Electrokinetic delivery of permanganate into low-permeability soils

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Abstract: A bench-scale study was conducted to investigate the feasibility of using electrokinetics as a method of delivering an oxidant into kaolin, a low-permeability soil. Potassium permanganate (KMnO4) was chosen as the oxidant, and in separate tests, KMnO4 was introduced at the anode, the cathode and both electrodes to investigate (1) the extent of oxidant transport via electroosmosis and electromigration and (2) to investigate the stability of the oxidant at each electrode location. Separate tests were performed under different voltage gradients to explore the effect of electric potential on oxidant transport and stability. Results indicate that (1) electromigration is not as effective as electroosmotic advection for the transport of permanganate into the soil and (2) permanganate may not be stable under the pH-redox conditions that are imposed by the application of electric potential. Additional research is being conducted to explore the stability of permanganate under electrokinetic environments and to determine whether a substantial amount of permanganate can be injected into low-permeability subsurface conditions.

Keywords: electrokinetics; chemical oxidation; permanganate; oxidant; soils; remediation; organics; clays.


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1 Introduction

In situ chemical oxidation is a viable remediation approach for the clean-up of organic pollutants at contaminated sites. The choice of in situ chemical oxidation over other in situ treatment methods such as bioremediation, surfactant flushing and thermally enhanced recovery is motivated by the ability of chemical oxidation to be engineered to accommodate site-specific conditions, to be implemented quickly with commercially available equipment and materials and to yield measurable results in short period of time (ITRC, 2000; Siegrist et al., 2001; USEPA, 1991, 1998). Numerous studies have been reported on the development and applications of Fenton’s reagent, ozone and permanganate oxidation systems for in situ treatment of organic contaminants in soils and groundwater (Siegrist et al., 2001). Permanganate may be chosen over other oxidants such as hydrogen peroxide or ozone for one or more of its inherent advantages. Compared to other oxidants, permanganate can be effective over a wider pH range. It oxidises organic contaminants through electron transfer rather than free radical processes and thus has a slower rate of reaction in the subsurface, which facilitates delivery and transport. Additionally, it has lower gas and heat evolution and a lower risk of fugitive emissions.

For chemical oxidation to be effective, the permanganate has to make contact with the contaminants, and therefore should be distributed uniformly throughout the contaminated zone (Siegrist et al., 1999, 2000). The use of wells, fracturing and injection probes to introduce permanganate solution into a low-permeability subsurface environment may not be very effective because of low hydraulic flow (advective transport) and/or slow diffusion process. Electrokinetic remediation is an attractive method for the treatment of low-permeability soils as the processes that govern electrokinetic contaminant transport are not easily hindered by low hydraulic conductivity (Reddy et al., 1997). This study was therefore conducted to support the notion of using electrokinetics as a means of permanganate delivery into a low-permeability soil to oxidise organic contaminants.

Electrokinetic remediation involves the installation of electrodes into multiple wells that have been strategically placed throughout a contaminated zone. An electric potential is then applied to induce two main transport mechanisms: electroosmosis and electromigration. Electroosmosis is the flow of water (or solution) through a charged soil medium under the influence of an electric field (Reddy et al., 1997). Electromigration involves the movement of ions under electrostatic attraction towards an anode or a cathode, depending on the charge of the ion. In low-permeability media with a surface charge, electric conduction involves the one-way movement of counter-ions, which are ions with a charge that is opposite to the mineral surface charge (Reddy et al., 1997). These ions carry waters of hydration and bulk water with them, generating electroosmotic flow. Both electromigration and electroosmosis have the potential to transport the negatively charged permanganate ion ($\text{MnO}_4^-$) through a low-permeability soil. If the solution is delivered at the cathode, then electromigration should transport permanganate ions towards the anode. If the permanganate solution is delivered at the anode, then it may be transported via electroosmosis towards the cathode.

The purpose of this study was to investigate the feasibility of using electrokinetics to deliver permanganate into a low-permeability soil. A series of bench-scale electrokinetic experiments was conducted using kaolin, a low-permeability soil with low reactivity.
The effects of delivery from the anode compared to delivery from the cathode on permanganate distribution, as well as the impacts of increased voltage gradient and test duration were investigated.

2 Background

The primary redox reactions for permanganate are given as follows:

\[
\begin{align*}
\text{MnO}_4^- + 8H^+ + 5e^- & \leftrightarrow Mn^{7+} + 4H_2O \quad \text{(for pH < 3.5)} \\
\text{MnO}_4^- + 2H_2O + 3e^- & \leftrightarrow \text{MnO}_2(s) + 4OH^- \quad \text{(for pH = 3.5 to 12)} \\
\text{MnO}_4^- + e^- & \leftrightarrow \text{MnO}_4^{2-} \quad \text{(for pH > 12)}
\end{align*}
\]

The first half-reaction is dominant under pH conditions that are less than 3.5. The second half-reaction is dominant under typical environmental conditions and applies over a wide pH range. The third reaction represents what may happen to the permanganate greater than a pH of 12. These three reactions show the reduction of Mn to progressively higher oxidation states with increasing pH. It is necessary to consider any subsequent reactions that may take place. The Mn\(^{2+}\) cations formed under low pH can be oxidised to MnO\(_2\) by excess permanganate as follows:

\[
2\text{Mn}^{2+} + 2\text{MnO}_4^- + 2H_2O \leftrightarrow 5\text{MnO}_2(s) + 4H^+
\]

In most acidic solutions, the Mn\(^{4+}\) in MnO\(_2\) can be reduced slowly to Mn\(^{2+}\) as follows:

\[
\text{MnO}_2(s) + 4H^+ + 2e^- \leftrightarrow \text{Mn}^{2+} + 2H_2O
\]

Apparently under any pH condition, permanganate has the potential to oxidise some reductant. Fe\(^{2+}\) and Mn\(^{2+}\) are among possible reductants along with natural organic matter or target organic chemicals such as TCE, PCE and others (Roach, 2002).

The amount of permanganate that is needed to effectively oxidise a toxic organic chemical, such as TCE, is about 2:1 (Roach, 2002). Below is a combination of the dominant half-cell reaction at pH values of 3.5–12 with a half-cell reaction for the oxidation of TCE:

\[
\begin{align*}
2\text{MnO}_4^- + 4H_2O + 6e^- & \leftrightarrow 2\text{MnO}_2(s) + 8OH^- \quad \text{(for pH = 3.5 to 12)} \\
C_2\text{HCl}_3 + 8OH^- & \leftrightarrow 2\text{CO}_2 + 4H_2O + H^+ + 3Cl^- + 6e^- \\
2\text{MnO}_4^- + C_2\text{HCl}_3 & \leftrightarrow 2\text{MnO}_2(s) + 2\text{CO}_2 + 3\text{Cl}^- + H^+
\end{align*}
\]

The amount of permanganate needed to effectively degrade organic contamination is a function of the type and amount of contaminant present and other factors such as the amount of organic matter and reduced metal ions present in the soil that consume additional oxidant (Siegrist et al., 2001).

Oxidant delivery into the subsurface relies on different transport processes that are dependent on subsurface conditions. These processes are termed advection, mechanical dispersion and molecular diffusion. Advection of a MnO\(_4\) front is often accelerated by
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Pressurised injection into the porous vadose zone or by ambient water flow below the water table (Siegrist et al., 2001). Mechanical dispersion involves the spreading of an otherwise sharp MnO\textsuperscript{4−} front due to microscopic velocity variations in a porous medium (Siegrist et al., 2001). Molecular diffusion, however, is an important process for the distribution of oxidant into low-permeability zones. It can occur when hydraulic fractures are filled with permanganate, wells are used for groundwater flushing operations and injection probes are used for potassium permanganate (KMnO\textsubscript{4}) solution delivery but it is a slow process and is generally not reliable for distribution more than a few decimetres, even for months of time (Siegrist et al., 2001). To address this problem, this study investigates the injection of permanganate into low-permeability soil under applied electric potential.

3 Experimental methodology

3.1 Test set-up

Figure 1 illustrates the electrokinetic reactor used for all the tests performed in this study. The components of the reactor included an electrokinetic cell, two electrode compartments, two electrode reservoirs, a power source and a multimeter (Reddy and Shirani, 1997). The electrokinetic cell, made of Plexiglas, had an inside diameter of 6.2 cm and a total length of 19.1 cm. Each electrode compartment included a valve to control the flow into the cell, a slotted graphite electrode and a porous stone. Small holes in the electrode compartment contained the electrode pins and the filter paper was placed in between the soil sample and the electrode. The electrode reservoirs were 3.8-cm inner diameter Plexiglas tubes and they were connected to the electrode compartments using Tygon tubing. There were exit ports in the electrode compartments to which thin tubes were attached to allow the escape of gas and liquid. Any liquid from these tubes was redirected to the respective electrode reservoir. A power source was used to apply a constant voltage to the electrodes, and voltage and current were monitored using a multimeter during the testing.

3.2 Materials

The clay used in this study was kaolin, a low reactivity soil. The kaolin was obtained from EM Science, CAS 1332-58-9. This kaolin was characterised in detail and its properties are listed in Table 1. Potassium permanganate salt was obtained from JT Baker Chemical Company, Phillipsburg, NJ.

3.3 Testing procedure

The required amount of potassium permanganate salt to produce a 1% solution was weighed and dissolved in deionised water. Approximately, 1100 g of dry kaolin soil was used for each test. The soil was mixed with predetermined amount of deionised water to yield initial moisture content of 35% and then placed into the electrokinetic cell in layers and tamped uniformly into the cell with a hand compactor. The electrode compartments were then connected to each end of the electrokinetic cell. The reservoirs were filled with deionised water or 1% KMnO\textsubscript{4} solution and the fluid levels in each reservoir were
maintained to ensure a low constant hydraulic gradient or to eliminate any hydraulic gradient depending on the desired testing conditions. A constant voltage gradient of either 1 or 2 VDC/cm was then applied, depending on the test. A baseline test under hydraulic gradient alone (without the application of electric potential) was also conducted. At the end of each test, the soil specimen was extruded and sectioned into 0–4 cm (section 1), 4–8 cm (section 2), 8–12 cm (section 3), 12–15.5 cm (section 4) and 15.5–19.1 cm (section 5) slices starting from the anode. Each soil section was placed into its own glass jar. For each section, about 10 g of soil was mixed with 10 ml of deionised water and shaken thoroughly by hand (ASTM D4972). After the solids settled, the pH of the soil–water mixture was measured.

The amount of permanganate that had migrated into the soil was traced through analysis for total manganese. Total manganese was extracted from the soil using the USEPA 3050 extraction procedure (USEPA, 1986). About 1–2 g of a representative sample of each soil section was weighed in a flask and then mixed with 10 ml of 1:1 nitric acid (HNO₃).
The flask was covered with a watch glass, heated to about 95°C and refluxed for 15 min. The sample was cooled, 5 ml of concentrated HNO₃ was added and flasks were refluxed again for 30 min. That step was repeated once, and then the flasks were covered with ribbed watch glasses to allow evaporation of the liquid. When the liquid reached a volume of about 5 ml, the sample was cooled. Then, 2 ml of deionised water and 3 ml of 30% hydrogen peroxide (H₂O₂) were added. The mixture was heated until the effervescence caused by the reaction between the peroxide and solution was observable. Samples were cooled and 1 ml of peroxide was added repeatedly until effervescence was minimised. The sample was cooled and 5 ml of concentrated HNO₃ with 10 ml of deionised water were added and the mixture was refluxed for 15 min. The contents of each flask were diluted to 100 ml and centrifuged to separate solids from liquids. The supernatant was poured into a glass vial and capped. Total manganese was determined using an Atomic Absorption Spectrophotometer (AAS).

Table 1  Summary of the properties of kaolin

<table>
<thead>
<tr>
<th>Property</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineralogy</td>
<td>Kaolinite: 100%</td>
</tr>
<tr>
<td></td>
<td>Muscovite: trace</td>
</tr>
<tr>
<td></td>
<td>Illite: trace</td>
</tr>
<tr>
<td>Particle size distribution (ASTM D422)</td>
<td></td>
</tr>
<tr>
<td>Gravel</td>
<td>0%</td>
</tr>
<tr>
<td>Sand</td>
<td>4%</td>
</tr>
<tr>
<td>Silt</td>
<td>18%</td>
</tr>
<tr>
<td>Clay</td>
<td>78%</td>
</tr>
<tr>
<td>Atterburg limits (ASTM D2487)</td>
<td></td>
</tr>
<tr>
<td>Liquid limit</td>
<td>50%</td>
</tr>
<tr>
<td>Plastic limit</td>
<td>27.4%</td>
</tr>
<tr>
<td>Plasticity index</td>
<td>22.6%</td>
</tr>
<tr>
<td>Specific gravity (ASTM D854)</td>
<td>2.6</td>
</tr>
<tr>
<td>Hydraulic conductivity (ASTM D5084)</td>
<td>1.0 × 10⁻⁸ cm/sec</td>
</tr>
<tr>
<td>USCS classification (ASTM D2487)</td>
<td>CL</td>
</tr>
</tbody>
</table>

3.4  Testing program

A total of five tests were conducted with the variables given in Table 2. Test 1 (T1) was a baseline test conducted without applied electric potential. Instead, a hydraulic gradient of 0.1 (2/19.1 cm) to 0.15 (3/19.1 cm) was applied to simulate typical field conditions. This test was performed to examine MnO₄⁻ migration under a hydraulic gradient and compare this to the other tests that were conducted with the applied electric potential.

Test 2 (T2) was performed for 21 days, with 1% KMnO₄ in the cathode and deionised water in the anode. An electric potential of 1 VDC/cm was applied. Test 3 (T3) was also conducted with 1% KMnO₄ solution in the cathode reservoir and deionised water in the anode, but an electrical potential of 2 VDC/cm was applied for 25 days. Test 4 (T4) was
conducted at 1 VDC/cm for 25 days, with the same soil (kaolin); however, the 1% KMnO₄ solution was delivered from the anode instead of the cathode. This was done to investigate the use of electroosmosis, rather than electromigration, as a transport mechanism for permanganate.

Table 2 Experimental programme

<table>
<thead>
<tr>
<th>Test</th>
<th>Soil</th>
<th>Voltage gradient (VDC/cm)</th>
<th>Cathode solution</th>
<th>Anode solution</th>
<th>Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>Kaolin</td>
<td>0</td>
<td>1% KMnO₄</td>
<td>DI water</td>
<td>4</td>
</tr>
<tr>
<td>T2</td>
<td>Kaolin</td>
<td>1</td>
<td>1% KMnO₄</td>
<td>DI water</td>
<td>21</td>
</tr>
<tr>
<td>T3</td>
<td>Kaolin</td>
<td>2</td>
<td>1% KMnO₄</td>
<td>DI water</td>
<td>4</td>
</tr>
<tr>
<td>T4</td>
<td>Kaolin</td>
<td>1</td>
<td>DI Water</td>
<td>1% KMnO₄</td>
<td>25</td>
</tr>
<tr>
<td>T5</td>
<td>2/3 fine sand, 1/3 kaolin</td>
<td>1</td>
<td>1% KMnO₄</td>
<td>1% KMnO₄</td>
<td>14</td>
</tr>
</tbody>
</table>

It should be noted that only kaolin was used for tests 1–4, but a different soil profile, simulating heterogeneous conditions, was used for test 5 (T5). The soil for this test was comprised of three adjacent layers. One-third of the EK cell was filled with fine sand (obtained from Ottawa, IL), about 360 g of kaolinite were tamped over the fine sand to fill the middle section, and the final third was filled with more fine sand. The test duration was 14 days, and 1% KMnO₄ was introduced at the cathode only at the beginning of the test. Two changes were made to reservoir solutions during testing. After three days, when the KMnO₄ solution did not appear to be penetrating the kaolin in the middle layer of the cell, the cathode solution was replaced with a 13:1 mixture of 1% KMnO₄ solution and acid (0.1 M HNO₃) in attempt to create a low pH condition. After four days, while continuing to replenish the slightly acidic solution at the cathode, 1% KMnO₄ solution was added to the anode (instead of deionised water) and replenished regularly throughout the remainder of the test (the last ten days).

4 Results and discussion

4.1 Homogeneous soil conditions (tests 1–4)

The measured current and flow in tests 2–4 are shown in Figures 2 and 3, respectively. In test 3, the current rapidly increased to about 65 mA during the first four hours of testing and then began to drop (Figure 2). In tests 2 and 4 the same pattern was observed, but the current did not reach values as high as in test 3, and this may be attributed to the difference in applied voltage between the tests. The change in current reflects changes in soil conductivity.

The electroosmotic flow pattern is similar in tests 2 and 3. Flow from anode to cathode increased rapidly towards the beginning of the test, and then the rate of increased flow volume began to decrease. Around this time, test 3 was stopped, but test 2 was continued until the flow ceased completely (Figure 3). In test 4, for which the KMnO₄ solution was added at the anode, the flow exhibited a more linear trend, following the initial rapid increase.
Figure 2  Measured current with time for EK tests 2–4

Figure 3  Measured flow with time for EK tests 2–4
Soil pH was relatively higher near the cathode for tests 2–4 marking the position of the ‘high pH front’, whereas lower pH values near the anode mark the path that was followed by the ‘acid front’ (Figure 4). The widest range of pH values was found in test 3, where soil pH ranged from 2.5 near the anode to almost 7 near the cathode. Test 2 ranged in pH from 3 to 5.5 whereas test 4 ranged in pH from about 3 to 7.5. The wider pH range for test 3 was associated with the higher electrical potential that was used for that test (2 VDC/cm). Soil pH levels in test 1 remained close to the initial value as no electrical potential was applied in this test. The pH changes observed in tests 2–4 are the direct result of hydrogen ion production at the anode and hydroxyl ion production at the cathode, creating acidic and basic conditions, respectively (Reddy et al., 1997).

Figure 4  Soil pH distribution for EK tests 1–4

For tests 1–3, manganese was only found near the cathode (in section 5) of the soil sample (Figure 5). For all these tests, the KMnO₄ solution was introduced in the cathode. It is to be expected that in test 1, there would be a very little permanganate migration because of low hydraulic conductivity (1.0 × 10⁻⁸ cm/sec) of kaolin and not applying electric potential. However, the diffusive transport from the cathode resulted in increase in Mn concentration in soil near the cathode region. In tests 2 and 3, however, the permanganate migrated into the soil for a short period of time due to electromigration and diffusion and then stopped. To offer a possible explanation, it is necessary to point out the dominant half-reaction for permanganate, which applied in a pH range of 3.5–12 (Siegrist et al., 2001).

\[ \text{MnO}_4^- + 2\text{H}_2\text{O} + 3e^- \rightarrow \text{MnO}_2(s) + 4\text{OH}^- \]

It is possible that in the cathode the electrons being fed into the system by the power supply were accepted by many of the MnO₄⁻ ions, thereby reducing them to MnO₂ solids, as in the above-mentioned reaction. This occurrence could have prevented permanganate
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migration in two ways. Firstly, if the permanganate had been reduced to MnO₂, it would no longer have a charge, and therefore would not electromigrate into the soil under the applied electric potential. Also, the newly formed MnO₂ may reduce soil permeability at the soil–electrode interface, and over time prevent any unreacted permanganate from migrating into the cell as well.

In test 4, the permanganate solution was introduced at the anode. As shown in Figure 5, the manganese distributed through the entire soil from anode to cathode. It existed at a concentration of about 210, 93, 85, 11 and 45 mg/kg in sections 1–5, respectively. Also, unlike any of the other tests, all of the soil near the anode (section 1) was stained pink, which is the colour of a dilute permanganate solution. Further away from the anode (section 2), the soil was also discoloured, but appeared brown, which is the colour of MnO₂(s) according to Ricart et al. (1999).

Figure 5  Manganese distribution for EK tests 1–4

Considering a significant increase in manganese concentration observed in test 4, the only test in which KMnO₄ solution was added to the anode, one might conclude that the transport of this solution via electroosmosis is more effective than transport of the ions via electromigration. For this test series, the flow of water from anode to cathode acted as a better carrier for permanganate ion than the force of electrostatic attraction that was meant to carry the ion through the soil in tests 2 and 3.

The manganese concentrations in soil in test 4 were still significantly less in near the cathode (soil sections 4 and 5), and there was no significant discoloration of the soil in these locations. The pink colouration of the soil near the anode (in section 1) suggests that the permanganate (MnO₄⁻) was still stable, or it was still in the same form when it was immobilised. The soil pH levels near the anode (in sections 1 and 2) were about 3 (Figure 4) and previous studies have shown that anionic species such as...
chromate (CrO$_4^{2-}$) can adsorb to the soil surfaces under such low pH conditions (Reddy and Parupudi, 1997; Reddy et al., 2001). It therefore seems feasible that some anionic permanganate species (enough to change the colour of the kaolin) may have adsorbed to particle surfaces in test 4.

As mentioned, the soil in section 2 was brown in colour, suggesting the presence of manganese oxides. A possible explanation for this phenomenon involves the electrolysis reaction that takes place at the anode during EK, along with two other reactions mentioned by Siegrist et al. (2001). The electrolysis reactions at the anode generate H$^+$ ions and free electrons (Reddy et al., 1997). This half-reaction is given as follows:

$$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(g) + 2\text{e}^- \text{ (anode)} \quad \text{(reaction a)}$$

Also, one must consider the half-reaction for the reduction of manganese under low pH conditions (Siegrist et al., 2001):

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \text{(reaction b)}$$

and the combination of (a) and (b),

$$4\text{MnO}_4^- + 12\text{H}^+ \leftrightarrow 5\text{O}_2 + 4\text{Mn}^{2+} + 6\text{H}_2\text{O} \quad \text{(reaction c)}$$

and finally the subsequent oxidation of Mn$^{2+}$ by excess permanganate (Siegrist et al., 2001),

$$2\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \leftrightarrow 5\text{MnO}_2(s) + 4\text{H}^+ \quad \text{(reaction d)}$$

If permanganate adsorbs to kaolin particle surfaces and exhausts the adsorption capacity of the kaolin, there will be excess permanganate exposed to the products of the electrolysis reactions that were occurring at the anode and migrating towards the cathode under the influence of electroosmotic flow. The electrons generated from the electrolysis reactions may cause the reduction of permanganate ion to Mn$^{2+}$ (reaction c), and those ions may then proceed to migrate towards the cathode under the influence of both electroosmotic flow and electrostatic attraction.

However, before the ions could move much further they were immobilised, as indicated by the colour change and the chemical analysis. This suggests that the Mn$^{2+}$ ions were oxidised by excess permanganate to form MnO$_2$ solids (reaction d) and they were immobilised. The MnO$_2$ solids reduce the pores and cause a reduction in hydraulic conductivity at that location, further hindering flow and ion migration. The formation of MnO$_2$ precipitates is consistent with the brown colouration that was observed in the soil.

4.2 Heterogeneous soil conditions (test 5)

As described in Section 3.4, test 5 contained a layered sand–kaolin–sand profile. The kaolin section was placed in the centre of the EK cell. The test was conducted under three different conditions: initially using 1% KMnO$_4$ solution at the cathode, next using 1% KMnO$_4$ and acid combination in the cathode and finally using the 1% KMnO$_4$ and acid combination at the cathode and 1% KMnO$_4$ at the anode. The changes in current that occurred under these heterogeneous conditions were quite different from
patterns observed in the homogeneous tests (Figure 6). The current actually dropped in the beginning before it began to increase. Also, it remained quite low, never exceeding 8 mA.

**Figure 6** Measured current in test 5 simulating heterogeneous soil condition

As shown in Figure 7, the flow rate from anode to cathode increased significantly when the 1% KMnO₄ solution was introduced at the anode (after about four days). Additionally, the flow rate seems to be boosted each time the solution was replenished, implying that these flow changes were a result of increases in ionic concentration that were associated with the initial introduction of KMnO₄ solution at the anode side, and with each replenishment (Figure 7).

**Figure 7** Measured flow in test 5 simulating heterogeneous soil condition
The soil pH and Mn concentrations in test 5 were different from the tests 2–4 due to differences in soil profile (Figures 8 and 9). An acid front and base front were not observed in test 5. Soil pH for test 5 never exceeds 4, and it drops to about 2.5 near the cathode. This low pH region is likely the result of the added acid at the cathode.

Figure 8  Soil pH in test 5 simulating heterogeneous soil condition

Figure 9  Manganese distribution in test 5 simulating heterogeneous soil condition
The highest concentrations of manganese in soil (Figure 9) were found near the anode and cathode, that is, in sections 1 and 5 (about 100 mg of Mn/kg dry soil for each section). These sections were both composed of fine sand. The kaolin clay in the centre of the soil profile (i.e. sections 2 and 4) contained Mn concentrations at 10–50 mg/kg. These are the two kaolin sections that were in contact with the fine sand. For the centre section, section 3, less than 1 mg/kg of Mn was detected, so the solution apparently did not completely penetrate the clay.

Although the soil conditions were different for this test, the reactions hindering the migration of permanganate under electrical potential may be the same. Under the low soil pH conditions that were present in the soil near the anode, it is possible that Mn$^{2+}$ was formed near the anode by the same reaction that was mentioned in the previous section (reaction c) to explain the phenomenon that took place in test 4. Mn$^{2+}$ could have then reacted with excess permanganate to form MnO$_2$ solids before it was able to completely penetrate the clay. At the cathode end, MnO$_4^-$ may have reacted with electrons near the cathode to produce MnO$_2$, as described for tests 2 and 3.

4.3 Transmission Electron Microscope/EDX analysis

The manganese that was transported into the kaolin in test 4 left a significant pink or brown discolouration on the kaolin (depending on its position in the cell). The soil sections that showed the most discolouration, and where the most manganese was detected, were examined with the Transmission Electron Microscope (TEM) to locate and characterise any visible manganese phases at the soil particle surface. The highest concentrations of manganese in the kaolin were in sections 1 and 2 of test 4, so samples from these sections were analysed. TEM images and EDX spectra were both collected.

Two images from test 4 and the corresponding EDX spectra are shown in Figure 10. Figure 10(a) shows a cluster of kaolin particles. A mottled surface appearance is visible on one of the grains towards the centre of the image, but this is a feature that was also observed on a clean sample of the kaolin (Roach, 2002). A trace of manganese was detected in this particle, as shown in the corresponding EDX pattern (Figure 10a), but no separate solid phases were visible in the image. Figure 10(b) shows a flakier, less hexagonal particle that is predominantly silica and alumina according to the EDX pattern. Mn also appears on this EDX spectrum, but again there are no visible signs of a separate solid phase on the surface of this particle.

MnO$_2$ solids, a common product of reduction of permanganate, should be easily distinguishable from any crystalline kaolinite grain or amorphous silica particle (Roach, 2002). However, the EDX detection of manganese without a visible solid phase suggests that the manganese is adsorbed onto particle surfaces as a thin coating. These results are not consistent with the observed brown colouring of the soil in section 2 or the proposed reactions that hindered the mobility of the permanganate ion.
Figure 10  (a) TEM image and EDX spectrum of kaolinite from section 1 of test 4 and  
(b) TEM image and EDX spectrum of kaolinite from section 2 of test 4

5 Conclusions

On the basis of this study, the following conclusions may be drawn. When the permanganate solution was delivered from the cathode end, the ions in the solution migrated into soil about a centimetre from the cathode (section 5) and then stopped. This may be due to the reduction of permanganate to MnO$_2$ solids in the electrode compartment, and the subsequent blocking of the soil–electrode interface at the cathode, which may have eventually prevented the migration of any unreacted permanganate into the soil. It is also possible that the electroosmotic flow (from anode to cathode) was hindering electromigration of permanganate ions to migrate from cathode to anode (i.e. opposite direction). If the permanganate was reduced to Mn$^{2+}$ in soil near the cathode (section 5), it may precipitate due to high pH conditions existing near the cathode due to electrolysis reactions.

When the permanganate solution was delivered from the anode end, more efficient migration of manganese was observed, but the permanganate was still eventually immobilised. Permanganate may have been adsorbed to the kaolin in the soil near the
anode (section 1), leaving a pink coating on the kaolinite grains. Then, some unadsorbed permanganate could have been reduced to Mn$^{2+}$ and subsequently oxidised to MnO$_2$, leaving a brown deposit in soil far away from the anode (e.g. section 2).

Under heterogeneous (layered) soil conditions, the permanganate was still not able to penetrate a kaolin lens. Data collected from this test could possibly be explained in a manner that is similar to tests 2 and 3 conducted using homogeneous kaolin soil profile. It is also possible that electromigration and electroosmotic flow are opposing each other. Changes in the composition of the cathode and anode solutions during testing (the addition of acid and addition of permanganate, respectively) also complicate the interpretation of test 5 results.

Finally, the addition of KMnO$_4$ solution at the anode (T4) significantly increased the rate of electroosmotic flow towards the cathode, and the manganese was better distributed throughout the cell. This implies that for these test conditions, electroosmotic flow was a more efficient transport mechanism for permanganate ion than electromigration.

References


