Investigations on the Phenomena of Accumulation and Mobilization of Heavy Metals and Arsenic at the Sediment-Water Interface by Electrochemically Initiated Processes

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Dedicated to My Beloved Mother Badri Shyama Amatya
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Abbreviations and Acronyms

AAS — Atomic Absorption Spectrometry
AES — Atomic Emission Spectrometry
AMD — Acid Mine Drainage
Ag — silver
As — arsenic
Ba — barium
C — carbon
Cd — cadmium
cm — centimeter
CN — Cyanide
Co — cobalt
Cr — chromium
Cu — copper
DC — Direct Current
DIN — German standard methods
EAS — Emission Atomic Spectrometry
EC — Experimental Column
Eh — Redox potential
e. g. — for example
Fe — iron
FAAS — Flame Atomic Absorption Spectrometry
g — gram
H — Hydrogen
HS5 — Hydride System 5
I — Current
IC — Initial concentration
ICP — Induced Couple Plasma
Igeo — Geo-accumulation Index
K — potassium
kg — kilogram
L — Litre
M — molar
m — metre
mg — milligram
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<td>Mg</td>
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<tr>
<td>Mn</td>
<td>manganese</td>
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<tr>
<td>mS</td>
<td>microsiemens</td>
</tr>
<tr>
<td>mV</td>
<td>millivolt</td>
</tr>
<tr>
<td>Na</td>
<td>sodium</td>
</tr>
<tr>
<td>Ni</td>
<td>nickel</td>
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<tr>
<td>O</td>
<td>oxygen</td>
</tr>
<tr>
<td>Pb</td>
<td>lead</td>
</tr>
<tr>
<td>pH</td>
<td>negative logarithms of hydrogen ion activity</td>
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<tr>
<td>Pt</td>
<td>platinum</td>
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<tr>
<td>PVC</td>
<td>polyvinyl chloride</td>
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<td>RC</td>
<td>reference column</td>
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<td>RFA</td>
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1 Introduction

Metals occur naturally and are commonly found as contaminants in areas where industrial and municipal effluents are discharged. Aquatic sediments/environments are often polluted by heavy metals due to the temporal variations in anthropogenic input of contaminants via atmospheric deposition, catchment runoff, effluent inflow and dumping from industrial transportation, mining, agricultural and waste disposal sources [EPA, 1989]. The transfer of contaminants associated with settling inorganic particulates and/or biotic detritus from the water column to the sediments, no disturbance of sediments by physical mixing, slumping or bioturbation after deposition, no post-depositional degradation or mobility of the contaminants and the establishment of a reliable time axis. Therefore, metal contamination in aquatic environment is one of the problems. Rivers, coastal waters, sediments, soils, etc. were mostly contaminated by industrial and mining activities. Recently, the metal discharged from the industries have been controlled in the most developed countries. Even so, till the heavy metals dispersed in river sediments still need to be dealt with. Mainly, characterization, transformation, transport and fate of metal contaminants in the sediment to the aquatic environment need to be studied, because the sediment has great capacity to accumulate the contaminants. Exploitation and utilization of mines discharges heavy metals into the environment and contaminates neighboring aquatic ecosystem. Weathering of sulphides generates highly acid mine drainage (AMD) which further releases large amount of metals.

Metal aquatic toxicity depends upon valancy, relative hardness or softness referred to as type A, and type B and differences in relative toxicity (i.e., extremely toxic to relatively nontoxic). Type A metal cations, with electron configurations resembling inert gases, are referred to as hard metals and have low reactivity owing to their relatively low electron acceptance potential. Anions such as fluoride or oxyanions (ligands having oxygen as a donor, e.g., $OH^-$, $CO_3^{2-}$) react with these cations to form insoluble precipitates. Less reactive anions such as halides (e.g., $F^-$, $Cl^-$ and $I^-$) and sulfur or nitrogen donor, are rarely complex with hard cations. Type B metal cations are reactive owing to their relatively high electron accepting potential. Most heavy metals are in type B metals.

There are several heavy metals such as $Cr$, $Fe$, $Co$ and $Ni$ are important to human beings. Much concern has been expressed about such ‘toxic’ metals as $Hg$, $Ag$, $Ba$, $Se$, $Cd$, $Pb$, $Cr$, $Ni$, $Zn$, $Cu$, $Fe$, $Mn$, $Co$, $As$, etc. being spread throughout the world.
Arsenic: As has been recognized as poison due to toxic properties of some of its compounds. The toxicity of As—compounds is not universal. Generally, trivalent As is much more toxic than the pentavalent form [Harvey, 1965 and Schröder and Balassa, 1966]. A small amount of arsenic sulfides is obtained in conjunction with silver, lead, copper, nickel, cobalt, iron etc. Especially, it exists as arsenopyrite in nature. Large amount of arsenic produced is used in manufacture of pesticides such as lead arsenate, calcium arsenate and copper acetate meta-arsenate, as well as in wood preservatives, such as Wolman salts. As in different forms is induced naturally or from anthropogenic sources to the sediments, soils, or aquatic systems. This may cause cancer and other hazardous diseases to living beings including human beings.

Cadmium: Cd is extremely toxic to all living beings because this is not extracted [McKee and Wolf, 1963]. Therefore, Cd is recognized as one of the dangerous environmental pollutants. Cd occurs in nature largely as the sulfide, greenockite or as impurity in zinc, copper and lead ores. Cd—pigments are used in paints, inks and plastics. Cd—salts are used in fluorescent tubes, television tube, some types of batteries, insecticides and herbicides. All these activities release Cd in the environment. Itai-itai diseases, severe endemic illness, even cancer are due to accumulation of Cd mainly in kidney, liver, pancreas and thyroid of human.

Cobalt: Vitamin B_{12}, which contains cobalt is essential to human beings. But, only exposure to pure cobalt may lead to partial or completely loss of smell, gastrointestinal problems, dilation of heart, secondary thrombosis, increase in erythrocytes in the blood, and decrease in uptake of iodine by thyroid [Domingo, 1989]. Till there does not appear to be any evidence for carcinogenicity of cobalt in human beings. Co occurs as Co_{3}S_{4}, CuCo_{2}S_{4}, CoAs_{2}. Relatively large residues are found in coal and uranium mines. Co is utilized in manufacture of alloys, primarily where strength, resistance to high temperature and to oxidation by hot gases are needed. It also applies as a drying agent, oxidizing catalyst, etc. From these activities, Co comes to the environment.

Chromium: Chromium is one of the essential trace elements, forming part of the antidiabetogenic factor although there is sufficient evidence for respiratory carcinogenicity in men [Korallus, 1986]. Cr(VI) compounds are more toxic than Cr(III) compounds for men. From Cr(VI), men can suffer from nausea, diarrhea, liver, kidney damage, internal hemorrhage, dermatitis, skin ulcer, respiratory problems including cancer. Till there is no evidence of carcinogenicity of Cr(III) compounds, either soluble or insoluble forms [US Environmental Protection agency, 1989 and Langard,
Cr is found as \((Fe, Mg)O(Cr, Al, Fe)_2O_3\), in chromite form in nature. More than 60% of Cr is used to make stainless steels; high-speed steels, other alloys, high temperature steels, nonferrous alloys, chrome bricks or magnesia-chrome bricks, chrome plating, tanning agents, pigments, catalysts, wood preservatives, corrosion inhibitors, etc. These applications contaminate the surroundings, if it is not properly controlled.

**Copper:** \(Cu\) occurs as chalcopyrite, metallic copper, chalcocite and bornite. \(Cu\) is an important metal for enzymatic reaction in the mammals. It is applied as electrical writing, the production of alloys such as bronze and brass, antifouling paint, construction, plumbing and a host of minor applications. This is second metal, which is applied in the world in the different purposes. So, there is more possible to contaminate the environment. It is not detected any carcinogenic potential of copper by the International Agency for Research on cancer. Yet, it was reported about its acute and chronic toxicity. They are epigastric burning, nausea, vomiting, diarrhea, accumulation of \(Cu\) in liver, brain, kidney, etc. [CARSON et al., 1987].

**Iron:** \(Fe\) is an essential heavy metal for both animals and plants to the oxygen transport. Although iron is very small toxic, chronic inhalation of \(Fe\) produces a benign, non-fibrotic pneumoconiosis. Sometimes, vomiting, gastrointestinal bleeding, etc. cause by acute exposure to \(Fe\). \(Fe\) can control the other elements according to its concentration and oxidation state. It is bad to have large concentration of \(Fe\) in soil, water or in sediment because it helps in increasing polyphenol oxidise activity, leading to production of oxidised polyphenols, formation of oxygen radicals etc. and acts as adsorption medium for many toxic elements. It is used in many different purposes and is the most abundant in the earth. It occurs mainly as magnetite, siderite, limonite, hematite.

**Manganese:** \(Mn\) occurs as pyrolusite, rhodocrosite, manganite, hausmannite, biotite mica, ramsdellite and amphiobile in nature. It is always found with iron and other precious metal ores. The main use is in iron alloys, nonferrous alloys and dry cells. Anthropogenic emissions to the atmosphere are relatively small in comparison to natural emission [NRIAGU, 1989]. It is an essential metal in animals. It has chronic toxicity in central nervous system [SETH AND CHANDRA, 1988]. It was not reported about its carcinogenicity.

**Nickel:** \(Ni\) has the important function in metabolism under particular conditions like situations of deficiency in human and animal nutrition. It is very useful in making
stainless alloys and heat-resisting steel, cast irons, electroplating, chemicals and catalysts. About million tons of nickel have been dispersed into global ecosystem through man’s industrial activities. It is one of the dangerous elements because chronic effect can have potential of having the cancer. Many nickel refinery workers got the respiratory cancer. But there is no evidence of intake through the food or water [Coogan et al., 1989]. The acute effect of Ni-exposers could get dermatoses, atopic dermatitis and allergies.

**Lead:** Pb exists mainly in nature as galena, cerussite, anglesite and pyromorphite. It uses mainly for the production of electric batteries, petroleum, paints, ceramics, insecticides, electric cable insulations, hose, pipes, sheets, floor coverings and for the stabilization of vinyl plastics. Wastewaters form these industries discharges into natural water or water bodies. It is more toxic than Cr, Mn, Ba, Zn and Fe and less toxic than Cd, Hg. The primary symptoms of acute toxicity of Pb are fatigue, colic anemia, neuritis, seizures and other neurologic disorders. Chronic poisoning makes loss of appetite, constipation, metallic taste, anemia, weakness, insomnia, muscle and joint pains and colic. It has carcinogenic effects.

**Zinc:** Zn occurs both as sulfides and carbonates in nature. Mostly it occurs with lead deposits. It is an essential metal for mammals. It is used in galvanizing, brass production, manufacture zinc-base alloys, rolled zinc and zinc oxide and other different purposes. Nearly 50% from nature and 50% from anthropogenic release are responsible for polluting the atmosphere. Although Zn and its compounds are not considered as an element having carcinogenic effects in humans and other animals but it is proved that it shows fever, diarrhea vomiting, etc. as acute toxic symptoms. Occupation ally expose workers may get gastrointestinal disturbance and clinically latent liver dysfunctions.
2 Problems, Purposes and Objectives

2.1 Problems

The river Weiße Elster in Kleindalzig, Leipzig, Germany that carries 330000 tons sediment with metal content of 1296 t Zn, 164 t Cr, 94 t Pb, 81 t Ni, 79 t Cu, 14 t Co, 9.2 t Cd, and 2 t Ag was reported [MÜLLER et al., 1998]. It is highly contaminated by heavy metal if it is compared with Table 1 because the river Weiße Elster, which originates from the Erzgebirge Mountains (a former old silver mining area), runs through the Vogtland Hollow and Leipzig Lowland region; or the old coal and uranium mining area and flows into the Saale River near the city of Halle. The length of the river Weiße Elster is 248 km and the drainage area is $\sim 5400 \text{ km}^2$ [MÜLLER et al., 1998]. Due to the high heavy metals contamination, sediments could not be used as fertilizers in agricultural areas [LÖSER et al., 1999]. The contaminated sediment were deposited or dredged on neighboring site. It gave the serious environmental problems due to dissolution of heavy metals by contacting the anoxic sediment with air and converting in acidic conditions by oxidation processes. It is not practical to remove the dredged sludge by landfill disposal. Even so, the landfill disposal is one of the expensive methods with limited capacity and without sustainability [LÖSER et al., 1999, EVANGELIC, 1998 and AVEYARD AND HAYDON, 1973]. Then, there is essential to find out methods to decontaminate the heavy metal-contaminated sediments.

Decontamination methods of the heavy metal contaminated sediments:

1. Extraction with mineral acids [MÜLLER and RIETHMAYER, 1982 and STRASSER et al., 1995]:

   Extraction of heavy metals from contaminated sediment was done with the help of mineral acids like $HNO_3$, $HCl$, $H_2SO_4$, $H_3PO_4$, etc. In this method, these acids acidify the sediment. Due to decrease in $pH$, the heavy metals get mobilized from the sediment to water phase.

2. Extraction with organic acids such as acetic, citric and oxalic acids or with complexing agents [FRÖHLICH et al., 1999, HÖLL, 1995, STICHNOTHE et al., 1999 and THÖMING et al., 1996]:

   The mobilisation of heavy metals from the contaminated soil or sediment was carried out by forming complexes with complexing agents or organic acids.
Table 1: Valancies (available in aqueous phase), Standards for drinking water and sediment and Effects of Some Toxic Heavy Metals

<table>
<thead>
<tr>
<th>Metals</th>
<th>Valencies</th>
<th>Standard for drinking water* (mg/L)</th>
<th>Standard for sediment** (mg/kg)</th>
<th>Toxic effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>III, V</td>
<td>0.01</td>
<td>50</td>
<td>For excess skin cancer risk of $6 \times 10^{-4}$ mg/L</td>
</tr>
<tr>
<td>Cd</td>
<td>II</td>
<td>0.003</td>
<td>5</td>
<td>Carcinogenic, Itai-Itai disease</td>
</tr>
<tr>
<td>Co</td>
<td>II</td>
<td>1.0</td>
<td>-</td>
<td>Based on acute gastrointestinal effects. Dilation of heart</td>
</tr>
<tr>
<td>Cr</td>
<td>II, III, VI</td>
<td>0.05</td>
<td>100</td>
<td>Carcinogenic, damage kidney, skin ulcer</td>
</tr>
<tr>
<td>Cu</td>
<td>I, II</td>
<td>2.0</td>
<td>200</td>
<td>Based on acute gastrointestinal effects</td>
</tr>
<tr>
<td>Fe</td>
<td>II, III</td>
<td>0.3</td>
<td>-</td>
<td>Based on acute gastrointestinal effects</td>
</tr>
<tr>
<td>Mn</td>
<td>II, IV, VII</td>
<td>0.5</td>
<td>-</td>
<td>Concentrations of the substance at or below the health-based guideline value may affect the appearance, taste, or odour of the water.</td>
</tr>
<tr>
<td>Ni</td>
<td>II</td>
<td>0.02</td>
<td>100</td>
<td>Dermatoses, carcinogenic</td>
</tr>
<tr>
<td>Pb</td>
<td>II, IV</td>
<td>0.01</td>
<td>100</td>
<td>Carcinogenic, loss of appetite, muscle and joint pain, etc.</td>
</tr>
<tr>
<td>Zn</td>
<td>II</td>
<td>5.0</td>
<td>400</td>
<td>Based on acute gastrointestinal effects</td>
</tr>
</tbody>
</table>


**LAGA Z2 limits [LAGA, 2002]

3. Size classification and treatment of fine fraction by flotation [VENGAUS AND WERTHER, 1996]:

The process of froth flotation entails crushing and grinding the ore to a fine size. The grinding is normally done in water with the resultant slurry called the pulp. The pulp is processed in the flotation cells, which agitates the mixture and introduces air as small bubbles. The ability of a mineral to float depends upon its surface properties. The ability to selectively float the separate minerals depends on the ore, the chemicals
used, and other factors e.g. \( pH \), size, etc.


A bacterial leaching process ("bioleaching") or microbial leaching is applied for the recovery of metals from solid materials such as incineration residues, galvanic sludge, or electronic scrap as well as metal-contaminated soils. Sulphur and sulphuric acid for leaching and nutrients for bacteria are used.

5. Chemical precipitation, membrane filtration, ion-exchange, carbon adsorption, and co-precipitation/adsorption by sorbents [Bailey et al., 1999]:

In the remediation, different types sorbents, chemicals, ion-exchangers were used to remove heavy metals from contaminated sediments.

Most of the above methods have different types of weaknesses such as requirement of chemicals for acidification, precipitations, co-precipitations, adsorption, bioleaching etc. It results in formation of sludge, which is difficult to dispose. Membrane filtration, ion exchange and carbon/charcoal adsorption system require a high investment and additionally, on site regeneration and reuse of required material has many problems associated with them.

2.2 Purposes

Electrokinetic remediation is an \textit{in-situ} process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil, sediment, sludge, etc. Targeted contaminants for electrokinetics are heavy metals, anions, and polar organics in soil, mud, sludge, and marine dredging [EPA, 1987 and EPA, 1989]. As a result of the application of this electric field, contaminants may be mobilised, concentrated at the electrodes and extracted from the sediment. Many vendors have marketed the potential of electrokinetic remediation for metals and other contaminated soil/sediments, however there are still problems in the field demonstration in a large scale due to some issues as control of contaminant movement, ability of cleanup goals. Concentrations that can be treated range from a few parts per million (ppm) to tens of thousands ppm. Electrokinetics are most applicable in low permeability soils or sediment. They are typically saturated and partially saturated clays and silt-clay mixture. The propose in electrokinetic remediation has been driven by the demand for technologies that are cost effective and will eliminate the long term liability.
2.3 Objectives

The main objective of this research work is to study the phenomena of accumulation and mobilization of heavy metals at the sediment-water interface by using electrochemically initiated processes intended as a preliminary step toward the design advance or field level work. This study was concentrated mainly on nine heavy metals; \( \text{Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn} \) and one semimetal; As.

The specific objectives are follows:

- Analyze the concentrations and \( \text{pH} \) of these elements in aqueous phase in dependence of time.
- Find out the rate of migration of these metals in the sediment.
- Determine the development of \( \text{pH} \) in the sediment and water.
- Measure the redox potential, oxygen content, conductivity and current in all experiment with time.
3 Basic Processes of the Electrokinetic Remediation

The principle of electrokinetic treatment is that a low direct current or a low potential gradient is applied through a pair of electrodes (cathode and anode). This mobilizes the charged species, ions and water to move toward the electrodes. Metal ions, positively charged complexes and organic compounds move toward the cathode. Anions such as chloride, cyanide, fluoride, nitrate, and negatively charged organic compounds move toward the anode. The current creates an acidic front at the anode and a basic front at the cathode by primary electrochemical reactions; called electrolysis of water \((eq. 1, 2)\). The \textit{in-situ} generation of acidic condition may help to mobilize sorbed metal contaminants for transportation to the collection system at the cathode.

\[
2H_2O - 4e^- \rightarrow O_2 \uparrow +4H^+ \quad \text{(anode)} \tag{1}
\]

\[
4H_2O + 4e^- \rightarrow 2H_2 \uparrow +4OH^- \quad \text{(cathode)} \tag{2}
\]

The contaminant transport induced during electrochemical treatment is based on the well-known electrokinetic processes that take part in wet porous medium under an electric field. Three primary transport mechanisms of contaminants through the sediment from one to another electrodes are Electrophoresis, Electroosmosis and Electromigration.

### 3.1 Electrophoresis

Electrophoresis is defined as the migration of charged colloids (not small ions) in solid-liquid mixture under an electric potential gradient (Fig. 1). If the current is applied across the suspension of the clay-water system, negatively charged clay particles migrate toward the anode. The un-restrained particle transport through water in poorly consolidated system will likely compact the soil to anode, and disintegrate it on cathode. In a compact system of porous plug, electrophoresis is of less importance due to restrained solid phase. But, in the process of soil decontamination, electrophoresis of clay colloids could still play an important role if chemical species of interest are adsorbed at migrating colloids. This was demonstrated whereby strongly sorbing lead was transported by mobile colloids [Grolimund et al., 1996].

### 3.2 Electroosmosis

The electroosmosis is the process of water transport through a continuous sediment or soil particle network in an electric field (Fig. 1). Typically sediment has a negative surface
3 BASIC PROCESSES OF THE ELECTROKINETIC REMEDIATION

Figure 1: Sketch diagrams of electrophoresis and electroosmosis

charge. To balance this charge a row of cations, such as sodium, calcium and magnesium, line up along the soil particle surfaces. There may be other ions in the bulk pore water solution, but these are typically balanced. Common counter-anions in soil water are chloride, sulfate and nitrate. Under the influence of a DC-field, the rows of cations on the soil particle surfaces start migrating towards the cathode by electrical attraction. The movement of this boundary layer of cations drags the bulk soil water with it.

3.3 Electromigration

Electromigration is the main mechanism for the electrochemical process, when the contaminants are ionic or surface charged (Fig. 2). The direction and rate of movement of an ionic species will depend on their charges, both in magnitude and polarity. Sediment typically has a negative surface charge. The metal ions are used to bind with negatively charged sediment. In an electric field, the metal ions move towards the cathode by leaving the surface of the sediment. This process accelerates by the primary reactions of electrochemical processes by acidification the sediment at the anode. The hydrogen ions can replace the metal ions from the sediment surface.

\[ nH^+ + \equiv (\text{Sediment})^{n-} Me^{n+} \rightarrow \equiv (\text{Sediment})^{n-} nH^+ + Me^{n+} \]  

Speciation and precipitation are major factors in mobilization and transport of heavy metal constituents by ion-migration component. The speciation is dependent upon a number of fairly well understood parameters including \( pH \), redox potential, and ion concentration. These same factors influence the equilibrium conditions relating to both the sediment and contaminants. In the electric field, metal ions could be oxidize by forming a redox barrier. The concept of redox barrier is that of a permeable reactive barrier driven by low voltage DC current. This is accomplished by installing closely spaced permeable electrodes transverse to flow through a targeted plume sequential oxidising and reducing conditions are generated.
about positive and negative electrodes respectively. The electrochemical ions might gain electrons at cathode to form solid metals. Due to pH barrier, metal ions might combine with OH\(^-\) or carbonate ions to precipitate. The most probable cases are the last two equations.

\[
4Me^{n+} + 4H^+ + O_2 \rightarrow 4Me^{(n+1)+} + 2H_2O \quad \text{(redox barrier)} \tag{4}
\]

\[
Me^{n+} + ne^- \rightarrow Me(s) \tag{5}
\]

\[
Me^{n+} + nOH^- \rightarrow Me(OH)_n \downarrow \quad \text{(pH-barrier)} \tag{6}
\]

\[
Me^{2+} + HCO_3^- + OH^- \rightarrow MeCO_3 \downarrow + H_2O \tag{7}
\]

(Me denotes a metal)
4 Experimental Methodology

The method that would be developed is aimed to be employed to reduce the concentration of heavy metals such as $Cd$, $Fe$, $Mn$, $Zn$, $Co$, $Cr$, $Ni$, $Pb$ in aqueous phase and in the sediment. The main working steps in the method would be the mobilization of these ions in the vicinity of the anode, followed by their immobilization at the sediment-water interface and finally remobilization by changing the electrode polarity. The trend seen in the result from these steps will be the basis to find out the feasibly of removal of heavy metals from sediments.
4.1 Function of the lab experimental facility (Experimental setup)

PVC-tubes (length: 0.6 m, width: 0.12 m) were filled with 1200 g sediment (about 20% of the total volume) from the river Weiße Elster, near Kleindalzig, Germany and the river Bagmati at Thapathali, Kathmandu, Nepal and tap water (about 80% of the volume) (Fig. 5). The initial physico-chemical parameters of the sediment samples are shown in Table 2 and Table 3 and the quality of the overlying water in Table 4. The electrodes were installed after filling the columns in accordance to the experimental variants as required (Fig. 6).

![Diagram of experimental assembly](image-url)

- DC controller
- Sampling pipes with Pt-wires
- Aqueous phase
- Sampling
- Sediment-water interface
- Dimensions of the tube:
  - Diameter: 12 cm
  - Height: 60 cm
  - Depth of sediment: 12 cm
- Pressure stabilization
- Measuring points I, II
- Cathode
- Anode
- Sediment core

Figure 5: Schema of experimental assembly (after WOLF, 2002)
### Table 2: Physico-chemical parameters of the used sediment of the river Weiße Elster

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Method</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>DIN 38404-C5</td>
<td>5.85</td>
</tr>
<tr>
<td>Redox potential*</td>
<td>DIN 38404-C5</td>
<td>166 mV</td>
</tr>
<tr>
<td>Conductivity</td>
<td>DIN 38404-C5</td>
<td>2.64 mS/cm</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>TOC Analyzer</td>
<td>9.4 mass %</td>
</tr>
<tr>
<td>Total sulphur content</td>
<td>RFA</td>
<td>15 mg/kg</td>
</tr>
<tr>
<td>$As$</td>
<td>AAS</td>
<td>29 mg/kg</td>
</tr>
<tr>
<td>$Cd$</td>
<td>AAS</td>
<td>30 mg/kg</td>
</tr>
<tr>
<td>$Co$</td>
<td>AAS</td>
<td>40 mg/kg</td>
</tr>
<tr>
<td>$Cr$</td>
<td>AAS</td>
<td>236 mg/kg</td>
</tr>
<tr>
<td>$Cu$</td>
<td>AAS</td>
<td>295 mg/kg</td>
</tr>
<tr>
<td>$Fe$</td>
<td>AAS</td>
<td>68449 mg/kg</td>
</tr>
<tr>
<td>$Mn$</td>
<td>AAS</td>
<td>600 mg/kg</td>
</tr>
<tr>
<td>$Ni$</td>
<td>AAS</td>
<td>276 mg/kg</td>
</tr>
<tr>
<td>$Pb$</td>
<td>AAS</td>
<td>238 mg/kg</td>
</tr>
<tr>
<td>$Zn$</td>
<td>AAS</td>
<td>2724 mg/kg</td>
</tr>
</tbody>
</table>

*Measured with a $Ag/AgCl$ (saturated)-electrode and referring to $pH = 7.0$

### Table 3: Physico-chemical parameters of the used sediment of the river Bagmati

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Method</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>DIN 38404-C5</td>
<td>2.56</td>
</tr>
<tr>
<td>Redox potential*</td>
<td>DIN 38404-C5</td>
<td>168 mV</td>
</tr>
<tr>
<td>Conductivity</td>
<td>DIN 38404-C5</td>
<td>2.88 mS/cm</td>
</tr>
<tr>
<td>Total organic carbon</td>
<td>TOC Analyzer</td>
<td>8 mass %</td>
</tr>
<tr>
<td>Total sulphur content</td>
<td>RFA</td>
<td>17 mg/kg</td>
</tr>
<tr>
<td>$As$</td>
<td>AAS</td>
<td>2 mg/kg</td>
</tr>
<tr>
<td>$Cd$</td>
<td>AAS</td>
<td>0.4 mg/kg</td>
</tr>
<tr>
<td>$Co$</td>
<td>AAS</td>
<td>7 mg/kg</td>
</tr>
<tr>
<td>$Cr$</td>
<td>AAS</td>
<td>50 mg/kg</td>
</tr>
<tr>
<td>$Cu$</td>
<td>AAS</td>
<td>75 mg/kg</td>
</tr>
<tr>
<td>$Fe$</td>
<td>AAS</td>
<td>54280 mg/kg</td>
</tr>
<tr>
<td>$Mn$</td>
<td>AAS</td>
<td>246 mg/kg</td>
</tr>
<tr>
<td>$Ni$</td>
<td>AAS</td>
<td>36 mg/kg</td>
</tr>
<tr>
<td>$Pb$</td>
<td>AAS</td>
<td>44 mg/kg</td>
</tr>
<tr>
<td>$Zn$</td>
<td>AAS</td>
<td>232 mg/kg</td>
</tr>
</tbody>
</table>

*Measured with a $Ag/AgCl$ (saturated)-electrode and referring to $pH = 7.0$
Voltage and distances of the electrodes from the sediment surface could adjust by the external control instruments. There were two fixed measuring points for the determination of $pH$ value and $O_2$-concentration in the aqueous phase. One measurement point was directly at cathode, the other at the sediment-water interface. Two sampling tubes were fixed for the drawing water samples. At the end of each of these tubes a platinum wire were positioned for the measuring the redox potential. A small fermenting tube was installed to ensure pressure balance. A second similar column without power supply was used as a reference system. All the experiments were carried out at room temperature without light in order to prevent formation of undesirable oxygen through the growth of autotrophic organisms such as algae. The electrodes were placed horizontally (Fig. 6).

### 4.2 Arrangement of the electrodes in the columns

#### 4.2.1 Electrode material

The cathode material should have a high hydrogen overvoltage as opposed to the anode material, which should have small oxygen overvoltage. The anode should remain stable...
under conditions of current flow. A further important criterion is that the material should not have ecotoxicological nature. Anything that may be released by anodic dissolution during the process should not produce any environmentally harmful reaction products. That’s why conductive polymer (polyethylene with carbon black) with a specific resistance of about $20 \Omega cm^{-1}$ were used as an electrode material. The middle coverage of the electrode in relation to the sediment surface area was about 20%. The lower coverage area up to 12% did not affect the migration of iron and manganese significantly [WOLF et al., 2002].

### 4.2.2 Distance between the electrodes

The distance between the electrodes is one of the important factors that affect the ions migration. The distance between the electrodes was determined on the one hand through Ohmic voltage drop and on the other hand through the possibility of electric short circuit. In all electrode system of the study, the two electrodes were installed with a distance of 8 cm.
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4.2.3 Electrode arrangement

According to the real working field, one must think about the positions and conditions of the electrodes. The arrangement highly depends on the type of contaminants and treatment aims. Therefore, following arrangement were made in this research to see the fundamental effects on heavy metals:

i. **Reference column**: The arrangement of electrodes was the same as in Fig. 5 and 6. But, there was no supply of current. From this, it was found that there is migration of heavy metals in contaminated places without current supply. It gives the natural phenomenon of the heavy metal polluted areas.

ii. **Anode placed at and cathode 8 cm above the sediment-water interface**: for mobilisation of the most metals ions from the contaminated sediments or soils at the interface by slow acidification the sediment. So, one can remove the contaminant from the interface by pumping or other methods.

iii. **Cathode at and anode 8 cm inside the sediment-water interface**: for the immobilisation of the most metals ions from the contaminated sediments or soils at the interface. In this arrangement, the distributed contaminants are concentrated to a small layer which can be removed easily.

iv. **Cathode 4 cm above and anode 4 cm inside the sediment-water interface**: This arrangement was between the cases of (ii) and (iii). One might expect mix-results of the cases ii and iii. The sediment acted as the buffering substance zone. So, the cathode produces $OH^-$ ions.

v. **Anode 4 cm above and cathode 4 cm below the sediment-water interface**: In this arrangement $H^+$ ions will move towards the sediment. The metals will be expected to mobilize in the aqueous phase.

vi. **Same as (iv), but with CaCO$_3$**: The CaCO$_3$ can be used to control the pH of the sediment surface. It helps to held the $pH$ - value of the environment constant at about 8.0.

vii. **Same as (iv), but with counter anode**: The counter anode was added to neutralise the $OH^-$ ions generated at the cathode, so that the $pH$ of the overlying water can not rise up to high values.
The supplement of a second anode over the cathode in the aqueous phase should oxidise the contaminants, dissolve the precipitation products over the cathode and diminish the vertical expansion of the alkaline front. After BASEL, 1912 and GERISCHER AND MAUNER, 1970 were confessed that the anodic electrochemical ammonium oxidation results only at strongly alkaline conditions ($pH \sim 14$). This $pH$ was reached during the electrochemical influence in the laboratory reactor in a short time. In this column, three electrodes were installed (Fig. 7).

The current $I_2$ over the second anode was regulated by means of a potentiometer ($R = 10 \: k\Omega$, placed linearly). The distance between second anode and cathode was held deliberately small, so that the material carrier ways of the reduction products of the cathode to the second anode as low as possible remain. The distance amounted between second anode and cathode was 2 cm. On the other hand the distance between anode in the sediment and cathode was 8 cm. Current flow through cathode is proportional to the material composition of the solution for the development of hydrogen and/or hydroxide ions. The current-flow over the second anode is the difference of the total current flow and current flow over the first anode.

viii. Same as (iv), but with various voltages ($U = 0V, 2.5V, 3V, 4V$): With increase in the voltage supply, the rate of reaction should be increase. Therefore, this type of arrangement was installed.

ix. Cathode 2 cm below and anode 10 cm below the sediment-water interface: When both electrodes, cathode and anode were inside the sediment, the contaminants could not come out to the interface. The gas-development at the electrode regions did not
disturb the system, because the gases formed might come out to the aqueous phase through the seepage.

x. Other conditions same as (iv), but with 3 meter long column: This arrangement was nearer to environmental situation.

4.3 Sample technique, preparation methods and analysis

Samples of sediments from the river Weiße Elster in Kleindalzig, Leipzig, Germany and the river Bagmati at Thapathali, Kathmandu, Nepal were collected by the sludge pit trap method on 01.03.2001 and 18.07.2001, respectively (Figs. 3, 4). Care was taken that the samples did not come in contact with the metallic parts of the dredge. The trend of mobilization and accumulation can, however, be estimated from the metal concentration in the water samples at the interface. For that purpose 10 ml aliquot (that is about 0.1 % of the total volume) was drawn out periodically from the sample port and the contents of the metal ion determined to monitor the changes in composition. The drawn volume was replaced with the same volume of tap water after sampling. The oxygen concentrations were measured approximately 35 cm above the sediment surface near the cathode.

The samples were put into airtight polyethylene bags and stored at 4°C until the chemical analysis was performed.

4.3.1 Sediment

4.3.1.1 pH, Redox Potential and Conductivity

The German standard methods (DIN-methods) were used with some minor modifications for the determination of the \( pH \)-value [DIN 38404 - C5], the redox potential [DIN 38404 - C6] and the electrolytical conductivity of the sediment suspension [DIN 38404 - S8]. For the measurement of the \( pH \)-, \( Eh \)-value and the electrolytical conductivity, ten grams of the sediment or soil sample was added to 50 ml of distilled water and stirred well for five minutes. The redox potential was determined with a MultiCal \( pH \)-meter 526 with Pt 4805-S7/120-Electrode (WTW, Weilheim). The suspension was stirred at frequent intervals for 0.5 hours. The \( pH \)-value was measured with a microprocessor controlled \( pH \)-meter \( pH \) 96 (WTW, Weilheim). The conductivity was measured with a microprocessor controlled conductivity meter LF196 (WTW, Weilheim) on the clear supernatant.
4.3.1.2 Water content

The water content of the fresh sediment was determined by German standard method [DIN 51582]. One gram of the fresh sediment was heated at 105°C in an oven for 1 hour, cooled in a dessicator and weighed. The percentage of the water was calculated from the difference between the fresh and the dried sample.

4.3.1.3 Total Organic Carbon (TOC)

Ten grams of 125 μm sized powdered dried sample was treated with 10 ml of 4M HCl and allowed to stand for 4 hours. The mixture was dried in an oven at 60 − 70°C for 16 hours. The TOC was measured with the help of TOC measuring instrument (TOC Boat sampler method, Model 184 (S)).

4.3.1.4 Buffer capacity

The buffer-capacity of the sediment was determined by the following method. About 10 g of the sediment and 100 ml distilled water were mixed. Under continual stirring, the pH-value of the initial solution was measured. For the characterization of the buffer capacity a series of measurements was incorporated in such a way, that depending on the added amount of hydrochloric acid, the equilibrium pH-value was determined and represented graphically. The buffer capacity determined according to the reference states, pH = 8.2 (\(K_{S4.2}\)) and pH = 4.3 (\(K_{S4.3}\)). The specification of the buffer capacity with the corresponding equilibrium-pH-value occurs in the unit mmol H⁺/kg sediment.

Calculation of the buffer-capacity of the sediment

\[ K_{S4.3} = \left[ \frac{x \text{ ml} \text{ 0.1 N or 0.01 N HCl}}{100 \text{ y}} \right] \text{(mmolH⁺/kg)} \]  

Where,
\[ x = \text{ ml added 0.01 N HCl (at 0.1 N HCl multiply with 10)} \]
\[ y = \text{ mass of the used sediment in kg} \]
\[ K_{S4.3} = \text{ buffer capacity of the sediment with reference pH-value 4.3} \]

4.3.2 Physico-chemical properties of the sediment

The pH-value of the interstitial water of the river Bagmati with pH = 2.56 was considerably smaller that of the river Weiße Elster which was 5.85 (Table 5). The conductivites, redox
4 EXPERIMENTAL METHODOLOGY

Table 5: Physico-chemical parameters of the interstitial water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>River Weiße Elster</th>
<th>River Bagmati</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.85</td>
<td>2.56</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>2.64</td>
<td>2.88</td>
</tr>
<tr>
<td>Redox potential (mV)*</td>
<td>+166</td>
<td>+168</td>
</tr>
<tr>
<td>Water content of the sediment (%)</td>
<td>34.5</td>
<td>31.2</td>
</tr>
<tr>
<td>TOC - content of the sediment (%)</td>
<td>9.4</td>
<td>8</td>
</tr>
</tbody>
</table>

*) measured with a Ag/AgCl (saturated)-electrode and referring to pH = 7.0

potentials and total organic compound were, however, almost equal. The reason behind this might be, that the basicity of the subsoil of the Bagmati and the cleft water influxes from the catchment area, have a relatively small proton buffering capacity. In this case, the acid rain was not neutralized during the interaction with the sediment material.

4.3.3 Sequential Extraction

The knowledge of the bonding forms of the metals at the sediment is a precondition for the assessment of the availability of the metals, because bonding type and its stability are factors for the bio-relevancy, toxicity and the mobility of metals. The sequential extraction is a method of consecutive chemical solution steps (Table 6).

Sequential extractions were carried out using the following reagents according to the method of Förstner and Calmano 1982 and Dinelli and Tateo 2001.

- Reagent I: Ammonium acetate (1M)
- Reagent II: Sodium acetate/acetic acid (1M)
- Reagent III: Oxalic acid-Ammonium oxalate (0.1M)
- Reagent IV: Hydrogen peroxide-Ammonium acetate (1M)
- Reagent V: Aqua regia

Each sample was treated in the following way:

A. Sequential extraction method

i. One gram of fresh sample was weighed out into a small centrifuge tube. Ten ml of reagent I was added and the mixture shaken in the shaker for 2 hours. The mixture was centrifuged for 20 min at 4500 rpm and the supernatant was filtered and the filtrate was analysed for metal content (S1).
Table 6: Chemicals for extracting - extractable bonding form of metals [FÖRSTNER AND CALMANO, 1982 and DINELLI AND TATEO, 2001]

<table>
<thead>
<tr>
<th>Medium</th>
<th>Binding forms</th>
<th>Steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium acetate ($pH = 7.0$)</td>
<td>Freely exchangeable metal ions: metal ions or complexes bound by cation exchange as well as released by metabolism processes from living cells</td>
<td>S1</td>
</tr>
<tr>
<td>Sodium acetate/acetic acid ($pH = 5.0$)</td>
<td>Metal carbonates: carbonates, mainly calcareous spar, as well as metals extractable through acids</td>
<td>S2</td>
</tr>
<tr>
<td>Oxalic Acid - Ammonium oxalate ($pH = 3.0$)</td>
<td>Metal oxides and hydroxides: iron and aluminium hydroxides arisen during the decomposition of silicates</td>
<td>S3</td>
</tr>
<tr>
<td>Hydrogen peroxide-Ammoniumacetate ($pH = 2.0$)</td>
<td>Metal sulphide and organo-metallic form: after the oxidation of sulfides and organic material exchangeable metals</td>
<td>S4</td>
</tr>
<tr>
<td>Aqua Regia ($T=120^\circ C; 5h$)</td>
<td>Residual digestion: residual / all mineral constituents</td>
<td>S5</td>
</tr>
<tr>
<td>AquA Regia ($T=120^\circ C; 5h$)</td>
<td>Residual digestion: residual / all mineral constituents</td>
<td>S5</td>
</tr>
</tbody>
</table>

Note: $R$(rest) = Total - (S1+ S2+S3+S4+S5)

ii. Ten millilitre of the reagent II was added to the residue from step i shaken for 5 hours. The mixture was centrifuged for 20 min at 4500 rpm and the supernatant was filtered. The filtrate was analysed for the metal content (S2).

iii. Fifty millilitres of reagent III was added to the residue from step (ii) and shaken under day light for 24 hours. The mixture was centrifuged for 20 min at 4500 rpm and the supernatant was filtered. The filtrate was analyzed for metal content. (S3).

iv. Fifty millilitres of double-distilled water was added to the residue from step (iii), shaken for 20 min and centrifuged at 4500 rpm for 20 min. The supernatant was discarded. Fifteen millilitres of reagent IV was added to the sediment and the mixture heated to $85^\circ C$ for 2 hours. Fifteen millilitres of reagent I was added to the mixture and shaken for 12 hours. The mixture was centrifuged for 20 min at 4500 rpm and the supernatant was filtered. The filtrate was analyzed for metal contents (S4).
v. The residue was heated with 20 ml reagent V at 120°C for 5 hours. The mixture was diluted to 50 ml with double-distilled water and then filtered. The filtrate was analysed for metal contents (S5).

B. Single extraction method

One gram of the fresh sediment sample was heated with 20 ml reagent V at 120°C for 5 hours. The solution was diluted to 50 ml with double-distilled water and filtered. The filtrate was analysed for metal contents (Total).

All solutions were directly analysed for metals by flame-(FAAS) and graphite-furnace (EA) methods except for arsenic, which was done by hydride method (HS) in Atomic Absorption Spectrometer AAS5 and AAS-ICP (ZEISS, Jena). For quality control, analytical blanks and duplicates were run together using the same procedures and reagents. Care was taken during handling of samples and measurement to prevent them from coming into contact with dust and metal ion contaminants.

It allows conclusions on the distinction depending on the solubility of the metals from bonding forms with that over the metal behaviour individuals in the corresponding medium as well as their distribution in the environment.

When the total heavy metal contents of the sediments of both the rivers were compared with the Clay-stone standard after Turekian and Wedepohl, 1961 and/or with the CLARKE values (middle geogenic element contents in the earth crust), the degrees of enrichment lied for typical mining industry relevant heavy metals in the Weiße Elster sediment in the range of 2 - 12, but in case of zinc in order of approx. 29 (Table 7) [Basel, 1912]. In the contrast to this, however the maximum degrees of enrichment, particularly in the heavy metals like Cu, Zn, Pb, Cd were achieved to 2.5 for the sediment in the river Bagmati, the enrichment values of Mn, As, Cr, Ni and Co could not reach the mid-value of the Clay-stone standard.

In additional to the heavy metal content, the bonding form of heavy metals in the sediments was decisive for the assessment of the danger potential in the water [Gerischer and Mauner, 1970 and Turekian and Wedepohl, 1961] (Fig. 9). The content of mobilizable heavy metals in the exchangeable and carbonatic fraction amount was less than 15% except cadmium in the sediment of the river Bagmati which was over 20%. The
relatively small part in the exchangeable and carbonatic bound fraction is effected to the competition and/or to the impact of the protons. The carbonate buffer area ($pH > 6.2$) was already exhausted to the both cases. With the exception of lead, all metals in the fraction S3 (heavy metals bound to aluminum and/or ferrous hydroxides) in the sediment of the river Weiße Elster in comparison to the river Bagmati were always found much higher. That became understandable, that through former input of iron and manganese containing mining waters into the river Weiße Elster and precipitation and/or coprecipitation of iron and aluminium as hydroxides, resulted solid matters with very great surfaces and high sorption capacity. They were able to integrate heavy metals in the crystal structure and/or to bind it by sorption. In the sediment of the river Bagmati this sorbent did not exit in such a great masses so that the part of this fraction was considerably smaller.

The relatively small part of heavy metals bound sulphidically, except for cadmium in both systems and chromium in the river Weiße Elster indicated a considerable amount of oxygen supply in the sediments. During the analysis of the residual-fraction S5 of both sediment systems, it was clear that the heavy metal part in the sediment of the river Bagmati, in most of the cases, were higher than that of the river Weiße Elster. This indicates that a majority of the heavy metals in the river Bagmati was bound relatively strong in the mineral matrices and mobilized only under extreme chemical conditions. It was presumed
that this stable bounding form is predominantly geogenic. In the summery, the sediment of the river Bagmati in comparison to the sediment of the river Weiße Elster contained a considerably smaller heavy metal contents, those in addition relatively strong bounded at the sediment matrix and, therefore, it was relatively difficult to mobilize. In addition to that the influence of the mining waters on the heavy metal content were higher in the sediment of the river Weiße Elster, the heavy metals were found in the easy mobilized fraction. An exception forms here the relative immobile lead.

The Geo-accumulation-index $I_{\text{geo}}$ of the rivers Weiße Elster and Bagmati with respect to metal concentration in the sediment resulted that almost all heavy metals of the river Bagmati were within the Class I (Fig. 8) This implies that the sediment of the river Bagmati was moderately polluted without any load. Thus, we can conclude that, the river Bagmati was still far less polluted than the river Weiße Elster with respect to heavy metals content. The quantities of the enrichment factor (EF) and Geo-accumulation-index $I_{\text{geo}}$ can be calculated as follows:

$$EF = \frac{\text{mg Me/kg original sediment}}{\text{mg Me/kg sediment after clay standard}}$$  \hfill (9)

$$I_{\text{geo}} = \log_2 \left[ \frac{C_n}{1.5 B_n} \right]$$  \hfill (10)

Where,
- $EF$ = Enrichment Factor
- $I_{\text{geo}}$ = Geo-accumulation index
- $C_n$ = Concentration of metals in the original sediment
- $B_n$ = Geochemical background value (Claystone standard)

### 4.4 Voltage supply and observation periods

Heavy metals and arsenic transport in sediment were carried out for maximum 430 days in small scale by arranging the electrodes in different positions and conditions in the laboratory in six phases. Phases I, III, V were without and phases II, IV and VI with voltage supply (Table 8). In most case, the first phase was the equilibrium phase and the equilibrium was reached in about 35 days. Then, about 90 days, the voltage was supplied to the system (phase II). Same period of time, voltage was disconnected (phase III). Again the same 90 days the voltage was supplied to the system (phase IV). Unfortunately the current flows through the electrodes were not so much as that in phase II. So that, the phase V, voltage
### 4 EXPERIMENTAL METHODOLOGY

Table 7: Heavy metal contents (mg/kg) in the sediment after the sequential fraction method, enrichment factor and the Geo-accumulations Index

#### The river Weiße Elster

<table>
<thead>
<tr>
<th>extraction step</th>
<th>Metal Contents (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>S1</td>
<td>2.04</td>
</tr>
<tr>
<td>S2</td>
<td>183.00</td>
</tr>
<tr>
<td>S3</td>
<td>32625.00</td>
</tr>
<tr>
<td>S4</td>
<td>388.90</td>
</tr>
<tr>
<td>S5</td>
<td>35250.00</td>
</tr>
<tr>
<td>Rest</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>68448.94</td>
</tr>
<tr>
<td>EF</td>
<td>1.42</td>
</tr>
<tr>
<td>$I_{geo}$</td>
<td>-0.07</td>
</tr>
</tbody>
</table>

#### The river Bagmati

<table>
<thead>
<tr>
<th>extraction step</th>
<th>Metal Contents (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>S1</td>
<td>4100.00</td>
</tr>
<tr>
<td>S2</td>
<td>4000.00</td>
</tr>
<tr>
<td>S3</td>
<td>18652.00</td>
</tr>
<tr>
<td>S4</td>
<td>4.00</td>
</tr>
<tr>
<td>S5</td>
<td>27320.00</td>
</tr>
<tr>
<td>Rest</td>
<td>204.00</td>
</tr>
<tr>
<td>Total</td>
<td>54280.00</td>
</tr>
<tr>
<td>EF</td>
<td>1.13</td>
</tr>
<tr>
<td>$I_{geo}$</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

| Metal Contents (mg/kg) after Turekian and Wedepohl, 1961 |
|--------------------------|---|---|---|---|---|---|---|---|---|---|
| 48000                    | 850| 7 | 45| 95| 20| 90| 68| 0.3| 19 |
| CLARKE-value             | 2 | 47 | 200| 13| 83| 58| 0.13| 18 |

supply was only 60 days. Then, in phase VI, the current were checked to have increment in current through the system. It was not increase as in phase II.

#### 4.5 Methodology for the determination of the least working voltage

The working voltage required for the electrode system depends on the water quality, sediment composition, redox reactions at/nearby the electrodes, distance between the electrodes and the electrode material. The minimum voltage was determined by establishing
Table 8: Operational phases during the experiment

<table>
<thead>
<tr>
<th>Phase</th>
<th>Days</th>
<th>Voltage supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0-35</td>
<td>without</td>
</tr>
<tr>
<td>II</td>
<td>36-120</td>
<td>with</td>
</tr>
<tr>
<td>III</td>
<td>121-210</td>
<td>without</td>
</tr>
<tr>
<td>IV</td>
<td>211-300</td>
<td>with</td>
</tr>
<tr>
<td>V</td>
<td>301-360</td>
<td>without</td>
</tr>
<tr>
<td>VI</td>
<td>361-430</td>
<td>with</td>
</tr>
</tbody>
</table>

a current-voltage curve in the pre-operational test. It was carried out by measuring the current with stepwise increment of voltage in the range of $U = 0$ to 10 V in the sediment-water system where the cathode is 4 cm above and the anode 4 cm below the sediment surface. The electrodes were first polarized in the anodic and then in the cathodic direction. Depending on inhibition of anodic and cathodic refluxes, a shift of the anodic and cathodic curve (hysteresis) was measured. It follows that the intersection point of the approximately linear rise of the $U$ - $I$ curve in the anodic direction with the abscissa at $I = 0$ A represents the minimum necessary voltage.
5 Results and Discussion of the Process Studies

5.1 Dependency of least working voltage on various sediment types

The measurement of minimum voltage was carried out in two different sediments from the river Weiße Elster and the Bagmati. From the graph (Figs. 9 and 10), it was observed that the minimum voltages were at about 2.9 V and 2.5 V respectively. Only during exceeding of these values the electrode polarization and overvoltage would be compensated and redox processes at the electrodes could be observed. Therefore, at our tests a voltage of \( U = 3 \text{ V} \) was used in the most cases.

![Graph showing current-voltage curve](image-url)

**Figure 9:** Current-Voltage curve for determination of the minimum voltage of the sediment-water system from the river Weiße Elster (electrode material: polyethylene with carbon black, distance between the electrodes: 8 cm, anode 4 cm below and cathode 4 cm above the sediment-water interface)
Figure 10: Current-Voltage curve for determination of the minimum voltage of the sediment-water system from the river Bagmati (electrode material: polyethylene with carbon black, distance between the electrodes: 8 cm, anode 4 cm below and cathode 4 cm above the sediment-water interface)

5.2 Reactions and processes at the sediment-water interface of various species in dependence of the position of the electrodes

5.2.1 Arsenic

5.2.1.1 Anode at the sediment-water interface and cathode in the aqueous phase

Electrochemical behaviours of arsenic at sediment-water interface was observed in batch system by arranging the electrodes in different positions and conditions in the laboratory in six phases. In phase I, the equilibrium state between sediment and water was given. The oxidation of As(III) to As(V) occurs at strongly acidic, high \( Eh \) and aerobic condition. In a study of ten major rivers in the southeastern USA, arsenate-As(V) was only the dissolved species found [Waslencn, 1979]. An acidic front was generated at the interface in the phase II in Fig. 11. The redox potential initially increased towards positive range by the influence of anode, then went up (\( \sim 0 \) to \( +45 \) mV), probably due to a slight positive polarisation at the sediment-water interface (Fig. 12). The \( pH \) also decreased from \( \sim 6 \) to
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

Figure 11: Temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in RC (without voltage), [Anode at the sediment-water interface and cathode in aqueous phase]
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

Figure 13: \( Eh - pH \) diagram of aqueous arsenic species in the system \( \text{As(III,V)-O}_2 - \text{H}_2\text{O} \) at 25\(^\circ\) C and 1 bar total pressure [FERGUSON AND GAVIS, 1972]

about 2 - 2.7 in this phase. Under these aerobic conditions the dominant species of As(V) are mainly \( H_3\text{AsO}_4^{\text{6-}}, H_2\text{AsO}_4^{-}, H\text{AsO}_2^{2-} \) and \( \text{AsO}_3^{3-} \) in dependence of \( pH \) (Fig. 13). It can be shown that a time-delayed mobilization of As(V) had taken place in the strong acidic medium. In phase III where the \( H^+ \) ions were neutralized by \( OH^- \) ions produced at the cathode a decrease of the As(V) at the sediment-water surface was observed. This could have been caused by the bonding of the negative charged species \( H\text{AsO}_2^{2-} \) and to a lesser degree of \( H_2\text{AsO}_4^{-} \) to \( Fe(\text{III}) \)-hydroxides and oxyhydroxides in the sediment. As the \( pH \) value did not decrease in the phase IV as much as in phase II (the deepest \( pH \)-value: 4.5) no mobilization of As(V) occurs in this phase. In phase VI, there was again a \( pH \)-decrease to 3. This could be the reason of the beginning of As(V) mobilization.

5.2.1.2 Cathode at and anode 8 cm below the sediment-water interface

When the cathode was positioned at the sediment-water interface and the anode 8 cm inside the sediment, during the application of voltage (Fig. 14). The sediment-water interface initially became alkaline and the redox potential fell from \( \sim -75 \text{ mV} \) to \(-488 \text{ mV} \) (Fig. 12). The \( pH \) increased from about 6 to a maximum value of 11.5 in phase II and to 9.5 and \( Eh \)
to -666 mV in phase IV, probably due to the production of OH⁻ ions. It was observed that there was no As mobilization in the current-influenced phases may be due to high pH value (Fig. 15). Under strong alkaline conditions As(V) exists as charged species of HAsO₄²⁻ and AsO₄³⁻ and As(III) as H₂AsO₄⁻ in the solution. The reason for no As mobilization might be by bonding these species to amorphous and crystalline iron containing species. In the currentless phases, significantly mobilization of As was measured, because of the As(III) mobilization at neutral and under acidic conditions it exists as a neutral complex H₃AsO₃. So that, low or no interactions with the solid phase are occured. In addition to pH, Eh also plays a significant role. At the phase III, Eh was in the negative range. It is clear that under mildly reducing condition arsenite predominate. The reference system is characterized by a slow mobilization of As-sulfides through oxidation processes as follows:

\[ As₂S₃ + 6O₂ + 6OH⁻ → 2H₃AsO₃⁰ + 3SO₄²⁻ \]  \hspace{1cm} (11)

\[ As₂S₅ + 10O₂ + 8H₂O → 2H₂AsO₄⁻ + 5SO₄²⁻ + 12H⁺ \]  \hspace{1cm} (12)

This is followed by a slow immobilisation of As by binding to Fe(III)-hydroxides containing solids at the days 242 - 421.
5.2.1.3 Anode 4 cm below and cathode 4 cm above the sediment-water interface

In the experiment the current flow through the system during phase IV was negligible in comparison to phase II (Fig. 16). The reason could be that the cathode in the phase IV maybe covered by a small insulating layer of carbonates or other precipitations. One can say that after phase II there was no much current. It was nearly 55% less than that of phase II. The redox potential fell on negative range (from 0 to -800 mV) in phase II (Fig. 12), probably due to the cathodic influence. In the current influenced phase II, the \( pH \) values increased upto 12 by the influence of the cathode. At this high \( pH \)-value no Ar- mobilization occurred, as described in cathode at and anode 8 cm below the sediment-water interface (Fig. 16).

5.2.1.4 Anode 4 cm above and cathode 4 cm below the sediment-water interface

The experimental column followed the similar trend as the reference column at phase I (Fig. 18). The \( pH \) and \( Eh \) (Fig. 12) had almost same values. The As - concentration at the interface was gradually increasing maybe due to slow oxidation of As or formation of ions even there was no voltage supply. At the phase II of EC with current, the \( Eh \) was in range of \(~ -64 \) to +15 mV and \( pH \) \~ 3.0 at the interface from 36 to 48 days. It was observed that the As - concentration was low. This could be due to time-delayed mobilization of high amount of As(V) species and low amount of As(III) species at the sediment-water interface.
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Figure 16: Temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage), and in RC (without voltage). [Anode 4 cm below and cathode 4 cm above the sediment-water interface]

interface. It is known (Fig. 15) that the As(V) species are likely absorbed at the sediment, which contains iron (III)- surfaces.

\[
\equiv FeOH + H_2AsO_4^{-} / (HAsO_4^{2-}) \rightarrow (FeOH_2^+)_{2/(3)} HAsO_4^{2-} / (AsO_4^{3-})
\]  
(13)

At days 48 - 76, the Eh increased to \(\sim +45\) mV whereas pH was \(\sim 5.5\). Under this condition, the mobilization of As increased up to 40 \(\mu\)g/L. This could be due to the formation of species of \(H_3AsO_4\). At weak acidic and aerobic conditions with low As- concentration (\(\sim 10\) \(\mu\)g/L) in 76-121 days, the following compound might be formed.

\[
H_2AsO_4^- + \equiv FeOH_2^+ \rightarrow \equiv FeOH_2^+ H_2AsO_4^-
\]  
(14)

After phase II, the pH, Eh and As - concentration remained almost constant throughout the process. This indicates that once the sediment is acidified the time needed for its neutralization is much longer than the acidification period.

5.2.1.5 Anode 4 cm below and cathode 4 cm above the water-sediment interface with \(CaCO_3\).

The buffer capacity of the sediment of the river Weiße Elster was \(K_{S_{1.3}} = 12\) mmol \(H^+ /\)kg (eq. 8).
Figure 17: Temporal changes of the current during the phases influenced by a constant voltage $U = 3\, \text{V}$.

Calculation of additional $\text{CaCO}_3$

The amount of $\text{CaCO}_3$ added in the solution should be calculated to know the exact amount to neutralise the acidic sediment.

\[ d = 12\, \text{cm} \quad \text{(diameter of the column)} \]

\[ \text{Area of Column (A)} = \frac{1}{4} \pi d^2 = 113\, \text{cm}^2 \]

\[ h = 4\, \text{cm} \quad \text{(height of the sediment)} \]

Volume of sediment up to the anode (V) = base area (A) \times height(h) = 452\,\text{cm}^3

Total volume of the sediment = 1357\,\text{cm}^3

Mass of the sediment used = 1800\,\text{g}

\[
\text{Density} = \frac{1800\, \text{g}}{1357\, \text{cm}^3} = 1.33\, \text{g/cm}^3
\]

mass of sediment up to anode used = 600\,\text{g}

\[ K_{\text{Si,3}} = 12\, \text{mmol H}^+ / \text{kg} \]

Therefore, for 0.6\,\text{kg} = 7.2\,\text{mmolH}^+$
Figure 18: Temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage), and in RC (without voltage), [Anode 4 cm above and cathode 4 cm below the sediment]

We know that,

\[
CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-
\]  

(15)

\[
CaCO_3 + 2H^+ \rightarrow CO_2 + Ca^{2+} + H_2O
\]  

(16)

1 mole of \(CaCO_3\) = 1 mole of \(H^+\) (production of 1 mole of \(HCO_3^-\))

7.2 mmol \(H^+\) = 7.2 mmol \(CaCO_3\)

= 720 mg (\(CaCO_3\) added to the column)

The \(pH\) was controlled through added 720 mg of \(CaCO_3\), even if the voltage was applied at the phase II (Fig. 19). As a result, the \(pH\) did not rise about 8.5 throughout the whole process. At beginning of 48 days in the phase II, the \(Eh\) decreased from \(\sim -70\) mV to \(-309\) mV (Fig. 12), the mobilization was not observed due to the time - delay mobilization. After 48 days, \(Eh\) decreased up to \(\sim -434\) mV and almost constant \(pH\) value, the concentration was constant. It is clear that the double bond oxygen in the arsenate/arsenite molecule influence their abilities to become ionized through the loss of hydrogen ions. A negative charge develops on the molecule when dissociation occurs. The double bond oxygen increases the capacity to delocalize that charge, easing the loss of hydrogen ions. Even so, the most probable reason for the mobilization may be formation of arsenite ions under these reducing potential and \(pH\) \(\sim 7.0\) conditions.
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

Figure 19: Temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage), and in RC (without voltage) [Anode 4 cm below and cathode 4 cm above the sediment-water interface with a CaCO₃ layer]

5.2.1.6 Anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode

In the first case, current distribution of 10% over the anode II (A2) and 90% over the anode I (A1) in the sediment showed no efficient result. The next two experiments showed similar effects (Table 9). Therefore, in the experiment, the second condition was taken.

Table 9: Distribution of current over the first and second anode

<table>
<thead>
<tr>
<th>Experimental no.</th>
<th>Current over the first anode ( I_1 \times 100% )</th>
<th>Current over the second anode ( I_2 \times 100% )</th>
<th>Effects on the sediment interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>10</td>
<td>No significant</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>40</td>
<td>pH ( \sim 8 )</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>50</td>
<td>pH ( \sim 8 )</td>
</tr>
</tbody>
</table>

The counter anode worked to neutralise the \( OH^- \) ions formed at the cathode. Under this condition, the \( pH \) and \( Eh \) ranges during the 51 days period of the experiment were \(~ 6.5\) to \(~ 9.0\) and \(~ -38\) to \(~ -309\) mV respectively (Fig. 20). No mobilization was seen due to time-delay mobilization. After 51 days, the mobilization was observed at the \( pH \) range between \(~ 9.6\) to \(~ 10.4\) and reductive condition \(~ -665\) mV in the phase II. The rate of
As-mobilization in the EC and RC seemed equal in the phase III. The influence of the counter anode was not effective in the phase IV. Always slow mobilization took place even on voltage supply.

Figure 20: Temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage), and in RC (without voltage). [Anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode]

5.2.1.7 Anode 4 cm above and cathode 4 cm below the sediment with various voltages

It was found that the rate of As-mobilization depends on the voltage between the electrode in the column. At phase II, there was a slight mobilisation when voltage of 3 V and 4 V were applied. But, when voltages of 0 V and 2.5 V were applied mobilization occurred continuously and at same rate. It showed that 2.5 V could not be used to mobilize As. When no voltage was supplied, mobilisation was the highest in the case of 4 V. The rate of As-mobilization was directly proportional to the voltage applied, the 3V could be taken for the all experiment because it showed similar or almost same action in mobilization only change in the rate (Fig. 21).
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

![Graph showing temporal changes in total As-concentration and pH-value at the sediment-water interface in the EC (with U = 0 V, 2.5 V, 3 V, 4 V without voltage), and in RC (without voltage)] [Anode 4 cm below and cathode 4 cm above the sediment-water interface with various voltages]

5.2.2 Cadmium, Lead and Zinc

5.2.2.1 Anode at the sediment-water interface and cathode in aqueous phase

In the currentless phase I, nearly neutral conditions were observed at the sediment-water interface. The heavy metal concentrations at the sediment-water interface were relatively low (about 40 μg/L Cd, 6 μg/L Pb and 6 mg/L Zn).

In the phase II (U = 3 V) the pH fell up to pH ~ 2.0, when a high increase in Cd, Pb and Zn - concentration was measured, because of the anodic $H^+$-production at the sediment-water interface. The Cd increased from 40 to 240 μg/L, Pb from 6 to 85 μg/L and Zn from 6 to 32 mg/L (Fig. 22). After about 7 days, when the pH increased slowly again because of the impact of the cathode, the $OH^-$ - ions produced at the cathode migrated towards the anode and partially neutralized the protons generated there.

The next currentless phase III was characterized by the further neutralization of the protons. It exhibited a nearly neutral condition at the sediment-water interface and relatively low heavy metal concentrations.
The phases IV and VI with repeated current influence (U = 3 V) showed a pH-decrease again, because of the 
$H^+$ production at the anode. However the pH decrease was by far not so high as in the phase II. The exact reason was unclear. It is assumed that the precipitation of heavy metal hydroxides and carbonates at the sediment-water interface has a raised buffering capacity. The anodically produced protons may be buffered through this layer.

The mobilization rate is characteristic of the individual ions:

**Cd:** The Cd-ion solubility rises as pH falls in the pH-range $< 10$ in equilibrium of $\text{Cd}(\text{OH})_2/\text{CdCO}_3$. Through the anodic influence the pH decreased up to 2 and the Cd-concentration increased. The minimum solubility is at about pH 10 for CdCO$_3$ and pH 11-12 at $\text{Cd}(\text{OH})_2$. At pH-values over 10 (up to pH 12.0), the solubility increases again, caused by the formation of soluble Cd-hydroxo and humic complexes.

**Pb:** The lead is transformed into strongly binding substances with the sediment and/or just in combination forms. Pb is bound most strongly among all the heavy metals by specific adsorption processes, particularly, with Fe-, Al- and Mn-oxides. It was seen that the high binding capacity of Pb in sediments increased with the pH. The Pb-solubility is dependent upon the pH-value and the redox conditions. Unlike Cd, Pb normally shows a very low solubility at pH values $> 5.0$ and is relatively immobile in sediments. The solubility and availability of Pb increases first with pH values $< 4.0 - 4.5$. In presence of humic acids or organic compounds, Pb is adsorbed nearly 90% at neutral pH. It was clearly observed in the phase III. The solubility increased from $\sim 20 \, \mu g/l$ to 35 $\mu g/L$ in the phase IV. Then very weak mobilization was observed in both phases V and VI.

**Zn:** It is well-known, that at a pH-range $< 7.0$ the solubility of hydroxides and carbonates of zinc increases with decrease in the pH. Besides, its affinity to humic substances and Mn- and Fe-hydroxides decreases very strongly at the range of $< 5.0$ [Dzombak and Morel, 1990]. For this reason Zn content of the soil solution rises with decrease in the pH. In phase III, there was a pH increase up to $> 6.0$, when the Zn did slightly or not mobilize. It is well known [Blume and Brummer, 1987] that the affinity of Zn to Mn- and Fe-oxides increases strongly with the rise in the pH to $> 7.0$. If the pH at the interface did not decrease below pH 3 (phase IV and VI) no significant Zn-mobilization occurred.
Figure 22: Temporal changes in total metal concentration of Cd, Pb, and Zn and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and RC (without voltage). [Anode at the sediment-water interface and cathode in aqueous phase]
5.2.2.2 Anode 8 cm below and cathode at the sediment-water interface

In the phase I, the EC followed the RC. Both systems had neutral pH (Fig. 23). After the application of voltage, the pH-value increased from \( \sim 6 \) to 12.0 in phase II, 6.6 to 9 in phase IV and 6.8 to 8.0 in phase VI due to the production of \( OH^- \) ions. This is a favourable range for \( Cd, Pb \) and \( Zn \) to be absorbed by the sediment and/or precipitated as explained before. In phase III, the pH values decreased from \( \sim 12.0 \) to \( \sim 6.6 \), in which \( Cd \) and \( Zn \) were mobilized from the sediment to the interface.

**Cd:** In the reference column, an increase in \( Cd \)-concentration caused by microbial sulphide oxidation was observed in the first 70 days by the following reaction.

\[
CdS + 2O_2 \rightarrow \text{heterotrophic microorganisms} \rightarrow Cd^{2+} + SO_4^{2-} \tag{17}
\]

After that, there was a slow decrease in \( Cd \)-concentration, because it is precipitated as \( Cd(OH)_2 \) at near neutral pH-conditions.

In the current phases, there is a precipitation and fast fixation of \( Cd \) in the form of \( Cd(OH)_2 \), or \( CdCO_3 \) by the \( OH^- \) ions produced cathodically, through the following reactions (eqs. 18, 19).

\[
Cd^{2+} + HCO_3^- + OH^- \rightarrow CdCO_3(s) + H_2O \tag{18}
\]

\[
Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2(s) \tag{19}
\]

In about 169 days, pH decreased to \( \sim 7.1 \), then the mobilization of \( Cd \) occurred. The concentration increased \( \sim 0.4 \mu g/L \) to \( 4 \mu g/L \). After this concentration came up to \( \sim 13 \mu g/L \). In phases IV, V, VI, the pH values \( > 8 \) were sufficient in order to fix the cadmium almost completely.

**Pb:** Relatively low initial \( Pb \)-values in the water were obtained at the equilibrium stage in the original sediment because of the strongly bonding of \( Pb \) as \( PbS \) at the sediment lattice at anaerobic conditions. The reason of the increase in the \( Pb \)-concentration in the reference was also due to the microbial oxidation of the sulphide. From the phase II where the concentration went down suddenly from \( \sim 9.7 \mu g/L \) to \( 0.13 \mu g/L \) due to pH increase from 6 up to 12, the concentration continuously went down to negligible value \( (0.03 \mu g/L) \) because the pH could not come to \( < 5 \) pH.
Figure 23: Temporal changes in total metal concentration of Cd, Pb and Zn and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [cathode at and anode 8 cm below the sediment-water interface]
The reason could be that the microbially formed sulfate reacted with the $Pb^{2+}$-ions to the relatively insoluble $PbSO_4$.

In the current phases a strong decrease of the $Pb$-concentration occurs, which could be a result of the $Pb(OH)_2$ precipitation (eq. 20). At $pH$ 11, significant amounts of $Pb$ can be detected in the solution. Here the critical $pH$-value of around 11 is exceeded, the formation of the soluble $Pb$-trihydroxocomplexes occurs (eq. 21).

$$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2(s) \quad (20)$$

$$Pb(OH)_2(s) + OH^- + H_2O \rightarrow [Pb(OH)_3H_2O]^-$$(21)

**Zn:** Zinc exists at $pH < 6.5$ as $Zn^{2+}$, $ZnOH^+$, $Zn(OH)_2^0$ [Gerischer and Mauner, 1970]. With the increase in the $pH$-value, oxides of Mn and Fe can adsorb particularly $Zn^{2+}$, $ZnOH^+$ and $Zn$-complexes so that the higher the $pH$ value the lower the $Zn$-concentration because $Zn$ is removed from the solution by the formation of solid $Zn(OH)_2$ (eqs. 22-24).

$$Zn^{2+} + OH^- \rightarrow ZnOH^+ \quad (22)$$

$$ZnOH^+ + OH^- \rightarrow Zn(OH)_2^0 \quad (23)$$

$$Zn(OH)_2^0 \rightarrow Zn(OH)_2(s) \quad (24)$$

At high $pH$-values of $>11$ significant amounts of the soluble $Zn$-complex $[Zn(OH)_3]^{-}$ are produced. This effect was observed at the end of the phase II at a small scale. In the currentless phases the $pH$-value decreased slowly because of the buffering effect of the precipitated solids. The increase in $Zn$ concentration was observed due to mobilization of $Zn^{2+}$ from sulphide phase in phase I (eq. 25).

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-} \quad (25)$$

### 5.2.2.3 Anode 4 cm below and cathode 4 cm above the sediment-water interface

In this experimental set up, the current flow through the system during phase IV is negligible in comparison to phase II (Figs. 24, 17). One must consider phase IV with very low
Figure 24: Temporal changes in total metal concentration of Cd, Pb and Zn and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [anode 4 cm below and cathode 4 cm above at the sediment-water interface]
current. In phase II the pH - value increases slowly to values of 12. In the same way the Cd- and Zn-concentrations sink to values near zero. Pb is only available at very negligible amounts at the sediment-water interface and hardly changes in its concentration. In the phases III, IV and V the Cd, Pb and Zn - concentration increases to values measured in the reference column.

### 5.2.2.4 Anode 4 cm above and cathode 4 cm below the sediment-water interface

In this experiment, the sediment-water interface got acidified continuously after current supply (Fig. 25). The degree of mobility of particular metals depends on the physicochemical state of their compound with respect to the sediment and pH-/redox-barrier formed by the electric field.

The following are the behaviours of the metals ions or the complexes under the experimental conditions:

**Cd:** Cadmium is freely present as divalent species up to pH 8.0, in absence of any adsorbents such as Mn- and Fe- oxides, phosphate, sulphide, etc. The Cd-adsorption at the sediment surface increases with pH beyond the threshold point (pH ≥ 7.0 for Cd). In presence of sorbents, the pH values required for precipitation of Cd change very low. Cd was observed unaffected by presence or absence of them in pH > 6.0. When the current was applied at phase II, the pH first reached 3.0, then up to 5.0 from the neutral stage of phase I, the mobilisation of Cd took place. The concentration increased from ~ 60 µg/L to 97 µg/L. At phase III, although the neutralisation at the interface occurred, the pH-value could not increase to pH 7.0. So the mobilization continued. This is the best arrangement for the mobilization of Cd from the sediment to the sediment-water interface by the following reaction.

\[
Cd - \text{sediment} + 2H^+ \rightarrow Cd^{2+} + 2H - \text{sediment}
\]  

(26)
Figure 25: Temporal changes in total metal concentration of Cd, Pb and Zn and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [anode 4 cm above and cathode 4 cm below at the sediment-water interface]
**Pb:** Lead is usually precipitated at \( p\text{H} > 4.0 \) [Gerischer and Mauner, 1970 and Blume and Brummer, 1987]. The \( p\text{H} \) suddenly decreased from \( \sim 6.0 \) to 3.0 and \( E\text{h} \) was also in positive range (Fig. 12) in 12 days of applying the voltage at phase II. At these conditions, the rate of mobilization increased from \( \sim 10 \, \mu\text{g/L} \) to 182 \( \mu\text{g/L} \). This was the favourable condition in this system. The \( p\text{H} \) increased to values up to 5.0 at the end of 67 days. It continued to phase III. It is known that at \( p\text{H} \) 6.0 the \( Pb^{2+} \)- and \( PbOH^+ \)-concentrations in solution are equal. Maybe this is the reason for mobilisation at the interface. The high \( Pb \)-mobilization at low \( p\text{H} \)-values results in its competition with the \( H^+ \)-adsorption to soil as follows:

\[
Pb - sediment + 2H^+ \rightarrow Pb^{2+} + 2H - sediment
\]  

(27)

**Zn:** The general trend of \( Cd \)-, \( Pb \)- and \( Zn \)-sorption at certain adsorbents such as humic acids, organic compounds, \( Mn \)- and \( Fe \)-oxides, etc. after [Gerischer and Mauner, 1970 and Blume and Brummer, 1987] is:

\[
Cd \geq Zn \geq Pb
\]

This sequence also depends on the \( p\text{H} \)-value. In the case of \( Zn \), significant adsorption in the sediment takes place only at \( p\text{H} \)-values higher than 5.5 - 6.0. Therefore, the phase II was the best condition for mobilization of \( Zn \) from the sediment to the interface. At phase III, where \( p\text{H} \) was about 6.0, only weak adsorption took place as follows:

\[
Zn - sediment + 2H^+ \rightarrow Zn^{2+} + 2H - sediment
\]  

(28)

**5.2.2.5 Anode 4 cm above and cathode 4 cm below the sediment-water interface (with a \( CaCO_3 \)-layer)**

In this experiment with the same electrode arrangement as in (iii), a calculated amount of \( CaCO_3 \) was added (5.2.1.5) to the sediment surface (Fig. 26). \( CaCO_3 \) is capable to buffer protons produced by the sediment-water interface (Fig. 15) As expected, the \( p\text{H} \) did rise to 7.5. A difference in solubility of \( Cd \), \( Pb \) and \( Zn \) was exhibited in this set of experiment:

**Cd:** At phase II, a \( Cd \)-mobilization was observed up to 39 days from \( \sim 36.4 \) to 52 \( \mu\text{g/L} \). The rate of mobilization slipped down slowly after this point, first \( \sim 41 \, \mu\text{g/L} \), then \( 10 \, \mu\text{g/L} \). This could be due to the start of the formation of \( CdCO_3 \).

\[
Cd^{2+} + CO_3^{2-} \rightarrow CdCO_3(s)
\]  

(29)
RESULTS AND DISCUSSION OF THE PROCESS STUDIES

Figure 26: Temporal changes in total metal concentration of Cd, Pb and Zn and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [anode 4 cm below and cathode 4 cm above at the sediment-water interface with a CaCO$_3$]
After applying current in the phase III, $CdCO_3$ could not dissolve due to its low solubility product of $CdCO_3$, as there are the high concentration of carbonate ions at the interface. Besides, once it was precipitated out, it was very difficult to form soluble ions.

$$CdCO_3 \rightarrow Cd^{2+} + CO_3^{2-}$$ (30)

$$K_{SO}(CdCO_3) = 5.3 \times 10^{-14} \text{mol}^2/\text{L}^2$$

$Cd$ - solubility = $2.3 \times 10^{-7} \text{mol}/\text{L}$

It can be shown the $Cd$ - immobilization by adding $CaCO_3$.

**Pb:** Pb in comparison with $Cd$ shows a different picture. The solubility of $Pb$ decreased slowly after the application of voltage. It could be humic acid that was in high amounts in the sediment was initially strongly desorbed, at phase I, at low pH. The trend went reverse at $pH > 6.5$, when soluble $Pb$-humate complexes were formed. The sediment had difficulty with soluble $Pb$-humates for retention on the solid phase. This was because the concentration slipped from $\sim 10 \mu g/L$ to $6 \mu g/L$. The solubility product of the $PbCO_3$ is little higher than that of $CdCO_3$. Even so, the slow immobilization was observed in phases III, IV and V.

$$PbCO_3 \rightarrow Pb^{2+} + CO_3^{2-}$$ (31)

$$K_{SO}(PbCO_3) = 7.4 \times 10^{-14} \text{mol}^2/\text{L}^2$$

$Pb$ - solubility = $2.7 \times 10^{-7} \text{mol}/\text{L}$

**Zn:** In the case of zinc, the mobilization increased with the increase in the $pH$ value as expected up to 169 days from $\sim 6.4 \text{ mg/L}$ to $12.1 \text{ mg/L}$ as the $pH$ reached up to above 8. $Zn(OH)^{+}$ and $Zn(OH)_2^0$ formed at the pH-range of 7 - 7.5. Therefore, $Zn$ is precipitated as $Zn(OH)_2$. After 169 days, the migration was not so rapid which could have been due to the decrease in $pH$. The reason why the concentration decreased continuously after 151 days was not clear. One is true that the concentration of $Zn$ came to very negligible after about 300 days and $pH$ was also stable.
5.2.2.6 Anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode

In this arrangement, a counter anode was placed 2 cm above the cathode, the cathode on the other hand 4 cm above and the anode 4 cm in the sediment. The measured concentration values of Cd, Pb and Zn and pH without/with voltage are shown in Figure 27. About 30% of total anodic current was passed through the counter anode to neutralise the \( OH^- \)-ions formed at the cathode. pH at sediment-water interface was reduced from \( \sim 12.0 \) to 10.5. The following results were obtained:

**Cd:** After application of voltage, the rate of mobilization of Cd decreased rapidly which could be due to the precipitation of hydroxide and carbonates at the pH-value of about 10.5.

\[
Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2(s) \tag{32}
\]

\[
Cd^{2+} + CO_3^{2-} \rightarrow CdCO_3(s) \tag{33}
\]

Strong negative redox potential was observed in all phases (Fig. 12), CdS might be also be formed by the following reaction at anaerobic conditions:

\[
Cd^{2+} + S^{2-} \rightarrow CdS(s) \tag{34}
\]

Even in the phase II, the mobility rate was almost constant due to the dissolution of the precipitated CdS-particles. This arrangement could be used to stop the Cd-mobilisation.

**Pb:** As usual, with the increase in pH, the immobilization increased maybe due formation \( Pb(OH)_2 \) at the phase II. The Pb - concentration at the interface decreased from \( \sim 8 \ \mu g/L \) to 1.5 \( \mu g/L \). The concentration continued decreasing at the phase III may be due to formation of more precipitates or absorption of Pb at soil particles at the interface.

**Zn:** The fixation of Zn rapidly increased with increased pH after applying the voltage at the phase I. After this phase, the concentration of Zn seems to be constant due to the inability of dissociation of the Zn-precipitates.
Figure 27: Temporal changes in total \( \text{Cd} \), \( \text{Pb} \) and \( \text{Zn} \) concentration and \( \text{pH} \)-value of the sediment-water interface in the EC (with \( U = 3 \text{ V} \)/without voltage), and in RC (without voltage). [Anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode]
5.2.3 Cobalt, Nickel and Copper

In the reference column (RC), the dissolved Co increased from 168 µg/L to ∼ 505 µg/L after approximately 136 days (Fig. 28).

Thereafter the concentration of Co slowly decreased until the end of the experiment. In the case of Ni (with 984 µg/L equilibrium concentration), the dissolution started increase extremely only after about 151 days from ∼ 1152 µg/L to 1185 µg/L (after about 226 days), then decreasing up to the end. The concentration of Cu gradually increased in all the experiment. Most metals are released from the sediment to aqueous phase by diffusion in exchangeable binding form. Since, diffusion is simple distribution method, it comes to the steady state. After this state, mobilized metals will be adsorbed and/or precipitated slowly. It was not clear why Cu mobilized gradually.

The experimental results of these metals with or without voltage supply in different arrangements as follows:

5.2.3.1 Anode at the sediment-water interface and cathode in the aqueous phase

The phase I was the equilibrium stage. Protons formed at the anode and the metal ions migrate from the sediment to the sediment-water interface during the voltage supply. After voltage supply at the phase II, within 3 days, the pH decreased suddenly from about 6 to 2.7. In the phase IV the pH could not go so deep as phase II. In the phases V and VI, pH values were constant. It might be due to coverage of precipitate on the electrodes. The observed current flow may be from the migration of protons and hydroxide ions (Fig. 17).

The rate of the mobilisation and accumulation of metals differs on their properties.

Co: The clear mobilization of Co was observed after supplying the current in the phase II. The concentration increase up from ∼ 76 µg/L to 1097 µg/L. The Co migration was by forming different soluble species of cobalt; Co$^{2+}$, CoOH$^{+}$. As expecting in the phase III, the mobilisation process was not fast as in phase II because at this phase, the neutralisation process was taken place. pH was about 6.5. So, the concentration was found in the range of 900 µg/L. At the phase IV with 3V, the pH values went down up to ∼ 4.24. The mobilisation was increasing from ∼ 836 µg/L to 931 µg/L. But it was not as much as in phase II. It might be happened due the coverage of precipitation of other metals or cobalt itself. It still had mobilities in the phase V
Figure 28: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [anode at sediment-water interface and cathode in the aqueous phase]
and VI. But the rate of mobilisation seems to be constant.

**Ni:** $pH < 5.0$ is the favourable range for Ni - migration. Therefore, at the phase II, Ni got the good mobilisation by forming Ni$^{2+}$ ions or soluble complexes. The concentration reached from $984 \mu g/L$ to $\sim 2370 \mu g/L$ at the reference state. The concentration decreased slowly down to $\sim 1326 \mu g/L$ because of neutralisation of the anodic-formed $H^+$ ions by alkaline front of cathode while supplying no voltage in the phase III. The $pH$ increased up to 6.0. From the $pH$ 6.0, the precipitations were occurred due to formation of insoluble surface complexes with iron and/or manganese oxides, humic acids or organic compounds. The concentration was little bit to $\sim 1933 \mu g/L$ in phase IV (with voltage) where $pH$ reached $\sim 4.2$. It is to be seen in the rest phases, the mobilities was remaining almost same, but the rate of mobilities was higher than that of copper.

**Cu:** At the phase II, the mobilization of Cu was very high. At $pH$ values $< 6.0$, Cu exist as $Cu^{2+}$, $Cu_2(OH)_2^{3+}$, $CuOH^+$ as the soluble Cu-complexes. There is only small amount of $Cu(CO_3)_2^{2-}$ [STUHM AND MORGAN, 1981]. After about 48 days, the concentration increase from $127 \mu g/L$ to $\sim 1401 \mu g/L$. In the phase III without voltage supply, the concentration of Cu decreased to $\sim 201 \mu g/L$ maybe due to formation of insoluble complexes with humic acids, insoluble organic compounds and surface complexes with Fe$^{3-}$ and Mn$^{3-}$ oxides. After phase III, only small mobilization took place up to 256 days in the phase IV. Then slow dissolution was occurred and the concentration reached to almost $\sim 368 \mu g/L$. After phase IV, the mobilization was constant. Once Cu is fixed to sediment, it dislikes to be desorbed from it and only very little amount migrates.

5.2.3.2 Anode 8 cm below the sediment-water interface and cathode at the sediment

The $OH^-$ ions formed at the cathode, precipitate out the metals, which released from the sediment surface. Here the $pH$ values at the interface increased from $\sim 7.0$ to 12.0 during the supply of voltage.

**Co:** The mobilization of Co decreases from $pH$ 6.0. Co forms the insoluble compounds such as $Co(OH)_2$, $Co(OH)_3$, $CoCO_3$ and different of its compounds absorbed with humic acids and organic materials above $pH$ 8.0. In current phase II, where cathodic conditions at the sediment-water interface were produced, the concentration remained very small in the range of $Co \sim 0.11-0.16 \mu g/L$. The $pH$ increased also the most
Figure 29: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with $U = 3\, \text{V}$/without voltage) and in the RC (without voltage) [cathode at and anode 8 cm below the sediment-water interface]
favorable condition for formation of insoluble compounds of Co (Fig. 29). At the phase III, the neutralization took place. The pH fell down to ∼ 6.5. The mobilization was observed. The concentration reached up to ∼ 262 µg/L. At the phase IV, once again the voltage was applied. First few days the mobility of Co remained constant. The concentration of Co decreased only when the pH was more than 8.0. After this, the other phases had an about constant neutral pH value or very weak acidic condition. Therefore, phases V and VI showed little mobilization.

Ni: The mobilization rate decreases to a constant value at pH > 6.0. After an initial mobilization in phase I, probably determined through the oxidation of sulfide, the mobilized Ni species precipitated at pH > 8-9, as insoluble compounds; Ni(OH)$_2$, NiCO$_3$ at the interface. In currentless phase III, the slight mobilization took place due to getting neutral pH values and forming Ni$^{2+}$ ions. The concentration reached from 77 µg/L to ∼ 383 µg/L. The similar trend was repeated in the phases IV, V and VI. But, the trend of mobilization at the interface was observed at very low rate.

Cu: The same tendency as Co and Ni showed by Cu. While in the current phases the Cu-concentration was nearly 8 µg/L at the interface because of fixation as hydroxide and carbonate at pH = 8-12, the concentration in the phases increased to maximal 268 µg/L at pH of 6.5. The important soluble species like CuHCO$_3^+$, CuCO$_3^0$, Cu(CO$_3$)$_2^{2-}$, Cu(OH)$_3^-$, Cu(OH)$_2^{2-}$ etc. or bound with organic materials, Fe$^-$ and Mn-oxides at phase II due to the increase the pH from ∼ 6.0 to 12.0. At the first stage of phase III, as the sediment is known to be rich in H$^+$ ions from the anodic front and OH$^-$ ions formed at the interface by the cathode neutralized this buffering capacity of the sediment. Next is that the H$^+$ ions migrate 2 times faster than OH$^-$ ions. Due to this reason the H$^+$ ions were successful to neutralize the OH$^-$ ions and slightly mobilized the Cu from the sediment. The phases IV, V and VI followed the same rules.

5.2.3.3 Anode 4 cm below and cathode 4 cm above the sediment

The conditions of this arrangement are similar to the arrangement of cathode at the sediment.

Co: The equilibrium concentration (∼ 156 µg/L) decreased tremendously in the phase II with current to ∼ 0.53 µg/L due to formation of hydroxide, sulphide, carbonates of Co by increasing in pH around 12.0. In neutralization and currentless phase III with
Figure 30: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [cathode 4 cm above and anode 4 cm below the sediment-water interface]
neutral pH, Co concentration increased from \( \sim 178 \mu g/L \) to \( 926 \mu g/L \) (nearly 5 times). After this phase, the slow immobilization took place came to \( \sim 500 \mu g/L \).

**Ni:** The Ni concentration decreased at the interface along the increase in pH value from \( \sim 154 \mu g/L \) to 18 \( \mu g/L \) in the phase II. The concentration increased about 4.9 times in the currentless phase III due to nearly neutral pH condition. The mobilization was slow after the phase IV and the concentration came to \( \sim 665 \mu g/L \).

**Cu:** The concentration decreased from \( \sim 47 \mu g/L \) to 9 \( \mu g/L \) when cathodic conditions developed in the phase II. In the phase III (Fig. 30), the concentration increased from \( \sim 165.4 \mu g/L \) to 712.9 \( \mu g/L \) i.e. nearly 4.3 times. After the phase III, the concentration decreased continuously up to \( \sim 200 \mu g/L \).

5.2.3.4 Anode 4 cm above and cathode 4 cm below the sediment-water interface

**Co:** Due to decrease in pH value Co is mobilized at the interface (phase II, Fig. 31). After about 90 days, the concentration of Co at the interface was 6 times higher in comparisation to the equilibrium concentration (from \( \sim 150 \mu g/L \) to 958 \( \mu g/L \)). The pH was in the range of 3 - 5.0. Therefore, the most available species of Co at these conditions are soluble. The pH is the most important factors for the mobilisation or immobilisation. It is no matter that there is a presence of the important factors for immobilization of Co like the organic matter, Fe/Mn - oxides. As it is also known that the humic acid or other organic matters up to pH 6.0 could absorb only 15% of Co the mobilisation [MOORE AND RAMAMOORTHY, 1984 and SCHNITZER AND HERNDORFF, 1981] after disconnecting the current in the phase III, mobilisation was till observed. At phase III, pH could not reach the neutral point (pH \( \sim 5.6 \)). The concentration slowly increased to \( \sim 1950 \mu g/L \).

**Ni:** Similar to Co, the Ni concentration increased slowly. The Ni concentration was less than that of Co. After about 90 days, the mobility was only 2.5 times higher then that of the equilibrium concentration (from \( \sim 746 \mu g/L \) to 2342 \( \mu g/L \)). At phase III, the slow mobilization in concentration was observed due only 16 % of Ni could be absorbed by the humic acid or other organic matters upto pH 6.0 [MOORE AND RAMAMOORTHY, 1984 and SCHNITZER AND HERNDORFF, 1981]. pH was 5.6.

**Cu:** Cu showed the different characteristics in the same conditions of column. At phase II, the concentration of Cu was suddenly increased from about 1950 \( \mu g/L \) to 142058 \( \mu g/L \). There were maybe high amounts of \( Cu^{2+} \) ions, specially \( CuOH^+ \) and
Figure 31: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [anode 4 cm above and cathode 4 cm below the sediment-water interface]
$Cu_2(OH)_2^{2+}$ ions. After this at the phase III, due to increase in the $pH$ value, the concentration decreased from $\sim 142058 \, \mu g/L$ to $38683 \, \mu g/L \, (\sim 82\%)$. It was found that $83\%$ of $Cu$ could be absorbed by organic and humic acids.

5.2.3.5 Anode 4 cm below and cathode 4 cm above the sediment-water interface (with a $CaCO_3$ - layer)

$Co$: Due to supply of the current at the phase II (Fig. 32), the anodically formed $H^+$ ions cannot initially migrate through the $CaCO_3$-layer to the sediment-water interface. Therefore, $CaCO_3$ added at the interface just came to equilibrium state to maintain the $pH$ at 8.2 (eq. 15). It took nearly 67 days. In the 10 days after current supply, only $H^+$ ions came in contact with $CaCO_3$. So,

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + CO_2 + H_2O \quad (35)$$

Therefore, $Co$ - concentration decreased from $\sim 171 \, \mu g/L$ to $90 \, \mu g/L$ in the first 3 days of current supply. Even $90\%$ of $Co$ could be absorbed in the sedimental organic matter at $pH$ 8.2, the slow mobilisation was observed maybe due to formation of soluble complexes (e.g. $CoHCO_3^+$, $Co(OH)_3^-$, $CoCO_3$).

$$Co^{2+} + HCO_3^- \rightarrow CoHCO_3^+ \quad (36)$$

$$Co^{2+} + 3OH^- \rightarrow Co(OH)_3^- \quad \text{(at alkaline conditions)} \quad (37)$$

$$Co^{2+} + CO_3^{2-} \rightarrow CoCO_3^0 \quad (38)$$

After 67 days, the concentration reached the value of $\sim 600 \, \mu g/L$.

At the phase III, neutralisation took place. The $pH$ reached $\sim 6.0$. This is the best condition for $Co$ to reach the soluble form. Only $15\%$ $Co$ could able to absorb by organic matter and humic acid [Moore and Ramamoorthy, 1984 and Schnitzer and Kerndorff, 1981]. $OH^-$ ions were coming towards the anode at this moment. So, $Co$ maybe formed soluble $[Co(OH)_{2}CO_3]^{2-}$ complexes including $Co(OH)^{+}, CoOHCO_3^-, CoHCO_3^+, CoCO_3$ at the interface. That’s why the concentration increased rapidly in this phase to $\sim 1102 \, \mu g/L$. At the phase IV, $pH$ reached the value 7.0. Slow immobilisation occurred by decreased in concentration of $Co$ by 48% i.e. $\sim 530 \, \mu g/L$. At the phase V, the increase in concentration to $\sim 622 \, \mu g/L$ has the same reasons as in the phase III.
Figure 32: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [cathode 4 cm above and anode 4 cm below the sediment-water interface with a CaCO₃ layer at the sediment-water interface]
Ni: Similar trend of the curve as Co observed in Ni because they have similar properties in absorption to and release from the sediment. In the interstitial water, Ni lies at pH 7.5 mainly as a Ni - ion (until 80%) and in organic Ni-complexes (until 20%). Dependent upon the content of carbonate, sulphate and phosphate in the interstitial water $NiCO_3^0$, $NiSO_4^0$, $Ni_3(PO_4)_2^0$, etc. are found as an important Ni - complexes in it [STICHER et al., 1987]. The concentration increased to $\sim 1945 \mu g/L$ in the phase II and in neutralization phase III, slowly increased to 2648 $\mu g/L$. Again showed slight immobilisation in phase IV and raised the concentration in phase V (as phase III).

Cu: At the phase II, in the first 3 days of voltage supply, the same character of curve is observed as in Co and Ni. After that Cu - concentration slowly increased from 38 $\mu g/L$ to 250 $\mu g/L$ maybe due to the complex formation of $CuCO_3$.

$$K_{SO}(CuCO_3) = 1.4 \times 10^{-10} mol^2/L^2$$

$$Cu - solubility = 1.2 \times 10^{-5} mol/L$$

It is not understood why the concentration not significantly decreased as neutralisation took place at the phase III to $\sim 241 \mu g/L$ from 250 $\mu g/L$. At phases IV and V, again concentration decreased.

5.2.3.6 Anode 4 cm below and cathode 4 cm above the sediment-water interface with variation of the voltages

In all three cases of Co, Ni, Cu at phase II, the first immobilisation started in the column at $U = 4 V$, then at $U = 3 V$. At phase III, the remobilisation took place first in the column with $U = 3 V$ then, at $U = 4 V$. The column with 2.5 V showed the similar trend as that of 0 V, because the minimum voltage was not reached.
Figure 33: Temporal changes in the total concentration of Co, Ni, Cu and pH-value at the sediment-water interface in the EC (with U = 0, 2.5, 3 and 4 V/wthout voltage) and in the RC [anode 4 cm below and cathode 4 cm above the sediment-water interface with various voltages U = 0, 2.5, 3 and 4 V]
5.2.4 Chromium

The concentration at the interface increased gradually from ~1.6 μg/L to 67.2 μg/L in the reference column (Fig. 34). The pH value was almost in steady state condition (~6.5) and Eh decreased gradually to the more negative range (~ -205 mV after 421 days). At pH ≥ 6.5, most Cr(VI) is present as chromate ions. It was noted that Cr(III) could be oxidised to Cr(VI) by reaction with MnO₂ (if available) [Moore and Ramamoorthy, 1983]. Although the reaction rate was not appreciable affected by dissolved oxygen, slightly acidic or basic pH water limited the oxidation rate. Maybe this is the cause that Cr released from sediment to interface.

![Figure 34: Temporal changes in total Cr-concentration and pH-values in sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC [anode at the sediment-water interface and cathode in aqueous phase]](image)

5.2.4.1 Anode at the sediment-water interface and cathode in the aqueous phase

In the case, at the phase II, the pH decreased in the range of 2-3.0 (Fig. 34). The concentration of Cr observed increase at the interface. It is known that Cr can exist in the sediment in forms of Cr(III) and Cr(VI). Cr(III) is less toxic than Cr(VI). Only Cr₂O₇²⁻ and CrO₄²⁻ adsorb at the iron oxide, aluminum oxide only at acidic or neutral pH and under oxic conditions (Fig. 35). The existance of Cr₂O₇²⁻ was not possible in this column because of extremely low and anaerobic condition. Dichromate is a strong oxidizing agent. That’s why, Cr₂O₇²⁻ is not taken into account in this text. However, Chromate in the
Figure 35: Dependence of Cr - species from $pH$ - $Eh$ value [Pourbaix, 1966]

Sediment can reduce to Cr(III) by accepting electrons from Fe(II) in anaerobic condition regardless of $pH$ and $Eh$ (eq. 39). The reaction rate is very slow in presence of organic matter under an environmental $pH$ and temperature conditions, but the reaction rate increases with decreasing in $pH$ value.

$$CrO_4^{2-} + 3Fe^{2+} + 8H^+ \rightarrow Cr^{3+} + 3Fe^{3+} + 4H_2O$$ (39)

The Cr(III) and/or Cr(VI) - mobilization rate was high at phase II.

At $pH$ - values, less than $pH$ 4.5, Cr(III) is the dominant species in chromium according to species distribution in aqueous phase.

$$[Cr^{3+}] > [CrO_4^{2-}]$$

At very low $pH$ value, $[Cr_2O_7^{2-}]$ and $[CrO_2^{2-}]$ are dominant species. They like to get attachment with sediment surfaces at positively charged sites. This attachment decreases with increasing in $pH$ value. Those ions maybe moved towards the cathode and $Cr^{3+}$ which mobilized at the phase II, completely precipitated as hydroxy-species at higher $pH$ value at the phase III (40-42).

$$Cr^{3+} + OH^- \rightarrow CrOH^{2+}$$ (40)

$$Cr^{3+} + 2OH^- \rightarrow Cr(OH)_2^+$$ (41)
\[ Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3^0 \]  \hspace{1cm} (42)

The same processes were repeated at phases IV, V and VI respectively.

5.2.4.2 Anode 8 cm below the sediment-water interface and cathode at the sediment-water interface

At the phase II (Fig. 36), the pH increased from 6.0 to 12.0. The redox potential was in negative range (Fig. 12). This condition favored Cr(III) to precipitate out as hydroxide (42), bicarbonate and/or carbonate.

\[ Cr^{3+} + CO_3^{2-} \rightarrow CrCO_3^\downarrow \]  \hspace{1cm} (43)

\[ Cr^{3+} + HCO_3^- \rightarrow Cr(HCO_3)^{2+} \]  \hspace{1cm} (44)

Cr(VI) got left from the surface of sediment, moved to aqueous phase. If there is Cr(VI) as the chromate in the water there is absorption at the interface at low pH - value or a mobilisation at high pH - value.

\[ [Cr^{3+}] < [CrO_4^{2-}] \]  \hspace{1cm} (45)

\[ (\equiv SOH_2^+)_2CrO_4^{2-} + 2OH^- \rightarrow 2 \equiv SOH + 2H_2O + CrO_4^{2-} \]  \hspace{1cm} (46)

Figure 36: Temporal changes in total Cr-concentration and pH-values in sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [cathode at and anode 8 cm below the sediment-water interface]
At phase III, the mobilization started due to neutralization and formation of Cr hydroxy-complexes (eqs. 40 - 42). The repetition processes were observed at the phases IV, V and VI, but mobilization rate was less in comparison to phases II and III due to less current supply.

5.2.4.3 Anode 4 cm below and cathode 4 cm above the sediment-water interface

At the phase II (Fig. 37), pH increased from 6 to 12.0. The redox potential was also in negative range. This conditions were better for Cr(III) to precipitate as hydroxides [Turekian and Wedepohl, 1961]. Cr(IV) got left the interface as shown [Calmano et al., 1994]. At phase III the mobilization started due to neutralization and formation of Cr hydroxy-complexes [Basel, 1912 and Gerischer and Mauner, 1970]. The phases IV, V, IV had constant mobilization due to no current flow. The broken down of current maybe due to coverage of metal hydroxides over the cathode.

![Figure 37: Temporal changes in total Cr-concentration and pH-values in sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [anode 4 cm below and cathode 4 cm above the sediment-water interface]](image-url)
5.2.4.4 Anode 4 cm above and cathode 4 cm below the sediment-water interface

At phase II (Fig. 38), after 3 days of current supply, pH decreased to 3.4. So, the Cr - mobilization was extremely high. It raised from 1.5 \( \mu g/L \) to 119 \( \mu g/L \). After 12 days, pH came to 3.5, the concentration of Cr at the interface was \( \sim 101 \mu g/L \). After 30 days, pH became constant about 5.0. The concentration decreased to \( \sim 60 \mu g/L \). It is obvious, when the first layer of the sediment is once acidified, it takes time to neutralize it. Thus, pH was like constant at the phase III. The mobilization rate was constant. \( OH^- \) - ions were buffered by the sediment. Therefore, pH value looked constant.

![Figure 38: Temporal changes in total Cr-concentration and pH-values in sediment-water interface in the EC (with U = 3 V/without voltage) and in the RC (without voltage) [anode 4 cm above and cathode 4 cm below the sediment-water interface]](image)

5.2.4.5 Anode 4 cm below and cathode 4 cm above the sediment-water interface (with a \( CaCO_3 \) - layer)

At the phase II (Fig. 39), pH increased slowly up to \( \sim 8.2 \) due to addition of \( CaCO_3 \) in 30 days after voltage supplying. The mobilization was very low due to time-delayed mobilization. May be there was competition of \( OH^- \) and \( CO_3^{2-} \) to form the insoluble compounds such as \( Cr(OH)_3 \). \( OH^- \) - ions cathodically formed could combine with \( Cr^{3+} \) - ions to form insoluble \( Cr(OH)_3 \) within those 30 days. After this, \( CO_3^{2-} \) are in equilibrium
Figure 39: Temporal changes in total Cr-concentration and pH-values in sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage)\[anode 4$ cm below and cathode 4$ cm above the sediment-water interface with CaCO_3\]

with $HCO_3^-$ and $CO_2$,$H_2$O

$$2H^+ + CO_2^- \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$$ (47)

At $pH$ 8.3 , 89% - 100% $HCO_3^-$ is found in the aqueous phase. This could form soluble. $Cr(HCO_3)^{2+}$, $Cr(HCO_3)_{3/2}$. Therefore, mobilization of Cr was observed after 30 days. Then, $pH$ also decreased to $\sim 6.0$. Here, use of $HCO_3^-$ might be high, so more $HCO_3^-$ might form to balance the equilibrium (Fig. 40). Therefore, $pH$ came down to $\sim 6.0$. From the solubility curve, $CaCO_3$ dissociates with decrease in $pH$ value. This also helps to make mobile $Cr$ from sediment to the interface at the phase III. This continued at the phase IV.

5.2.4.6 Anode 4$ cm below and cathode 4$ cm above the sediment-water interface with various voltages

It is obvious that the rate of any reactions (accumulation or mobilization) increases with increase in voltage supply. Thus, at phase II, after supplying voltages, the $Cr$ showed immobilization first in the column with $U = 4$ V, then $U = 3$ V (Fig. 41). At the phase III, the neutralization phase, mobilization started to build first in the column with $U = 3$ V, then with $U = 4$ V. The column with $U = 2.5$ V worked as without any current supplied.
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

Figure 40: Solubility of CaCO$_3$ as a function of pH [CARROLL AND MATHER, 1992]

Figure 41: Temporal changes in total Cr-concentration and pH-values at the sediment-water interface in the EC (with U = 2.5 V, 3 V, and 4 V/without voltage) and in the RC (U = 0 V) [anode 4 cm below and cathode 4 cm above the sediment-water interface with various voltages]
5.2.5 Iron and Manganese

5.2.5.1 Anode at the sediment-water interface and cathode in the aqueous phase

Fe: The concentration of iron at the sediment-water interface released from the sediment with and without voltage was measured (Fig. 43). The phase I was the equilibrium stage. At phase II, only after 39 days with voltage, concentration of iron increased slowly maybe due to time-delay mobilization. After 121 days, the Fe-ions concentration was more than 170 mg/L due to the pH below 2.0 and oxic conditions in which Fe(III) might form (48 - 50) at the anode.

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{48}
\]

\[
Fe(OH)_3 + 3H^+ \rightarrow Fe^{3+} + 3H_2O \tag{49}
\]

\[
Fe^{3+} \rightarrow Fe^{3+} + e^- \tag{50}
\]

Figure 42: Eh - pH diagram of Fe and Mn - species [STUMM AND MORGAN, 1981]
At phase III, the neutralisation took place without current supply, but the pH was till below 6.0. The mobilisation from the sediment continuously went up to \( \sim 345 \) mg/L. At phase IV, the redox potential decreased from -145 mV to -166 mV and oxygen content from 1.4 mg/L to 0.39 mg/L within 45 days of current supply. The mobilisation was continued up to \( \sim 518.35 \) mg/L from 345 mg/L due to Fe(III) microbial reduction at lower pH \((< 6.0)\).

The formation of iron (III) ions maybe as below:

\[
Fe_2O_3 + H_2O \rightarrow 2FeOOH
\]  

Figure 43: Temporal changes in Fe and Mn - concentration and pH-values at the sediment-water interface in the EC (with \( U = 3 \) V/without voltage) and in the RC (without voltage) [anode at the sediment-water interface and cathode in the aqueous phase]
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

\[ \text{FeOOH} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \quad (52) \]

\[ \text{Fe(OH)}_3^+ + \text{H}^+ \rightarrow \text{Fe(OH)}_2^+ + \text{H}_2\text{O} \quad (53) \]

\[ \text{Fe(OH)}_2^+ + \text{H}^+ \rightarrow \text{Fe(OH)}^2+ + \text{H}_2\text{O} \quad (54) \]

\[ \text{Fe(OH)}^2+ + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} \quad (55) \]

At phase V, the redox potential decreased from -249 mV to \(-400\) mV and increase in the oxygen content from 0.4 mg/L to \(\sim 2\) mg/L during neutralisation and migration processes, when there was no supply of current. The oxidation and acidification might take place. So the immobilisation of iron was observed. But the rate of mobilization increased maybe due to beginning of complexation as equations 53 - 55. The phase VI might follow the phase IV. The rate of mobilization seems to be low in comparison to IV phase maybe due to fewer amounts of microorganisms in less oxygen content environment and also by adsorption or precipitation in phase V.

**Mn:** At the phase I, concentration of Mn got equilibrium stage after 10 days. The mobilisation of Mn increased after 39 days by supplying current due to decrease in pH and increase in Eh. Maybe following reactions were carried out expect equations 48 - 52.

\[ \text{Mn(OH)}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad (56) \]

\[ 2\text{Mn}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + 4\text{H}^+ \quad (57) \]

In comparison to Fe, mobilization of Mn started faster just after current supply because of microbial microorganism’s mobilisation and less Mn affinity with organic and humic acid in low pH and high Eh value (Fig. 42). At pH 6.0, according to Irving - Williams order, the rate of precipitation is 100% for Fe and 43% for Mn . At the phase III, the concentration of Mn increased up to 40 mg/L after 169 days. After that, the oxygen content, redox potential increased, the mobilisation went down continuously up to the phase VI. In the phase VI, the concentration increased slight from \(\sim 19\) mg/L to 22 mg/L due to decrease in pH because of the current supply.
5.2.5.2 Anode 8 cm below and cathode at the sediment-water interface

**Fe:** The pH value increased from 6.0 to 12.0, oxygen content from 0.7 mg/L to 1.1 mg/L and redox potential decreased from $\sim\ -75$ mV to -309 mV when voltage was supplied after 121 days in the phase II.

$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^- \quad (58)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 (pH \sim 8) \quad (59)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 (pH > 8) \quad (60)$$

Figure 44: Temporal changes in $Fe$ and $Mn$-concentration and $pH$-values at the sediment-water interface in the EC (with $U = 3$ V) and in the RC (without voltage) [cathode at and anode 8 cm below the sediment-water interface]
Results and Discussion of the Process Studies

May be due to formation of hydroxides of Fe(II) or Fe(III), the mobilization was very low at high pH in range of 8 - 12 at the phase II. Therefore, the Fe_{total} concentration came to ∼ 22 mg/L. At phase III, the neutralization was taken place, the mobilization slowly increased by forming Fe^{2+}, Fe^{3+}, Fe(OH)_{2}^{+}, FeOH^{2+}, FeOH^{+} because pH went down from ∼ 12.0 to 7.0, redox potential from ∼ -309 mV to -240 mV and oxygen content slowly decreased. So the reduction occurred. The Fe concentration increased from 0.078 mg/L to 95 mg/L after neutralization for 90 days. Maybe there were formation of Fe(OH)_{2}^{+}, Fe(OH)^{2+}, Fe^{3+} or FeOH^{+}, Fe^{2+} (eqs. 61 - 62).

\[
Fe(OH)^{+} - OH^{-} \rightarrow FeOH^{2+} \quad (61)
\]

\[
FeOH^{+} - OH^{-} \rightarrow Fe^{2+} \quad (62)
\]

The voltage was again supplied in the phase IV. The pH increased from 6.6 to 9.5, not like in phase II where pH was about 12.0, maybe because of coverage of precipitates and redox potential went to positive values. Therefore, mobilization seems to be negligible. Same process was repeated in the phases V and VI.

Mn: At the end of the equilibrium phase I, the concentration of Mn is about 10 mg/L. After current supply at the phase II, the pH increased to more than 12.0. The redox potential went to the negative range. Due to also formation of hydrogen, the reduction and precipitation was more favorable. The fact is that there was formation of OH\(^{-}\) at interface and the interrupting of H\(^{+}\) from the anode was less due to presence of sediment between cathode and anode. The sediment act as buffer zone in this phase. Therefore, Mn was precipitated out (eq. 63).

\[
Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_{2} \downarrow \quad (63)
\]

At phase III, Mn was remobilized faster than Fe within 3 days. As the manganese has tendency to less precipitation even pH reaches about 8.0 [Sticher et al., 1987].

Precipitation,

\[
\text{at } 7.0 \quad Fe(> 95%) > Mn(16%) \quad (64)
\]

\[
\text{at } 8.0 \quad Fe(> 90%) > Mn(70%) \quad (65)
\]

In this phase, maybe there was a formation of Mn^{2+}, MnOH^{+} due to decrease of pH and redox potential went up to ∼ -240 mV. After current supply at the phase IV,
pH increased to 8.0, so that Mn again precipitated out. But, in this phase, the pH did not go up as the phase II, maybe due coverage of precipitates over the electrode so that current supply decrease. Although the current was not same in all phases, the trend of curves was similar in the phases II, IV and VI.

5.2.5.3 Anode 4 cm below and cathode 4 cm above the sediment-water interface

Due to alkaline condition, Fe and Mn were immobilised in the phase II (Fig. 45). After phase III, the current flow was very low, so the mobilisation was almost constant.

5.2.5.4 Anode 4 cm above and cathode 4 cm below the sediment-water interface

At the phase II, the anode showed the good effects on the sediment-water interface (Fig. 46). At first pH decreased to about 3.5, then almost constant at pH about 5.0 upto phase III. This condition showed the strong mobilization of both Fe and Mn maybe due to formation of Fe(II), Fe(III) and Mn$^{2+}$ as in equations 49, 50, 54 - 57.

5.2.5.5 Anode 4 cm below and cathode 4 cm above the sediment-water interface with a CaCO$_3$ layer

In this experiment, the CaCO$_3$ was added to stabilise the pH condition in the environment (Fig. 47). When the current was supplied to the system, suddenly pH increased up to 8.2. Then, after 91 days, the pH was within the range of 6-7.0. The redox potential was always in negative values (∼ -500 mV) and oxygen content was very low (∼ 0.1 - 0.6 mg/L) in all phases.

Fe: After applying current at phase II, the pH increased up to about 8.2. So that the iron maybe formed Fe(OH)$_3$ (especially) and Fe(OH)$_2$ more than FeCO$_3$ (eqs. 66 and 67). Therefore, mobilization was low.

\[
Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow \quad (66)
\]

\[
Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow \quad (67)
\]
After 91 days, carbonates dominated so that the concentration of iron increased at the interface due to Fe(II) - carbonates ($K_{SO}$ values ($FeCO_3$) = $3.13 \times 10^{-11}$ mol$^2$/L$^2$). Only after 301 days, due to the dominant of OH$^-$ - ions or other precipitating agents helped to decrease in mobilization of iron at the phase V. It was found that pH was around 6.2.

**Mn:** pH = 8 is favourable condition for mobilization. Therefore, Mn showed gradually mobilization due to formation of $MnCO_3$ or $Mn(OH)_2$. After 271 days, the mobilization seems to be constant.
5.2.5.6 Anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode

Current was passed through the system after equilibrium in phase II. At this phase, pH was within about 10. In the case of iron, mobilisation was decreasing trend and the concentration decrease to about 0.8 mg/L (Fig. 48). At phase III, due to neutralisation, increased in mobilisation was observed. At the phase IV, the situation was repeated. In case of Mn, even at high pH value, less mobilization was observed. Mobilisation was increased during the neutralisation process at the phase III.
Figure 47: Temporal changes in total Fe and Mn-concentration and pH-values at the sediment-water interface in the EC (with $U = 3$ V/without voltage) and in the RC (without voltage) [anode 4 cm below and cathode 4 cm above the sediment-water interface with $CaCO_3$]
Figure 48: Temporal changes in total $Fe$ and $Mn$-concentration and $pH$-values at the sediment-water interface in the EC (with $U = 3 \text{V}$/without voltage) and in the RC (without voltage) [anode 4 cm below and cathode 4 cm above the sediment-water interface with a counter anode]

5.2.5.7 Anode 4 cm below and cathode 4 cm above the sediment-water interface with various voltages

The observations were carried out at various voltages ($U = 0 \text{V}, 2.5 \text{V}, 3 \text{V}$ and $4 \text{V}$) at same conditions of the columns to see electrochemical oxidation of $Fe$ and $Mn$ by oxygen formed at the anode or direct oxidation at the anode by current supply (Fig. 49). The trend of the mobilization of $Fe$ and $Mn$ at the sediment-water interface under electrochem-
ical influence were same. The figures 47, 48 and 49 show the three cycles. In both Fe and Mn, 2.5 V did no effect on immobilisation. But, in case of Fe, very less mobilisation was observed at phase II with 3 V and 4 V. Then, only slowly mobilisation occurred without current after 15 days. The mobilization rate was higher in the case of 4 V than that of 3 V. In case of Mn, it was clearly seen that the less mobilisation took place at the 4 V - variant after 39 days whereas in 3 V - variant only after 76 days at the phase II. At phase III, the mobilisation took place immediately after stopping the current. The rate of mobilisation was higher in case of U = 3 V than that of U = 4 V.

Figure 49: Temporal changes in total Fe and Mn-concentration and pH - values at the sediment-water interface in the EC (with U = 0 V, 2.5 V, 3 V and 4 V/without voltage) and in the RC (without voltage)[anode 4 cm below and cathode 4 cm above the sediment-water interface with a various voltages]
5.3 Reactions and processes in the sediment

Fig. 50 shows the $pH$-profile of the experimental columns at various conditions: A; anode at the interface, B; cathode at the interface and C; anode 4 cm below and cathode 4 cm above the interface with respect to the reference column after about 180 days at $U = 3$ V. In Fig. 50 A, due to formation of hydrogen ions at the anode, $pH$ was low $\sim 5.0$ after 180 days of voltage supply at the interface. It shows that once the sediment is acidified, it takes long time to neutralize it. The $pH$-profile of the interstitial water also showed clearly that the acidic front reached the sediment horizon (0 to -4 cm depth) after 180 days. In this depth, the sediment buffered the acidification and it came to neutral $pH$ conditions.

Figure 50: $pH$ profiles after 180 days of voltage supply $U = 3$ V; A: anode at the sediment-water interface and cathode in aqueous phase; B: cathode at and anode 8 cm below the sediment-water interface and C: anode 4 cm below and cathode 4 cm above the sediment-water interface.
In Fig. 50B, the \( pH \)-profile of the interstitial water show that the alkaline front reached in the first sediment horizon (0 to -2 cm) after 180 days. In this area, \( pH \) available was \( \sim 9.0 \). This was neutralized by the hydrogen ions formed at the anode. It is know that hydrogen ions can move twice time faster than that of hydroxide ions. Therefore, from 4 cm depth from the interface had the \( pH \) value lower than 7.0. In Fig. 50C, the \( pH \)-profile of the interstitial waters showed the alkaline front reached in the first sediment horizon (0 to -2 cm) after 180 days as in Fig. 50B. But, the \( pH \) was not so high as in Fig. 50B or it came near to neutral \( pH \) value of \( \sim 7.5 \).

With the \( pH \) profile in the sediment, the distribution of the metals in the sediment also changes. Following explanations shows the distribution of different metals in the sediment.

### 5.3.1 Arsenic

The behavior of arsenate in soil seems analogous to that of phosphate because of their chemical similarity. Like phosphate, arsenate is fixed to \( Fe(III) \) - containing soil particles, and thus is relatively immobile. Iron (\( Fe \)), aluminum (\( Al \)), and calcium (\( Ca \)) influence this fixation by forming insoluble substances with arsenate. The presence of iron in soil is most effective in controlling the arsenate mobility. Arsenite compounds are 4 to 10 times more soluble than arsenate compounds at about \( pH \) 6.0 under oxidation condition [GULENS et al., 1979]. Under anaerobic conditions, arsenate may be reduced to arsenite. Arsenite is more subject to leaching because of its higher solubility. The adsorption of arsenite is also strongly \( pH \)-dependent because at high \( pH \) - value, the arsenite adsorbes in the sediment. Mostly, arsenite dominates under reducing and anaerobic conditions. The reference column (RC) also experienced the mobilization of As to the sediment-water interface with time. Therefore, concentration increased with the depth (0 - 5 cm) from \( \sim 0.0244 \) to \( 0.03 \) mg/g whereas the initial concentration (IC) was \( \sim 0.03 \) mg/g. In Fig. 51A, \( pH \) at the first sediment horizon (0 to -2 cm depth) decrease to 4.56, maybe this was the preferable condition to migrate arsenite to the anode. As the anode influenced up to 6 cm depth, it was observed that arsenite transported from sediment to sediment-water interface water. So, the concentration increased with depth (0 - 5 cm) from \( \sim 0.0134 \) mg/g to \( 0.035 \) mg/g. In case of Fig. 51B, the trend of arsenic was just similar to the case of Fig. 51A because, the anode might attract the anions. It is clear here that ions flow was toward the anode, which was 8 cm below the sediment. Up to depth of 0 - 2 cm, there was maybe great effect of the cathode placed at the interface, so the \( pH \) was also greater than 7.0. Due to this, \( As \) - mobilization was stopped. Accumulated ions maybe slowly migrated to the anode. Therefore, concentration increased from \( \sim 0.03 \) mg/g to \( 0.054 \) mg/g. In case of
Fig. 51C, the migrating arsenite toward the anode due to charge attraction was not found as in Fig. 51B. As concentration near the anode was same as in Fig. 51B ~ 0.054 mg/g. It was supposed the migration of ions from the interface into the water when the pH was almost in neutral conditions in the water phase.

Figure 51: As distribution profile after 180 days of voltage supply U = 3 V; A: anode at the sediment-water interface and cathode in aqueous phase; B: cathode at and anode 8 cm below the sediment-water interface and C: anode 4 cm below and cathode 4 cm above the sediment-water interface
5.3.2 Cadmium, Lead and Zinc

The adsorption of $Cd$, $Pb$ and $Zn$ onto soil/sediment and silicium or aluminum oxides is strongly $pH$-dependent. Increase as conditions become more alkaline. When the $pH$ is below 6.0 - 7.0, the metals desorbed and migrated into the water phase from these materials.

Figure 52: $Cd$, $Pb$, $Zn$ distribution profile after 180 days of voltage supply $U = 3 \text{ V}$; [anode at the sediment-water interface and cathode in aqueous phase]

$Cd$: Cadmium has considerably less affinity for the absorbents tested than zinc, and lead and might be expected to be more mobile in the environment than these materials. Studies have indicated that cadmium concentrations in sediments are generally at least an order of magnitude higher than in the overlying water. Addition of anions, such as humate or tartrate, to the dissolved cadmium causes an increase in adsorption [Blume and Brummer, 1987]. But most adsorption and desorption depend strongly on the $pH$ value.
**Pb:** It tends to accumulate in the soil/sediment surface, usually within 3 to 5 centimeters of the surface. Insoluble lead sulfide is typically immobile in as long as reducing conditions are maintained. The capacity of soil to adsorb lead increases with pH, cation exchange capacity, organic carbon content, soil, sediment/water - Eh (redox potential), and phosphate level. Lead exhibits a high degree of adsorption on clay-rich soil. Only a small percent of the total lead is leachable; the major portion is usually solid or adsorbed onto particles. Surface runoff, which can transport particles containing adsorbed lead, facilitates migration and subsequent desorption from contaminated sediment. Lead compounds are soluble at low pH and at high pH.

Figure 53: Cd, Pb, Zn distribution profile after 180 days of voltage supply U = 3 V; [cathode at and anode 8 cm below the sediment-water interface]
Zn: The sediments with carbonates or hydrous oxides, readily adsorb zinc. The greatest percentage of total zinc in polluted soil and sediment is associated with iron (Fe) and manganese (Mn) oxides. Rainfall removes zinc from soil because the zinc compounds are relatively soluble. As with all cationic metals, zinc adsorption increases with pH. Zinc hydrolyzes at a pH > 7.7. These hydrolyzed species strongly adsorb to the sediment surfaces. Zinc forms complexes with inorganic and organic ligands, which will affect its adsorption reactions with the sediment surface.

![Diagram](image-url)

Figure 54: Cd, Pb, Zn distribution profile after 180 days of voltage supply \( U = 3 \, \text{V} \); \([\text{anode} \ 4 \, \text{cm} \ \text{below} \ \text{and} \ \text{cathode} \ 4 \, \text{cm} \ \text{above} \ \text{the sediment-water interface}]\)

In the Fig. 52, soluble or exchangeable binding Cd, Pb and Zn mobilized slowly toward the sediment-water interface after 180 days in RC. The concentration increased with depth. The anode influenced up to 6 cm depth of the interface. The pH was in range of 4.68 - 6.59. Cd and Zn start to precipitate at pH > 7.0, Pb at pH > 6.0. Therefore, Cd, Pb and Zn were soluble in this case. All those metals might migrate to the interface. So, the concentration of those metals increased with increase in the depth. But, the rate of migration
to the interface was highest in *Cd*, then *Zn*. The last was *Pb*, proving the Irving-William order of stabilities of chelates.

In Fig. 53, the cathode had its effects up to 2 cm depth from the interface. After that hydrogen ions dominated the depth. Up to 4 cm depth, the *pH* was 9.05 to 6.52. Not *Cd*, *Pb* and *Zn* were mobilized. In 4 cm sediment depth, *Cd*, *Pb* and *Zn* mobilized. That’s why the concentration of those metals accumulated up to 4 cm depth. Immobilization rate was highest in *Pb*.

Fig. 54 shows that due to influence of both cathode and anode, the *pH* was in the range between 6.3 - 7.0. It was the case in between above Figs. 52 and 53. Those metals showed the mobility but not as in the case where anode was at the interface. *Cd* and *Zn* showed the similar properties. But it is not still clear about the causes that the enrichment of those metals in the vicinity of anode. In the case of *Pb*, a slow migration in the direction towards the interface.
5.3.3 Cobalt, Nickel and Copper

Co: The adsorption of cobalt onto soil/sediment is also strongly pH-dependent, increasing at more alkaline conditions. When the pH is below 6, cobalt is desorbed and mobilized by $H^+$ from these materials. Co has considerably less affinity for the absorbents; soil particles tested than nickel and copper and might be expected to be more mobile in the environment.

Ni: The mobility of nickel from the sediment also depends on the pH-value. With increase in pH, adsorption do also increase. The precipitation starts from pH 6.0. It is less mobile than Co, but more than Cu.

Cu: Soil retains copper (Cu) through exchange and specific adsorption [Blume and Brummer, 1987]. Copper adsorbs to most soil/sediment strongly but Cu is also

Figure 55: Co, Ni, Cu and pH distribution profiles after 180 days of voltage supply $U = 3 \text{ V}$ [anode at the sediment-water interface and cathode in aqueous phase]
mobile in the electric field than any other toxic metal, except lead (Pb). Copper, however, has a high affinity to soluble organic ligands. The formation of these complexes may greatly increase its mobility.

In the Fig. 55, the anode influenced up to 6 cm depth of the interface. The $pH$ was in range of 4.68 - 6.59. $Co$ and $Ni$ start to precipitate at $pH > 6.0$, whereas $Cu$ at $pH > 5.0$. Therefore, maybe $Co$, and $Ni$ were till mobile forms such as $Co^{2+}$, $Ni^{2+}$, or complexes etc. All those metals might migrate to the anode at the interface. So, the concentration of those metals increased with increase in the depth.

![Graphs showing Co, Ni, Cu distribution profiles after 180 days of voltage supply $U = 3$ V](image)

Figure 56: $Co$, $Ni$, $Cu$ distribution profiles after 180 days of voltage supply $U = 3$ V [cathode at and anode 8 cm below the sediment-water interface]
In Fig. 56, the cathode had its effects up to 2 cm depth from the interface. After that hydrogen ions dominated in the depth. Up to 4 cm depth, pH range was 9.05 to 6.52. Co, Ni and Cu did not mobilize. After 4 cm, all observed metals did mobilize. That’s why the concentration of those metals accumulated up to 4 cm depth. Fig. 57 shows that due to influence of both cathode and anode, the pH was in the range between 6.3 - 7.0. It was the case in between above two cases. Those metals showed the mobility but not as in the case where anode at the sediment. The trend of rate is same as in this case.

5.3.4 Chromium

The dichromate ions present a greater health hazard than chromate ions and both Cr(VI) ions are more toxic than Cr(III) ions. The two forms of hexavalent chromium are pH
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dependent; hexavalent chromium as a chromate ion \( \text{CrO}_4^{2-} \) predominates above \( p\text{H} \) 6; dichromate ion \( \text{Cr}_2\text{O}_7^{2-} \) predominates at very strong acidic conditions. This association decreases with increasing soil \( p\text{H} \). Iron and aluminum oxide surfaces adsorb the chromate ions at acidic conditions or neutral. \( \text{Cr}(\text{III}) \) is the stable form of chromium in soil. \( \text{Cr}(\text{III}) \) hydroxide precipitate at \( p\text{H} \) 4.5 and complete precipitation of the hydroxides occurs at \( p\text{H} > 5.5 \). In contrast to \( \text{Cr}(\text{VI}) \), \( \text{Cr}(\text{III}) \) is relatively immobile in soil. Regardless of \( p\text{H} \)

![Diagram](image)

Figure 58: \( \text{Cr} \) distribution profile after 180 days of voltage supply \( U = 3 \text{ V} \); [A: anode at the sediment-water interface and cathode in aqueous phase; B: cathode at and anode 8 cm below the sediment-water interface and C: anode 4 cm below and cathode 4 cm above the sediment-water interface]

and redox potential, most \( \text{Cr}(\text{VI}) \) in soil is reduced to \( \text{Cr}(\text{III}) \) under anaerobic conditions. The reduction reaction in the presence of organic matter proceeds at a slow rate under normal \( p\text{H} \) and temperatures, but the rate of reaction increases with decreasing soil \( p\text{H} \).
5 RESULTS AND DISCUSSION OF THE PROCESS STUDIES

In Fig. 58A, pH at the first sediment horizon (0 to -2 cm depth) went to 4.56, maybe this was the preferable condition to migrate chromate to the anode. Very little Cr(VI) and Cr(III) might migrate to the interface as Cr(III) has stopped transport after pH 5.5. In case of Fig. 58, the trend of Cr was just similar to the case of Fig. 58A because only chromate started to migrate towards the anode. In case of Fig. 58C, the anode might attract the anions.

5.3.5 Iron and Manganese

After duration of 180 days under the influence of the electric field, mobilization of Fe and Mn towards the uppermost sediment surface was recognized (Fig. 59). From there, they migrated to the sediment-water interface. So the concentration in the EC increased with the depth (0 - 5 cm), \[ Fe, \sim 43 \text{ mg/g to } 61 \text{ mg/g}, Mn, \sim 0.5 \text{ mg/g to } 1 \text{ mg/g} \], whereas in the RC, very low migration was observed. It is also proved the rate of dissolution is higher in Mn species than that of Fe. In case of Fig. 60, the acidic front developed at the anode; 8 cm below the sediment-water interface helped in dissolution the Fe and Mn species to form \( Fe^{2+}, Mn^{2+} \) and even \( Fe^{3+} \) (because oxygen got formation nearby the anode). Those ions might migrate to the cathode at the sediment-water interface. The influence of cathode maybe did not allow migrating from the interface. Therefore, Fe and Mn might precipitate. In Fig. 61, acidic front from anode might help to mobilize the Fe and Mn ions.

Figure 59: Fe, Mn distribution profiles after 180 days of voltage supply \( U = 3 \text{ V} \) [anode at the sediment-water interface and cathode in aqueous phase]
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Figure 60: $Fe$, $Mn$ distribution profiles after 180 days of voltage supply $U = 3$ V [cathode at and anode 8 cm below the sediment-water interface] around the anode. Maybe due to this cause, the concentration of $Fe$ and $Mn$ was high nearby the anode. The ions slowly migrated toward the cathode, positioned 4 cm above the sediment-water interface.

Figure 61: $Fe$, $Mn$ distribution profile after 180 days of voltage supply $U = 3$ V [anode 4 cm below and cathode 4 cm above the sediment-water interface]
5.4 Metal-distribution in the sediment, sediment-water interface and aqueous phase

After an electro-chemical polarization of 100 days was to be recognized of mobilization and fixation of metals in the sediment, interface and aqueous phase in the system by the protons formed at the anode and alkaline front at cathode in section when the systems were designed as: i. Cathode 2 cm and anode 10 cm inside the sediment-water interface

![Graph showing concentration profiles for Fe, Mn, and Zn](image)

**Figure 62:** Concentration profile of Fe, Mn, and Zn in pore water in the RC and EC after 100 days electrochemical polarization (C1) and ii. Cathode 4 cm above and anode 4 cm below the sediment-water interface with a 3 m long column in which 0.5 m was filled up with sediment and stirring time to time to have similar conditions as nature (CN) with voltage supply, $U = 4$ V.
In the area of the cathode, the highest concentration of metals (e.g., Fe, Mn and Zn) was measured in the interstitial water in C1. The concentrations of these metals decreased in the sediment-water interface and water phase. Directly at the interface, Fe, Mn and Zn - concentrations were negligible (0.4 mg/L Fe, 0.7 mg/L Mn, 0.8 mg/L Zn) in the experimental column. Here the alkaline front developed at the cathode helped to accumulate the metals nearby the cathode inside the sediment by precipitation. This pH-barrier prevented the diffusion and migration of the iron, manganese and zinc ions. The pH was higher than 7.0. The advantages of this arrangement are the accumulation of heavy metals inside the sediment and pH of aqueous phase in about 7.0 (Figs. 62 and 63). The pH in the reference column remained in the total period relative constantly to pH = 7. Whereas pH was in the range of 9.0 - 11.0 in the aqueous phase after applying the voltage in similar conditions as nature (CN). This was the best condition for most metals to precipitate. The concentration was high (6 mg/L Fe, 0.85 mg/L Mn, 1.3 mg/L Zn) at the interface. These concentrations are higher than in case of C1. The metals slowly diffused in the aqueous phase. It was found that the concentrations increased with the height of water from the sediment-water interface although the pH nearby the cathode was 11.0, whereas at surface water it was 10.0. The concentrations nearby the cathode were 1.4 mg/L, 0.5 mg/L, 0.3 mg/L for Fe, Mn and Zn respectively. It was measured 0.2 mg/L, 0.3 mg/L, 0.2 mg/L for Fe, Mn, Zn

Figure 63: Profile of pH in interstitial water in the RC and EC after 100 days electrochemical polarization
at the surface water 64. The reason is maybe the metals ions and precipitated could be decantation at the interface. Even the concentration were low at the surface-water, the $pH$ was still very high for aquatic environment. The trend of mobilization and accumulation was similar in small columns. So, it was proved whatever the curves shown in previous experimental systems would give similar results in nature if arrangements were same. Only the lower concentration of metals could be obtained at the surface-water, but the $pH$ could be same.

Figure 64: $Fe$, $Mn$, and $Zn$ concentration and $pH$ profiles in overlying water after 100 days of electrochemical polarization in 3 m long column
6 Summary

Pollution in surface waters by the discharge of metals from industries has been effectively controlled in the most developed countries. However, heavy metals dispersed in river sediments still remains a problem that needs to be addressed seriously.

Methods that are available for removal of heavy metals from contaminated sediments are:

1. Extraction with mineral acids [Müller and Riethmayer, 1982 and Strasser et al., 1995]
2. Extraction with organic acids or with complexing agents [Fröhlich et al., 1999, Höll, 1995, Stichnothe et al., 1999 and Thöming et al., 1996]
3. Size classification and treatment of fine fraction by flotation [Venghaus and Werther, 1996]
5. Chemical precipitation, membrane filtration, ion-exchange, carbon adsorption, and co-precipitation/adsorption by sorbents [Bailey et al., 1999]

Most of these methods have some or other disadvantages. They all incur high cost of chemicals. Use of methods like acidification, precipitation, co-precipitation, and adsorption, bio-leaching and other produce sludge that will need to be disposed. Membrane filtration, ion exchange and carbon adsorption requires a high investment. Besides on site regeneration and reuse of the materials have many problems associated with them.

Application of electro-kinetic remediation will eliminate the long-term liability that is incurred in land filling of contaminants. This is an in-situ process in which an electrical field is created in a soil matrix by applying a low-voltage direct current (DC) to electrodes placed in the soil, sediment or sludge that need to be treated. Targeted contaminants such as heavy metals, anions, and polar organics [EPA, 1989 and EPA, 1987] can be effectively treated at concentrations ranging from a few mg/L to g/L by this technology. It is most effective in low permeability soils or sediments that are typically saturated and partially saturated clays and silt-clay mixture.

The main objective of the present investigation is to study the phenomenon of accumulation and mobilization of heavy metals at the water-sediment interface by using Electrochemically initiated processes. It is intended as an initial step towards designing an advanced or
field level work. The study is focused on nine heavy metals, viz., Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn and one semi-metal: As.

The specific objectives are:

• to analyze the concentration and pH of the above elements in aqueous phase and in the sediment.

• to find out their rate of migration in the sediment itself

• to determine the change of pH in the sediment and water

It is envisaged that the study will be able to develop a cost-effective method for reducing the concentration of the heavy metals in aqueous phase as well as in sediments. The main working steps of the method would be the mobilization of the target ions in the vicinity of the anode, followed by their immobilization at the water-sediment interface and finally remobilization by changing the polarity. The trend seen in the results will be the basis to find out the feasibility of removal of heavy metals from sediments by this method.

Samples of sediments were collected from two rivers: a) river Weiße Elster at Kleindalzig, Leipzig, Germany and b) river Bagmati at Thapathali, Kathmandu, Nepal, by the sludge pit trap method on 01.03.2001 and 18.07.2001 respectively for the study. Their physical parameters (pH, redox potential, electric conductivity and water contents were determined by using German Standard Methods (DIN - methods).

The metal ion contents and their bonding states were determined in the samples prepared by sequential [Dinelli and Tateo, 2001] and aqua regia [Förstner and Calmano, 1982] extractions by AAS (flame, graphite or hydride methods as required).

The total heavy metal contents [Turekian and Wedepohl, 1961] and the degrees of enrichment lied for typical mining industry relevant heavy metals of the Weiße Elster sediment in the range of 2 - 12, but 29 for zinc [Basel, 1912]. In the contrast to this, the maximum degrees of enrichment, particularly in the heavy metals - Cu, Zn, Pb, Cd were achieved to 2.5 for the sediment in the river Bagmati; the enrichment values of Mn, As, Cr, Ni and Co could not reach the mid-value of the Clay-stone standard.

The content of mobilizable heavy metals in the exchangeable and carbonatic fraction amount was less than 15% in the sediment of the river Bagmati (except cadmium, which was over 20%). With the exception of lead, all heavy metals bound to aluminum and/or
ferrous hydroxides were always much higher in the river Weiße Elster in comparison to the river Bagmati. Relatively small proportion of the heavy metals was bound sulphidically, except for cadmium in both. A majority of the heavy metals in the river Bagmati was indicated to be bound relatively strongly in the mineral matrices and can be mobilized only under extreme chemical conditions.

Thus, we can conclude that, the river Bagmati was still far less polluted than the river Weiße Elster with respect to heavy metals content.

The pH - value of the interstitial water of the river Bagmati with \( pH = 2.56 \) was considerably lower than that of the river Weiße Elster which was 5.85 (Table 5). The conductivity, redox potentials and total organic compounds were, however, almost equal.

PVC - tubes (length: 0.6 m, width: 0.12 m) were filled with 1,200 g sediment (about 20% of the volume) and tap water (about 80% of the volume) (Fig. 5). The electrodes were installed after filling the columns in accordance to the experimental variants as required. The optimum distance required of the electrodes for the reactions was determined through Ohmic voltage drop and to avoid electric short circuit at the same time. The two electrodes were kept 8 cm apart.

**Electro-kinetic investigation:**

The sediment from the river Weiße Elster was used for the electrochemical investigation. Nine different types of cells with the following nine different arrangements of the electrode system were prepared were fabricated from columns of polyethylene of 5.5 cm diameter for finding out the tendency to migrate of the metal ions under different conditions.

1. Reference cell: Same arrangements of electrodes as in the experimental but without the supply of current were used as a control for giving the natural phenomenon of the heavily polluted places.

2. Anode placed at and cathode 8 cm in the water above the sediment-water interface: This cell was for building the slow mobilization of most of the contaminant metals ions at the interface by acidification of the sediment.

3. Cathode at and anode 8 cm inside the sediment-water interface. This arrangement was for immobilization of the most of the contaminant metals at the interface.
4. Cathode 4 cm above and anode 4 cm inside the sediment-water interface. This arrangement was between the cases of (ii) and (iii).

5. Anode 4 cm above and cathode 4 cm inside the sediment-water interface.

6. Same as (iv), but with CaCO$_3$. So as to maintain the pH of the environment at around 8.0.

7. Same as (iv), but with counter anode.

8. Same as (iv), but with varying voltages ($U = 0$ V, 2.5 V, 3 V, 4 V).

9. Cathode 2 cm below and anode 10 cm below the sediment-water interface.

10. Same as (iv), but the experiment was carried out in 3 - meter long column. This arrangement is approximate to the field situation.

Aliquots were drawn periodically and analyzed to monitor the changes in composition through the experimental period. The drawn volume was replaced with the same volume of tap water after each sampling.

The minimum working voltage was determined by establishing a current-voltage curve in the pre-operational test by measuring the current with stepwise increment of voltage in the range of $U = 0$ to 10 V. A voltage of $U = 3$ V was used in the most cases [Wolf et al., 2002].

The experiments were carried out for a period of a maximum 430 days. Electric voltage was passed and stopped intermittently so that there were six phases. The following changes in redox potential and $pH$ was observed in different cells:

1. Anode at the sediment-water interface and cathode in the aqueous phase.

At the end of phase I sediment and water reached an equilibrium. When electric voltage was applied (phase II) an acidic front was generated at the interface. The redox potential increased going up from $\sim 0$ to $+45$ mV, probably due to a slight positive polarization at the sediment-water interface. The $pH$ decreased initially from $\sim 6$ to about 2 - 2.7. After about 7 days, when the $pH$ increased slowly again probably because of the impact of the $OH^-$ ions produced at the cathode migrated towards the anode and partially neutralized the protons generated there. On stopping the
electric supply (phase III) the \( p\text{H} \) went up again. The phases IV and VI with repeated current influence (\( U = 3 \text{ V} \)) showed a \( p\text{H} \) decreases again, because of the \( H^+ \) production at the anode. However, the \( p\text{H} \) decrease was by far not so high as in the phase II. The exact reason was unclear. It is assumed that the precipitation of heavy metal hydroxides and carbonates at the sediment-water interface has a raised buffering capacity. The anodically produced protons may be buffered through this layer.

2. Cathode at sediment-water interface and anode 8 cm inside the water.

The sediment-water interface became alkaline on voltage supply. The \( p\text{H} \) increased from \( \sim 6 \) to 12.0 in phase II, 6.6 to 9 in phase IV and 6.8 to 8.0 in phase VI due to the production of \( OH^- \) ions. In phase III, the \( p\text{H} \) values decreased from \( \sim 12.0 \) to \( \sim 6.6 \).

3. Anode 4 cm below and cathode 4 cm above the water-sediment interface.

In this set up, the current flow through the system during phase IV was negligible in comparison to phase II (Fig. 20). The reason could be that the cathode in the phase IV maybe covered by a small insulating layer of precipitation of carbonates or other species. The redox potential fell on negative values (from 0 to -800 mV) in phase II, probably due to the cathodic influence. In the current influenced phase II, the \( p\text{H} \) - values increased up to 12.

4. Anode 4 cm above and cathode 4 cm below the sediment-water interface.

The experimental column followed the similar trend of the reference column at phase I The \( \text{Eh} \) was in range of \( \sim -64 \) to +15 mV and \( p\text{H} \) \( \sim 3.0 \) at the interface from 36 days to 48 days. In 48-76 days, the \( \text{Eh} \) increased to \( \sim + 45 \text{ mV} \) whereas \( p\text{H} \) was \( \sim 5.5 \). After phase II, the \( p\text{H} \) and \( \text{Eh} \) remained almost constant throughout the process.

5. Anode 4 cm below and cathode 4 cm above the water-sediment interface with \( CaCO_3 \).

The \( p\text{H} \) was controlled through the added \( CaCO_3 \), even when the voltage was applied at the phase II so that the \( p\text{H} \) did not rise above 8.5 throughout the whole process. In the phase II, at beginning to 48 days the \( \text{Eh} \) decreased from \( \sim - 70 \text{ mV} \) to -309 mV. After 48 days, \( \text{Eh} \) decreased up to \( \sim -434 \text{ mV} \) with the \( p\text{H} \) staying almost constant.
Table 10: Concentration Increment Ratio at sediment-water interface in 90 days with 3 V

<table>
<thead>
<tr>
<th>Metals</th>
<th>Anode at interface</th>
<th>Cathode at interface with ( \text{CaCO}_3 )4 cm above and Cathode 4 cm below the interface</th>
<th>Anode at 4 cm above and Cathode 4 cm below the interface</th>
<th>Cathode at 4 cm above and Anode 4 cm below the interface</th>
<th>with counter anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>44.00</td>
<td>-0.14</td>
<td>11.08</td>
<td>12.86</td>
<td>-0.11</td>
</tr>
<tr>
<td>Cd</td>
<td>0.75</td>
<td>-0.98</td>
<td>-0.66</td>
<td>0.55</td>
<td>-0.97</td>
</tr>
<tr>
<td>Co</td>
<td>68.62</td>
<td>-1.00</td>
<td>2.45</td>
<td>5.40</td>
<td>-1.00</td>
</tr>
<tr>
<td>Cr</td>
<td>86.50</td>
<td>-0.73</td>
<td>1.21</td>
<td>39.00</td>
<td>-0.52</td>
</tr>
<tr>
<td>Cu</td>
<td>7.94</td>
<td>-0.76</td>
<td>3.21</td>
<td>1.50</td>
<td>-0.76</td>
</tr>
<tr>
<td>Fe</td>
<td>87.57</td>
<td>-0.93</td>
<td>60.95</td>
<td>20.30</td>
<td>-0.96</td>
</tr>
<tr>
<td>Mn</td>
<td>2.17</td>
<td>-1.00</td>
<td>1.42</td>
<td>0.58</td>
<td>-0.97</td>
</tr>
<tr>
<td>Ni</td>
<td>1.41</td>
<td>-0.98</td>
<td>0.97</td>
<td>1.15</td>
<td>-0.98</td>
</tr>
<tr>
<td>Pb</td>
<td>13.17</td>
<td>-0.97</td>
<td>-0.45</td>
<td>17.11</td>
<td>-0.85</td>
</tr>
<tr>
<td>Zn</td>
<td>3.87</td>
<td>-0.97</td>
<td>0.71</td>
<td>26.89</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

6. Anode 4 cm below and cathode 4 cm above the water-sediment interface with a counter anode.

The counter anode worked to neutralize the \( OH^- \) ions formed at the cathode. The \( pH \) and \( Eh \) ranges during the 51 days period of the experiment increased from \( \sim 6.5 \) to 9.0 and decreased from \( \sim -38 \) to -309 mV respectively. After 51 days (in the phase II) the \( pH \) ranged between \( \sim 9.6 \) to 10.4 at reductive conditions (\( \sim -665 \) mV). The influence of the counter anode did not appear to be effective in the phase IV.

The batch-experiments were conducted at maximum current density of about 0.5 mA/cm\(^2\) in columns fitted with electrodes made from conductive polymers at room temperature in absence of direct daylight. The mobilization or accumulation of metals; As, Cd, Pb, Zn, Co, Ni, Cu, Cr, Fe and Mn at the sediment-water interface at different positions under different conditions of electrodes were determined by measuring \( pH \) and \( Eh \) - values, conductivity, oxygen and heavy metal concentrations in the water and sediment.

The experimental results suggest that the mobilisation and accumulation of arsenic species from the sediment depends highly on physicochemical factors e.g., \( pH \) values and redox potential, which develop an acidic front at the anode and an \( Eh \) barrier at the interface.
respectively due to the application of the voltage. The sorption of As is very high in the pH range (6.5 - 8.5). As expected, the high mobilisation of As was seen in the case of the experiment with anode at the sediment because pH was out of the range mentioned above. The best conditions for the As - immobilisation are high pH-values (cathode at the interface). These values show that the method using the electrochemical formation of pH- and Eh-barriers at the sediment and water interface has a good potential to accumulate arsenic (V) and to support the in – situ - cleaning of the sediments.

The trend of mobilization and accumulation of Cd, Pb and Zn was studied in a bench scale. The results show that the examined heavy metals are mobilized by the effects of the anodic polarization and transported by migration from the sediment into the sediment-water interface. By constructing a pH-barrier at the sediment-water interface, those metals were precipitated at the steep pH-gradient. The metals were accumulated at the sediment-water interface. In the arrangements where the cathode was positioned at the sediment surface, with counter anode and with calcium carbonates, did not allow those metals to migrate to the sediment-water interface. The results show the electrode arrangement-anode in the sediment-cathode in the water body with a relatively small distance between both electrodes to create a steep pH- and Eh-gradient is the best arrangement for the calculated mobilizing and enrichment of those heavy metals in a relative small layer. If necessary the electrodes can be combined with a counter anode to neutralize OH- -ions that alkalinised the water body. This will be a possibility to support the in-situ-cleaning of sediments by constructing a pH- and Eh-barrier to accumulate the heavy metals. After this it should be possible to mobilize them in a relative short time and to remove the concentrated heavy metals containing solution from the solid phase by reversing the polarity of the electrodes.

As expected, the highest mobilization effects of Co, Ni and Cu were generally observed when the anode was positioned at or above the sediment. Under such conditions, the mobilization effect was found to be inversely proportional to the pH-value. The main reason for this effect could be the acidification of the sediment-water interface by the formation of protons at the anode. In the opposite situation, where the cathode was positioned at the sediment, an immobilization of these metals was observed. The rate of mobilization or immobilization varied highly with the metals. The rate of mobilization follows Co > Ni > Cu.

The highest mobilization of Cr(III) or Cr(VI) was found when anode was placed at or above the interface where the acidic front was clearly observed. The best immobilization condition for Cr was in the columns where the cathode was at or above and anode below
the interface.

Both Fe and Mn - concentrations were found to be the highest at the interface when anode was placed at or above the interface due to anodic formation of protons. The best immobilization condition for Fe and Mn was in the columns where the cathode was at or above and anode below the interface. As Mn has lower tendency to precipitate out than Fe, the rate mobilization was always found high in the case of Mn. Similar trend of curves as the case of the column with cathode at interface was observed when the anode placed 4 cm below and cathode 4 cm above the interface. Similar trend of curves as the case of the column with anode at sediment was observed when the cathode was placed 4 cm below and anode 4 cm above the interface.

It is the important point to take into account of the distribution of metals in the sediment with pH profile in the sediment. After 180 days of current supply, it was found that pH of the sediment decreased when anode at the interface and cathode in the aqueous phase. The concentration of most metals were found to be low at the interface. pH - value were in the range of 6.5 - 8.5 when anode 8 cm or 4 cm below and cathode at or 4 cm above the interface. The metals were accumulated at the interface.

Alternative solution of balancing the \( OH^- \) ions in the system by arranging counter anode or reversing polarity for a short time which can balance pH in the system. pH could also be maintained at 7 - 8.2 by adding CaCO_3. A column with both cathode and anode placed inside the sediment was found to be the best condition to make heavy metal stable inside the sediment. Even in the long column with 3 m lengths, the pH distribution in the aqueous phase was same as in small column.

From using the various voltages, U = 0 V, 2.5 V, 3 V and 4 V in the same arrangement, it was proved that the effective voltages always could be calculated from the minimum working voltage curve. It was found that it must be \( \geq 3 \) V.

Electrochemical method is the best method to use for migration or accumulation of metal ions; but before using this method, one must think of type of ions whether it have to be removed from or accumulated in sediment. It is beneficial to gain knowledge of type of contaminants and the work whether it is for accumulation or mobilization from the sediment in order to choose the electrodes arrangements and if so, identify a proper solution.
Reference


DIN 38404 - C5.

DIN 38404 - C6.

DIN 38404 - S8.

DIN 51582.


Maximum permissible levels for land disposal of soils in Germany, LAGA (2002).


Declaration

I, Reena Amatya Shrestha, hereby declare that, the Ph. D. dissertation entitled "Investigations on the Phenomenon of Accumulation and Mobilization of Heavy metals and Arsenic at the Sediment-Water Interface by Electrochemically Initiated Processes" has been written by myself using practical research work and the literature cited in the reference under the guidance of my supervisors.

In this thesis, expert references have been made; there is no duplication of any other previous work already presented at any academic institute of higher education.

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