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Electrochemical Treatment of a Polluted Sludge: Different Methods and Conditions for Manganese Removal

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ABSTRACT

Five laboratory experiments to analyze the removal of manganese from a contaminated sludge by electromigration were carried out. The experiments differed in the arrangement of the remediation cells and the remedial conditions (current intensity or voltage drop constant, use of

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ion-exchange membranes, neutralization of basic environment at the cathode, and stirring in the electrode solutions). This was done in a way to compare the advantages of and differences between electrokinetic and electrodialytic remediation. Electrokinetic treatment was appropriate to remove 68% of the Mn from this polluted sludge when pH control was used in the cathode solution and a potential difference of 30 V was applied during 8 days.

Key Words: Manganese; Electrodialytic remediation; Electrokinetic remediation; Contaminated sludge.

INTRODUCTION

The uncontrolled release of acid mine drainage (AMD) is one of the serious impacts that mining exerts on the environment. The AMD often contains dissolved heavy metals (e.g., Cu, Pb, Ni, Cr, and Mn) in high concentrations due to the low pH.[1] This study deals with the treatment of sludge from a wastewater treatment plant contaminated especially with manganese. Manganese is a difficult metal to remove from the AMD because of high pH requirements for oxidation of Mn to form Mn oxide precipitates.[2] The manganese contamination was caused by the AMD from an open cast-lignite mine in As Pontes de García Rodríguez (Galicia, Spain), where the larger Spanish electricity producer, ENDESA, has a 1400 MW plant burning domestic lignite and imported sub-bituminous coal. The streams from the mine and a mine dump pass through the wastewater treatment plant, where most of the metals are precipitated, creating a sludge.

To remove the contaminating heavy metals from the sludge, electromigration can be proposed as a remediation tool. Electromigration has now been successful in a variety of cases, when the aim is to treat heavy-metal-contaminated soil and sludge. Several designs and conditions for electrochemical treatment exist at present.[3–5] One way to improve the remediation efficiency for soils is to introduce ion-exchange membranes in the process—electrodialytic remediation.[6–8]

The purpose of this work is to demonstrate the removal of manganese from the actual sludge by electromigration. Some previous published experiments showed that it was possible to remove manganese from spiked kaolin.[9,10] The objective, furthermore, was to test different electrochemical remediation arrangements, connecting experiences from electrokinetic remediation of Mn-contaminated sludge with the idea of electrodialytic soil remediation to obtain the best treatment.

MATERIALS AND METHODS

Electrokinetic Cells

The experiments were performed in two different electrokinetic cells: Universidad de Vigo (UV)-cell and Danmarks Tekniske Universitet (DTU)-cell.

The UV-cell was developed at the University of Vigo. The cylindrical glass cell contains a sample compartment of 100-mm length and 32-mm inner diameter. The two electrode compartments are placed at each end of the sample compartment, isolated from this one by separators (paper filter and porous stones, or ionic exchange membranes). Three auxiliary electrodes allow measuring of the electric field distribution along the sample. The gas produced by the electrode reactions is purged from the electrode compartments through a manual valve.[8]

The DTU-cell was developed at the Technical University of Denmark. The cylindrical polyacrylic cell contains a sample compartment of 100-mm length and 40-mm inner diameter. At the ends of the sample compartment are placed separators to isolate the sample from two concentration compartments, where the heavy metals should end up. Between the concentration compartments and the electrode compartments are placed ion-exchange membranes in a way that prohibit the heavy metals to participate in the electrode processes. In each of the four solution compartments, pumps apply recirculation of liquid and gas produced at the electrodes is removed in this way.[4]

Analytical Methods

The Mn concentration in the sludge was analyzed by x-ray fluorescence. Liquid samples were digested in accordance to the US Environmental Protection Agency Method 3010 [acid digestion of aqueous samples and extracts for total metals for analysis by flame atomic absorption (FAA) and inductive coupled plasma (ICP) spectroscopy], and FAA spectroscopy was used to analyze Mn. In acidic samples without turbidity, the digestion was omitted.

Methodology

Readings of the voltage drop between the current electrodes, the cell compartments, and the three auxiliary electrodes, were taken daily during the tests. Other measurements included the current intensity and the pH in the different compartments.

Upon completion of all experiments, samples were taken from all solutions and the sludge for chemical analysis. The sludge samples were divided into four or five sections of equal size. These samples were stored at 4°C for the analysis of water content, Mn concentration, and pH. Liquid samples from the cell compartments were collected for all tests and were analyzed for pH and Mn concentration.

Electrokinetic Remediation Experiments

Five different electrokinetic remediation experiments were carried out. Figure 1 depicts the experimental setup, and Table 1 summarizes the differences in process design and conditions. The contaminated sludge used in each experiment was taken from the same batch, and the initial Mn concentration was 898 mg Mn/kg dry matter (DM).

RESULTS AND DISCUSSION

The development in the current density for ED1 and EK1 was first a rise until a maximum and then a continuous decline to a lower value. This development is because the solutions initially were distilled water and did not contain dissolved ions to carry the current. Production of ions at the electrode surfaces resulted in a rise in the current density. The decrease after the maximum is caused by the following: (i) a decrease in the mobile ions concentration, which were removed first, and (ii) the high pH environment generated at the cathode side of the sludge. Most of the voltage drop for these experiments was placed between the cathode and the sludge section closest to the cathode.

In EKD1 and EKD2, the circulation of solutions and the control of pH resulted in a more uniform distribution of the current density and the potential over the whole remediation cell. Here the 90% of the total voltage drop was placed across the soil.

Table 2 lists the remediation results for the 5 experiments. From the table, it can be noticed that EK2 showed the highest average amount of Mn

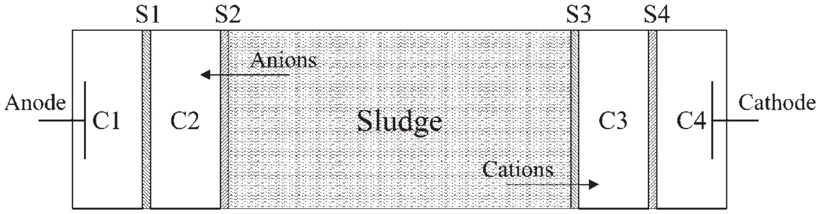

Figure 1. Experimental setup for remediation experiments. S1, S2, S3, and S4 are separators, and C1, C2, C3, and C4 are compartments.

Table 1. Operating conditions of the experiments.

Experiment 1: ED
- Cell: UV-cell
- Compartment 1 = compartment 2: distilled water
- Compartment 3 = compartment 4: distilled water
- Separator 1 and 4: nothing
- Separator 2: anion exchange membrane
- Separator 3: cation exchange membrane
- No circulation in compartments
- No pH adjustment
- Constant voltage drop (30 V)
- Electrodes: platinized titanium rods

Experiment 2: EK1
- Cell: UV-cell
- Compartment 1 = compartment 2: distilled water
- Compartment 3 = compartment 4: distilled water
- Separator 1 and 4: nothing
- Separator 2 and 3: porous stones and paper filter
- No circulation in compartments
- No pH adjustment
- Constant voltage drop (30 V)
- Electrodes: graphite plates

Experiment 3: EK2
- Cell: UV-cell
- Compartment 1 = compartment 2: distilled water
- Compartment 3 = compartment 4: distilled water
- Separator 1 and 4: nothing
- Separator 2 and 3: porous stones and paper filter
- No circulation in compartments pH adjustment ($pH < 2$)
- HNO_3 (conc)
- Constant voltage drop (30 V)
- Electrodes: graphite plates

Experiment 4: EKD1
- Cell: DTU-cell
- Compartment 1, 2, 3 and 4: HNO_3 (aq) ($pH < 2$)
- Separator 1 and 3: cation exchange membranes
- Separator 2: paper filter
- Separator 4: anion exchange membrane
- Circulation in all compartments
- pH adjustment ($pH < 2$)
- Constant current (1.15 mA)
- Electrodes: platinized titanium rods

Experiment 5: EKD2
- Cell: DTU-cell
- Compartment 1, 2, 3 and 4: HNO_3 (aq) ($pH < 2$)
- Separator 1 and 3: cation exchange membranes
- Separator 2: paper filter
- Separator 4: anion exchange membrane
- Circulation in all compartments
- pH adjustment ($pH < 2$)
- Constant voltage drop (30 V)
- Electrodes: platinized titanium rods

Table 2. Remediation results for the five experiments.

Experiment	Time (d)	Mn moved[a] (%)	Mn in catholyte[b] (%)	Mn remaining in the sludge (%)	Electrons transferred (mol)	Power consumption (W · h)
EK1	23.44	11.01	0.85	98.87	0.00591	2.374
ED1	22.88	19.62	0.2	99.80	0.00843	6.776
EKD1	22.23	20.21	0.61	97.5	0.024358	15.995
EK2	8.17	74.06	68.1	30.88	0.41169	331.06
EKD2	37.8	24.18	3.47	96.39	0.05617	45.164

[a] Average value calculated in the zone of the sludge, where manganese concentration decreased.

[b] Percentage of Mn collected in the cathode solution in respect to initial amount of Mn in the sludge.

transported, about 74%. Here, 68% of the initial Mn content in sludge reached the cathode solution, whereas, in the rest of the experiments, the Mn was found to be transported between the sludge sections, but it was not removed from the whole of the sludge. Experiment EK2 also showed the highest power consumption, the highest total charge passed through the sludge, and the shortest remediation time.

Figure 2 shows the relative distribution of Mn in each sludge section for the 5 experiments. Experiments ED1, EK1, and EKD1 show that, only in the section of the sludge closest to the anode, the Mn migrated toward the cathode (as cation) and the electric current reduced the concentration. The manganese precipitated and accumulated around the section, where a pH jump was observed. Comparing EKD2 with EKD1, it can be seen that a longer time of remediation (e.g., more charge passed through the sludge) provokes the movement of the accumulation front toward the cathode. Therefore, it could be expected that by further treatment, the Mn front would reach compartment 3 (cathode side). In EK2, no accumulation occurred, and, furthermore, the removal efficiency of Mn was uniform across the sludge sections, ranged from 72% to 78%. No significative transport of Mn toward the anode was detected. Only in the experiment EKD1, 1.5% of the initial Mn was found in the anode compartment and 1% in the experiment EK2. These values are rather low and insignificant compared with the movement

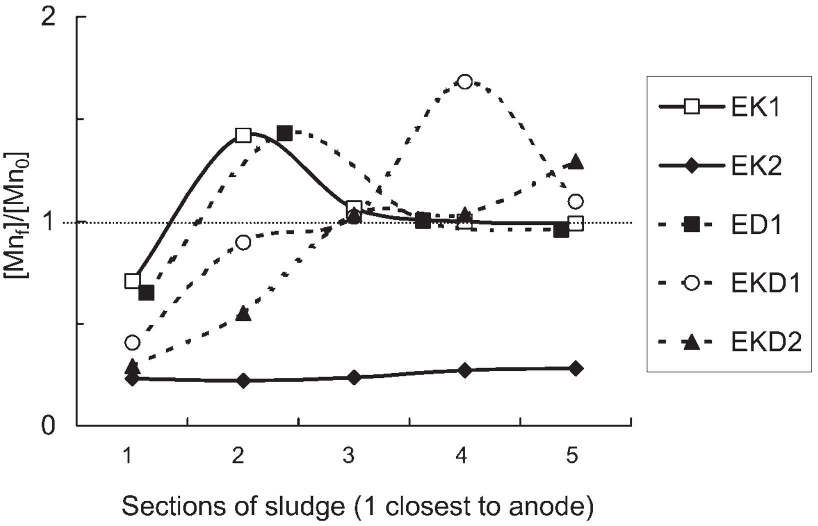

Figure 2. The normalized concentration of Mn of each sludge section at the end of the electrochemical remediation experiments.

toward the cathode. In the rest of the experiments, no Mn was detected in the anode compartment.

Figure 3 shows the distribution of pH in the sludge sections after remediation. A low pH helps the dissolution of Mn oxides, which is the most probable speciation of the Mn in the sludge. Therefore, the acidic front was beneficial and that was the reason to remove the anion exchange membrane 2 (see Fig. 1) and to place a passive membrane to allow H^+ to pass into the sludge. In all experiments, the pH was lowered at the anode end of the sludge sample. In EKD2, the acidic front reached further than in EKD1, EK1, and ED. In EK2, the acidic front passed all through the sample, and a constant level of 3.9–4.0 was achieved. This explains why no accumulation of Mn was observed in EK2.

Table 3 shows the initial concentration for a variety of elements and removal efficiency for experiment EK2. The content of elements other than Mn in the sludge was found to have influence on the removal efficiency, especially those present in higher concentrations. Two of them were Ca and Fe. The sludge had initially a high $CaCO_3$ content. In all experiments, a decrease in the Ca concentration in the sludge was noticed. The low pH

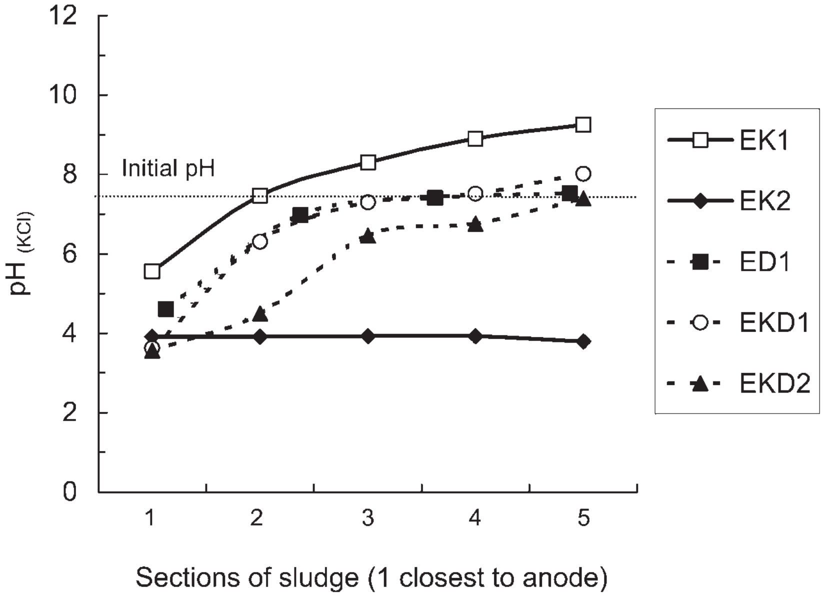

Figure 3. pH of each sludge section at the end of the electrochemical remediation experiments.

Table 3. Initial composition of the sludge and removal efficiency for experiment EK2.

Element	Concentration (mg/kg dry matter)	Removed from soil (%)
Al	76,700	0
Fe	42,300	27
Si	21,400	0
K	14,500	0
Ca	10,200	68
Na	5,860	24
Ti	5,560	0
Mg	4,110	24
Cl	3,080	44
Ba	1,050	37
Mn	898	74
S	761	10
Cr	691	88
Zr	588	0
P	373	89
Rb	318	22
Sr	261	33
Zn	239	60
Ni	179	44
Cu	157	60

starting at the anode side of the sludge dissolved the carbonate. In the experiments ED1, EK1, EKD1 and EKD2, no reduction in the Fe concentration was observed, whereas, in EK2, the Fe concentration was lowered by 27%. This can be explained by the very low final pH in the sludge, and, therefore, it indicates dissolution of Fe oxides. The dissolved Ca and Fe cations competed with the Mn cations to carry the current, e.g., in EK2, of the total charge passed through the sludge (0.41169 mmol equivalents, only 2.2 mmol equivalents were spent in transporting Mn^{2+}. This corresponds to a Mn^{2+} transport number of 0.0053 which is a low value when compared with H^+, NO_3^-, Ca^{2+} (transport number: approx. 0.075), and Fe^{3+} (transport number: approx. 0.066) among others which have carried the electric current. From Table 3, it can be seen that apart from Mn, other heavy metals and elements are present in the sludge, and experiment EK2 was effective for their removal too. However, elements such as Al, Si, K, Ti, and Zr that are forming the crystalline structure of different minerals, showed no migration, since those minerals did not suffer any alteration in the acidic environment of experiment EK2.

CONCLUSIONS

Five remediation experiments that used DC current as a cleaning agent were carried out under different operation conditions. Two methods (electrokinetic and electrodialytic treatments) were tested by using two experimental arrangements with the Mn-polluted sludge.

Electrokinetic treatment was appropriate to remove the Mn of this polluted sludge (up to 68%) when pH control was used in the cathode solution and a potential difference of 30 V was applied during 8 days. The same experiment also has shown the highest power consumption, shortest remediation time, and highest amount of charge passed through the sludge sample.

Electrodialytic treatment also was appropriate when acid front was allowed to enter the sludge from the anode side. For this method, longer treatment time was required than for electrokinetic method.

From all experiments, a factor was found to be important: a great influence of pH attained after treatment on Mn transport across the sludge sections. A low pH meant a migration of Mn from those sections.

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