Improvement in electrokinetic remediation of Pb-contaminated soil near lead acid battery factory

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Abstract: To improve the conventional electrokinetic remediation of Pb-contaminated soil, the Pb-contaminated soil near a lead acid battery factory in the Pearl River Delta region of China was electrokinetically remedied with polarity exchange technique. The variations in Pb removal efficiency and the soil pH value with the treatment time and the exchange polarity interval were determined. It is found that the removal efficiency of Pb reaches a maximum of 87.7% when the voltage gradient is 1 V/cm and the exchange polarity interval is 48 h. This value is far higher than that obtained with conventional electrokinetic remediation (61.8%). Additionally, the “focusing effect” which appears in the conventional electrokinetic remediation can be avoided, and thus additional chemicals are not needed for the polarity exchange technique. The mechanism of Pb electromigration behavior in soil during the treatment with the polarity exchange technique was described.

Key words: electrokinetic remediation; polarity exchanges; Pb-contaminated soil

1 Introduction

Anthropogenic activities have caused the accumulation of heavy metals in the soil [1−3]. Soil pollution is directly related to a country’s rapid industrial and economic development [4−7]. Soil contaminated by heavy metals, especially lead (Pb), has recently been found to be present in the Pearl River Delta (PRD) region of China [8]. Pb is a common contaminant in the soil near lead acid battery factories. Accumulated Pb in soil poses threats to human health by contaminating crops and groundwater [9−11].

Over the past few decades, electrokinetic remediation (EKR) has emerged as a promising in-situ strategy for treating contaminated soils. The EKR technique has been demonstrated to be successful and cost-effective in removing a wide variety of heavy metals in both bench and field-scale studies [12,13]. The advantages of this EKR technique include low power consumption, and confinement of the pollutants in the electrode chambers thus making it easier for subsequent treatment [14]. In the electrokinetic remediation processing, the applied current yields water electrolysis at both the anode and the cathode [15]:

Anode: \( 2\text{H}_2\text{O} \rightarrow \text{O}_2(g) + 4\text{H}^+ + 4\text{e}, \quad E_0 = 1.229 \text{ V} \) (1)

Cathode: \( 4\text{H}_2\text{O} \rightarrow 2\text{H}_2(g) + 4\text{OH}^- + 4\text{e}, \quad E_0 = -0.828 \text{ V} \) (2)

Consequently, \( \text{H}^+ \) and \( \text{OH}^- \) ions are generated at the anode and the cathode, respectively. The generation of \( \text{OH}^- \) ions at the cathode leads to the precipitation of the heavy metals, which is called the “focusing effect” [16], and this effect is the main barrier to the electrokinetic remediation of heavy metal contaminated soil [13,17].

Many studies have been performed to control the soil pH value and enhance the capability of electrokinetic remediation for the removal of heavy metal, including adding strong complexing agents such as EDTA into...
soil [18,19] and using ion exchange membranes (IEM) to control the pH value and zeta potential [20]. An electrokinetic remediation by reversing polarity was reported previously to remove manganese (Mn) from kaolin with the voltage gradient of 3 V/cm [21]. The polarity was reversed according to a pH indicator color transition (e.g., exchange polarity once soil turned to alkaline, and change polarity back to original position once pH value decreased). The removal of metal was improved by the modified techniques, but the additional chemicals or devices resulted in secondary contamination.

In this study, the application of the new polarity exchange technique without additional chemicals for the removal of Pb from soil near a lead acid battery factory in the Pearl River Delta (PRD) region of China was reported. The new polarity exchanging was not only based on the pH value variations, but also depended on the heavy metal distribution in the soil. The variations of the Pb removal efficiency and the soil pH value with treatment time and exchanged polarity interval were determined.

2 Experimental

2.1 Electrokinetic cell

The EKR experiments were carried out in a rectangular translucent plexiglass test cell (Fig. 1). Its dimensions are 26.0 cm in length, 10.0 cm in width and 10.0 cm in height. The soil was filled into the cell up to a length of 20.0 cm. A constant voltage of 20 V (1 V/cm) was applied with a DC power source. A filter paper and an o-ring were used between the electrode chambers and the soil cell to avoid leakage. Both the anode and cathode were graphite electrodes, which were inserted into each electrode chamber and connected with the DC power. A graphite electrode with a surface area of 54 cm² (2 × 3.0 cm × 9.0 cm) covered the whole soil cross-section to provide electric current evenly. The electrode chambers were filled with distilled water, which was cycled by pumps to avoid concentration gradients within the compartments.

2.2 Soil preparation

The soil samples were collected from the soil near a lead acid battery factory in the PRD region. The composition of the experimented soil is shown in Table 1 and 2. The soil is composed of several kinds of minerals. 3Mg4SiH2O is the predominant one, and accounts for 58.5% of the total mineral content. The tested soil of the coastal plain displays a sandy texture. It can be attributed to the silt loam according to the United States Department of Agriculture (USDA) classification system. It is slightly alkaline, typical of soil from the Pearl River Delta region of China. The mineralogy analysis by the X-ray diffraction (Fig. 2) indicates the presence of chlorite clay (58.5%, corresponding to 26.7°), feldspar (15.1%, corresponding to 20.9°) and mica (12%, corresponding to 35.8°).

The low cation exchange capacity (~5.3 cmol/kg, due to low organic matter and clay contents) suggests

Table 1 Texture composition of soil specimen (mass fraction, %)

<table>
<thead>
<tr>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.3</td>
<td>62.4</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 2 Minerals components of soil specimen (mass fraction, %)

<table>
<thead>
<tr>
<th>Chlorite</th>
<th>Mica</th>
<th>Smectite</th>
<th>Kaolinite</th>
<th>Pinguite</th>
<th>Feldspar</th>
<th>Picrite</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.5</td>
<td>12.0</td>
<td>4.4</td>
<td>3.6</td>
<td>2.7</td>
<td>15.1</td>
<td>3.7</td>
</tr>
</tbody>
</table>
that the Pb ions are not highly absorbed onto the soil particles, which is propitious for the migration of Pb ions in the soil [22].

The measured Pb content is 0.116 % (mass fraction) for the collected soil samples. The soil moisture content is approximately 9.1% (mass fraction). The initial soil pH is 7.7. For each electrokinetic test, about 1000 g of dry soil sample was loaded into the electrokinetic cell. Tap water was used as the electrolysis solution.

2.3 Methodology

The soil sample was divided into five sections within the cell, named S1–S5 moving from anode to cathode. Table 3 provides the experimental conditions of EKR1–EKR9. Experiments No. EKR1–EKR4 were conventional electrokinetic treatment experiments with treatment time of 24, 48, 96 and 192 h without polarity exchange. Experiments No. EKR5–EKR9 were the polarity exchange electrokinetic treatment experiments and were conducted for 192, 48, 96, 144 and 192 h, respectively. The polarity direction was exchanged periodically in order to enhance the removal efficiency during the polarity exchange electrokinetic remediation. At the same time, the solution was refilled.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Exchange polarity interval/h</th>
<th>Treatment time/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKR1</td>
<td>Conventional technique</td>
<td>24</td>
</tr>
<tr>
<td>EKR2</td>
<td>Conventional technique</td>
<td>48</td>
</tr>
<tr>
<td>EKR3</td>
<td>Conventional technique</td>
<td>96</td>
</tr>
<tr>
<td>EKR4</td>
<td>Conventional technique</td>
<td>192</td>
</tr>
<tr>
<td>EKR5</td>
<td>96</td>
<td>192</td>
</tr>
<tr>
<td>EKR6</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>EKR7</td>
<td>48</td>
<td>96</td>
</tr>
<tr>
<td>EKR8</td>
<td>48</td>
<td>144</td>
</tr>
<tr>
<td>EKR9</td>
<td>48</td>
<td>192</td>
</tr>
</tbody>
</table>

The soil pH was measured in the five different sections by a pH meter (the mass ratio of soil and water is 1:2.5). The samples were air-dried and passed through a 100-mesh screen (0.149 mm), then digested with HF–HNO₃–HClO₄ for the determination of heavy metal concentration. An atomic absorption spectrophotometer (AAS) was used to determine the content of total Pb. The pH value and Pb content were measured for two samples from each section, and two standard soil samples (i.e., soil with a controlled content of heavy metals) were analyzed for quality control.

3 Results and discussion

3.1 Conventional electrokinetic remediation

The conventional electrokinetic remediation with the unchanged electrode was carried out at a constant potential of 20 V for 192 h. Figure 3 shows the current density variation with respect to the treatment time. The current density started at 0.17 mA/cm², increased up to 0.88 mA/cm² after 3 h, and then continued to increase to a maximum value of 1.18 mA/cm². This trend indicates that the charge transport increases. After reaching this maximum value, the current density decreased for the remainder of the experiment and reached a value of 0.18 mA/cm² at 192 h. The decay in current density is due to the combination of the OH⁻ and H⁺ ions, yielding H₂O and thus removing the ions that transport charge to the electrode chambers [21].

Figure 4 presents the pH values after 48, 96 and 192 h treatment. The soil pH value decreased to about 3 at region S1 which was close to the anode, and...
increased to approximately 11 at region S5 which was close to the cathode. This trend is due to the electrolysis of water which produced H\(^+\) ions at the anode and OH\(^-\) ions at the cathode [23]. The regions S3–S5 were alkaline with the pH value above 7. These regions where OH\(^-\) and Pb\(^{2+}\) combined resulting in the precipitation of Pb are called as the “focusing effect”.

The standard concentrations of Pb\(^{2+}\) after the treatment for 24, 48, 96 and 192 h are shown in Fig. 5. Approximately 61.8\% of the total Pb content was removed after 192 h treatment. It was observed that Pb\(^{2+}\) effectively migrated through the soil towards the cathode, resulting in most of the Pb\(^{2+}\) precipitates at regions S4 and S5 because of the alkaline soil condition. The concentration variations indicate that Pb\(^{2+}\) moves to the cathode and accumulates. Similar results were obtained in the previous study which showed that Cr\(^{3+}\) and Ni\(^{2+}\) migrated towards the cathode and accumulated either as precipitates or adsorbates at the sections closest to the cathode where high pH conditions existed [24]. No significant differences were observed for Pb\(^{2+}\) concentrations distribution after 96 and 192 h treatments, which indicated that the ion migration was retarded.

3.2 Polarity exchange

To control the “focusing effect”, the pH values in regions S2–S5 were reduced by exchanging the polarity, and the oxidation of water would take place in the alkaline zones and produce H\(^+\) ions. The polarity was exchanged every 96 h and every 48 h based on the distribution of heavy metals after the conventional electrokinetic remediation and the soil pH value. The solution in both electrode chambers was changed at the same time as the polarity was exchanged to keep the extracted metal away from the soil.

Experiment No. EKR5 was conducted with a polarity exchange interval of 96 h. Figures 6(a) and (b) show the remnant concentrations of Pb\(^{2+}\) in the soil and the pH values, respectively, after polarity exchange electrokinetic remediation for 192 h treatment. After reversing polarity, the previous cathode became to be the anode. When water oxidation occurred, H\(^+\) was produced and the soil pH value was lowered, with Pb precipitates re-dissolved, and Pb\(^{2+}\) migrates towards the new cathode. The soil pH values in regions S1–S5 were controlled in the range of 7–9. Approximately 77.1\% of total Pb content was removed. Compared with the conventional technique using the same voltage gradient and the same treatment time (61.8\%, Fig. 5), the removal of Pb was enhanced. The improved removal is attributed to the fact that the precipitate of Pb\(^{2+}\) in the alkaline soil is alleviated by exchanging the polarity. The Pb\(^{2+}\) concentration variation indicates that the operation for a longer time period at reversing polarity leads to easier migration of Pb\(^{2+}\) near the two poles soil sections (S1 and S2, S4 and S5) compared with other sections. The oxidation/reduction may be significant in bench-scale experiments due to the increased impact of the boundaries on the overall process.

![Fig. 5 Pb\(^{2+}\) remnant after conventional electrokinetic remediation](image)

**Fig. 5** Pb\(^{2+}\) remnant after conventional electrokinetic remediation

![Fig. 6 Pb\(^{2+}\) distribution (a) and pH value (b) in soil after polarity exchange electrokinetic remediation for 192 h with polarity reverse interval of 96 h](image)

**Fig. 6** Pb\(^{2+}\) distribution (a) and pH value (b) in soil after polarity exchange electrokinetic remediation for 192 h with polarity reverse interval of 96 h

To assess the impact of polarity exchange interval on the removal efficiency, the polarity exchange interval decreased to 48 h (the experiments were still conducted for 192 h). Figure 7 shows the time-dependent current
The current density variation in polarity exchange electrokinetic remediation with an exchange interval of 48 h. The current density fluctuated periodically. It increased after each polarity exchange due to the precipitates re-dissolving and thus providing more ions for current transport. The current density increases to a peak of 1.21 mA/cm². The electric current density dropped to about 0.22 mA/cm² at 192 h because the dissolved ion concentration decreased over time.

Figures 8 and 9 show the Pb²⁺ distribution and the soil pH value, respectively, after polarity exchange with an interval of 48 h. The soil pH value at region S1 was close to or above 5, which was higher than that with the conventional technique (Fig. 4). At the same time, the soil pH value at region S5 decreased, as shown in Figs. 9(b)−(d), and the pH value at region S3 was higher than that at other sections after the polarity exchange treatment. The pH value range for all soil sections is 5−9.

Compared with polarity exchange with an interval of 96 h under the same voltage gradient and the same treatment time (77.1% of total Pb content was removed shown in Fig. 6), approximately 87.7% of total Pb content was removed by polarity exchange for 192 h with an interval of 48 h (Fig. 8(d)). So, the removal efficiency was enhanced. It is postulated that the accumulation of Pb in S3 is the hindering mechanism for the removal of Pb under the polarity exchange condition.

The significant differences between the data in Figs. 5, 6 and 8 were analyzed by the analysis of variance (ANOVA). Approximately 13.1%, 14.0%, 12.4%, 82.4% and 74.0% of the Pb contents for regions S1−S5 were retained after the conventional electrokinetic remediation without polarity exchange for 192 h treatment, as shown in Fig. 5. 15.9%, 19.8%, 31.8%,
24.3% and 22.4% of the Pb contents for regions S1−S5 were retained after polarity exchange electrokinetic remediation for 192 h with polarity reverse interval of 96 h, as shown in Fig. 6. 7.3%, 12.3%, 18.6%, 14.4% and 8.8% of the Pb contents for regions S1−S5 were retained after polarity exchange electrokinetic remediation for 192 h with polarity reverse interval of 48 h. The average values were 39.18%, 22.84% and 12.28% for the data shown in Figs. 5, 6 and 8, respectively. The data above were analyzed by ANOVA. The F test of ANOVA shows that there is evident difference between the three groups data shown in Figs. 5, 6 and 8, and there is also evident difference between every two groups data shown in Figs. 5, 6 and 8. Therefore, the polarity exchange technique improves the removal efficiency of Pb²⁺. The polarity exchange electrokinetic remediation for 192 h with polarity reverse interval of 48 h obtained the best removal efficiency (Fig. 8(d)).

The electrical conductivity (EC) experiments were carried out and the results are presented in Fig. 10. The EC was higher for the two regions (S1 and S5) near the electrode chambers compared with that for regions S2−S4. This trend was observed because there was more H⁺ near the anode, and there were more OH⁻ and Pb²⁺ near the cathode [25]. Compared with the EC of the conventional electrokinetic remediation, the EC for polarity reverse (interval of 48 h after 192 h treatment) was inverted. The EC was lower for regions S1 and S5 since there were not many H⁺ or OH⁻ ions after polarity reverse, and the EC was higher for region S3 because the...
precipitates re-dissolved (higher concentration of Pb\(^{2+}\) ions). Therefore, the EC for polarity reverse coincided with the Pb\(^{2+}\) distribution and the pH value shown in Figs. 8(d) and 9(d), respectively.

### 3.3 Mechanism with polarity exchange

The pH values and conductance of remnant Pb\(^{2+}\) in treated soils varied linearly after polarity exchange with an interval of 48 h. Its mechanism lies in the fact that OH\(^-\) ions are confined in the cathode compartment. Consequently, the acidic fronts steadily move towards the cathode. Thereafter, H\(^+\) ions must react with negative groups in soil solution and on soil particles during its forward movement. The chemical reaction behavior of H\(^+\) ions in soil during polarity exchange process is similar to that in an electrokinetically driven chromatogram [26]. After the polarity exchange, the previous cathode becomes the anode, H\(^+\) is produced and the soil pH value is lowered, with Pb precipitates re-dissolving and Pb\(^{2+}\) ions migrating towards the cathode. H\(^+\) ions are produced at the anode and continuously supply into the treated soil similar to a mobile phase. Likewise, the soil particles react as a stationary phase. When the pH value of mobile phase decreases, heavy metals with positive charge will accelerate electro-migration towards the cathode like elution. Many types of reactions occur during the remediation, including desorption, ion exchange, decomplexation, dissolution, destruction of the active sites on the soil surface and diffusion from the inner sites of the crystal lattices. However, the most important aspect in electrochemical soil remediation is the soil pH value [19]. Often it is an acidic front, which develops in the soil from the anode towards the cathode during EKR, used for mobilizing many heavy metals. When meet with an acidic front, Pb in non-charged species can be ion-exchanged by hydrogen ions.

\[ \text{Pb}^{2+} + 2\text{H}^+ = \text{PH}_2^+ + \text{Pb}^{2+} \quad (3) \]

The lower the soil pH value becomes, the more positive charges the Pb fractions have. Pb\(^{2+}\) with net positive charges will expedite to electro-migrate towards the cathode. To some extent, linear model pH value may be the main mechanism that can account for linear model of Pb removal velocity in the polarity exchange process. It is the low pH value that is helpful to releasing heavy metals from the soil particles and speed up the electro remediation effect [27], especially near the anode. This can also illustrate why EKR with polarity exchange brings about effective treatment effect.

### 4 Conclusions

1) The application of conventional electrokinetic remediation obtains about 61.8% of total Pb removed from the soil near a lead acid battery factory in the Pearl River Delta region of China after 192 h treatment.

2) The polarity exchange technique improves the removal efficiency of Pb\(^{2+}\) and results in the soil pH value in the range of 5–9. 77.1% and 87.7% of total Pb are removed by polarity exchange technique with polarity exchange intervals of 96 and 48 h, respectively. The improved removal efficiency is attributed to exchanging polarity which prevents the precipitation of Pb\(^{2+}\) in the alkaline soil and the re-dissolution of the precipitates.

3) The additional chemicals and complex equipment are not required for the polarity exchange electrokinetic remediation, which is an improved and economical remediation method for the Pb-contaminated soil.

### References


为了改进传统电动修复铅污染土壤效率，采用交换电极电动修复技术对珠江三角洲区域一铅酸电池厂附近铅污染土壤进行修复。研究去除效率和土壤 pH 值的变化与修复时间及交换频率的关系。结果表明：当工作电压梯度为 1 V/cm，交换间隔为 48 h，铅去除效率最大值达到 87.7%，远远大于传统固定电极方向运行模式的去除效率(61.8%)。另外，采用交换电极电动修复可以消除传统固定电极方向运行出现的“聚焦效应”，而且不用添加化学试剂，讨论了交换电极技术中铅在土壤中电迁移的机理。

关键词：电动修复；交换电极；铅污染土壤

(Edited by Mu-lan QIN)