA cm^{-2} (experiments C–F) are shown in Table 4. From Table 4 it is seen, that the fastest remediation occurred during the first day, where 45 mg Cu/kg was removed and the Cu removal rate clearly decreased with increasing duration. The decrease must be due to the bonding of Cu to the sediment, because the final concentration reached is still much higher than the initial Cd concentration and Cd was removed well, and thus the decrease in removal rate cannot be linked solely to a decrease in transference number. The part of Cu that was not removed must be bound strongly to the sediment. By sequential extraction conducted with sediment from other harbours: Port-en-Bessin, France [18]; Richards Bay Harbour, South Africa [19] and Bjørvika, Norway [3] it was found that Cu binds strongly to the sediment, and a high fraction of the Cu is in the residual fraction of the sequential extraction. Thus in general Cu must be expected to bind strongly to harbour sediments.

Also the Cd removal rate is decreasing over time but is at the same level during the first 3 days where after it decreases dramatically, but at this time the concentration in the sediment was only 0.1 mg Cd/kg and the transference number must be low.

Comparing the result from the chemical extraction (Fig. 2) to the result obtained by electro-dialytic remediation (Fig. 5) it can be seen, that especially Cu removal by the electro-dialytic method is convincing. At the lowest pH (0.3) less than 50% Cu could be extracted in HNO_3 but during the electro-dialytic experiment more than 80% Cu was removed from the sediment at pH 2.6.

From Fig. 4 it is seen that pH in the sediment suspension stabilized at a value of about 1.8 and 2.5 after some days of electro-dialytic treatment. A comparison of the lowest concentration obtained in the electro-dialytic experiments to the concentration in the sediment after the chemical extraction experiments (at a similar pH of 1.7–1.8) is shown in Fig. 6. It must be remembered that the liquid to solid ratio was different; 4 in the electro-dialytic experiments and 10 in the chemical extraction experiments which may favour extraction in the latter, though no clear dif-

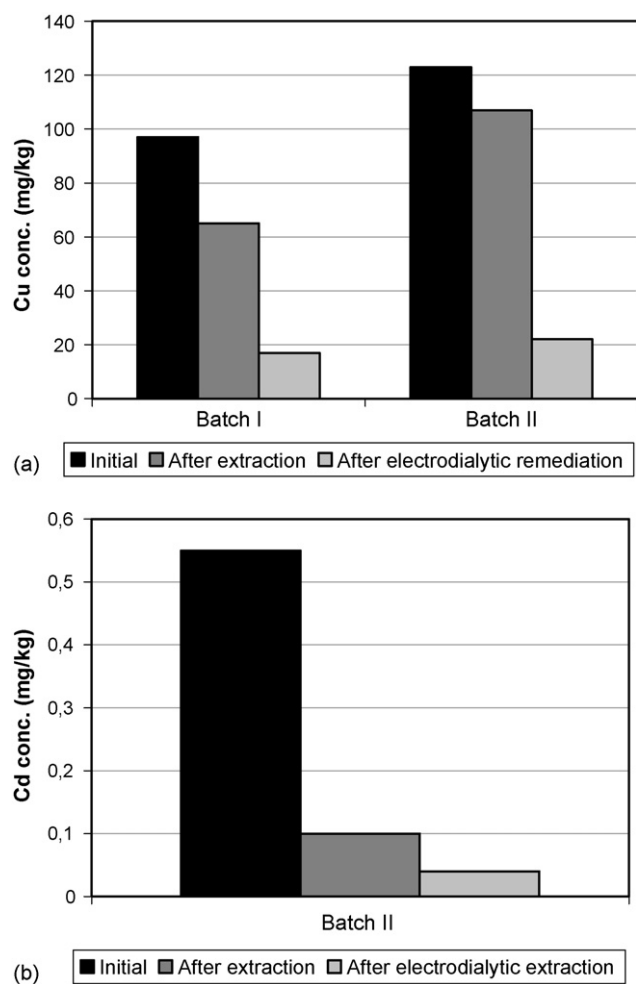


Fig. 6. The initial concentration, concentration after extraction in HNO_3 at pH about 2 and the lowest final concentration obtained in the electrochemical experiments: (a) Cu and (b) Cd.

ference in acid extraction at pH 1.8 for different liquid to solid ratios (between 4 and 16) was found for another sediment [10]. It is clearly seen that the concentration is lower after electrochemical treatment than after chemical extraction. The reason for this may be that equilibrium will not be obtained during the electrochemical experiments since Cu and Cd are continuously removed and more is forced into solution. Continuous removal is not happening in the chemical extraction experiments and after some time equilibrium will be reached in these experiments. However, it is possible that equilibrium was not reached during the 48 h of the chemical extraction experiments in this investigation and more Cd and Cu could be extracted over time.

5. Conclusion

Both Cd and Cu were successfully removed from Greenlandic harbour sediment during the electrochemical treatment. The more charge passed through the sediment suspension, the lower final concentration was obtained. The removal rate for both Cd and Cu decreased considerably after 3 days with an applied of 0.5 mA cm^{-2} , and the major part of the Cu and Cd removal process occurred within these 3 days. The Cu concen-

tration was reduced with 74% and the Cd concentration with 80% during these 3 days.

The lowest Cu concentration reached was 16 mg Cu/kg, which corresponds to a removal percentage of 82% compared to the initial concentration of 97 mg Cu/kg. The highest removal percentage of Cd was 93% which corresponds to a decrease in concentration from 0.55 mg/kg to 0.03 mg Cd/kg. The lowest OSPAR concentration was met for Cd, thus the treated sediment can be considered without toxicological effect from Cd. For Cu, on the other hand, this lowest concentration was not met, but the concentration was decreased from the range where toxicological effects must be expected to the lower range, where further investigation are necessary to consider the risk.

In comparison with chemical extraction the electrochemical method removed more Cu and Cd at comparable pH values. After chemical extraction in HNO_3 at pH about 1.8–1.9, 67% and 87% Cu was left in the sediment, respectively, in the two sediment samples of the investigation. After electrochemical treatment 18% Cu was left in the sediment at similar pH. In the case of Cd 40% was left in the sediment after chemical extraction but 7% was left after electrochemical treatment. The electrochemical treatment is thus mobilizing and removing more of both Cu and Cd than chemical extraction, probably due to non-equilibrium.

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