

GEOCHEMISTRY OF CHROMIUM DURING ELECTROKINETIC REMEDICATION

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Abstract: Remediation of chromium contaminated clays has been a difficult task due to the complex geochemistry of chromium. Chromium exists either as an anion or a cation in the soils depending on the pH and redox conditions. The behavior and eventual removal of these chromium species during electrokinetic remediation depends on various geochemical processes including oxidation/reduction, adsorption/desorption, and precipitation/dissolution. In this study, the effect of the initial form of chromium in the soil on electrokinetic remediation is evaluated. In addition, the effects of the soil type as well as the reducing and oxidizing agents on the speciation and migration of chromium under induced electric potential have been assessed. This study showed that a detailed understanding of the geochemistry of chromium is critical for the design of the electrokinetic remedial systems.

1. INTRODUCTION

Chromium is a common heavy metal found at many contaminated sites in the United States. Chromium exists in two valence states, trivalent, Cr(III), and hexavalent, Cr(VI). Cr(VI) is more toxic and mobile as compared with Cr(III). Chromium contamination has been caused mainly by past industrial activities such as electroplating, wood preservation, leather tanning, and metal finishing.

There are three conventional strategies to address the problem of chromium contamination in soils. The first strategy is to remove contaminated soil by excavation and then dispose of it in a permitted landfill. The second strategy is to remove or recover chromium from the soil by using ex-situ processes such as soil washing or in-situ processes such as soil flushing. The third strategy is to immobilize or stabilize chromium in the soil by reducing Cr(VI) into Cr(III) either ex-situ or in-situ. This may be accomplished either chemically by using reducing agents such as Fe^{2+} and sulfides or biologically by using a variety of microorganisms. However, these conventional strategies may be inefficient, ineffective or cost-prohibitive in remediating low permeable clayey soils.

Recently, in-situ electrokinetic remediation has been shown to be a promising technique for the removal of heavy metals from contaminated clays. The performance of electrokinetic removal of heavy metals such as lead and cadmium has been extensively studied; however, only limited studies have been performed to study the removal of chromium (Hamed et al., 1991; Lindgren et al., 1992; Pamukcu and Wittle, 1992; Acar and Alshawabkeh, 1993; Probststein and Hicks, 1993; Acar and Alshawabkeh, 1996; Haran et al., 1996; Li et al., 1997; Reddy and Parupudi, 1997; Reddy et al., 1997; Reddy and Shirani, 1997; Reddy et al., 1999). Chromium, when in Cr(VI) form exists as oxyanions, and when it is in Cr(III) form it exists as cationic hydroxides. Therefore, under an induced electric potential, Cr(VI) migrates towards the anode and Cr(III) migrates towards the cathode. The

speciation and extent of chromium migration depends on the initial form, soil type, and naturally occurring reducing and oxidizing agents. Therefore, a detailed understanding of the geochemistry of chromium is essential for the development of an effective electrokinetic remedial strategy.

This paper first presents an overview of the geochemistry of chromium and then assesses geochemical effects on chromium migration during electrokinetic remediation based on bench-scale electrokinetic experimental results. The effects of: the initial form of chromium, the soil type, and the naturally occurring reducing and oxidizing agents, on the speciation and migration of chromium under an induced electric potential have been examined.

2. GEOCHEMISTRY OF CHROMIUM

Geochemistry of chromium has been studied by several investigators (Bartlett and James, 1979; Fendorf and Zasoski, 1992; Rai et al., 1989). The speciation or the form of chromium, Cr(III) or Cr(VI), and the phase in which it exists, whether in aqueous, adsorbed or precipitated (solid) phase, depends on various geochemical processes. The most important of these geochemical processes include oxidation/reduction, adsorption/desorption and precipitation/dissolution.

The redox chemistry of chromium depends on the Eh and pH conditions (Pourbaix, 1974). Under highly oxidizing conditions, chromium usually exists in Cr(VI) form. When the soil pH is less than 6.3, Cr(VI) exists as HCrO_4^- ; however, at a soil pH greater than 6.3, it exists as CrO_4^{2-} . Under low oxidizing or reducing conditions, chromium exists as Cr(III). When the pH is less than 6, Cr(III) exists as cationic species Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$; when the pH is greater than 6, Cr(III) exists as amorphous $\text{Cr}(\text{OH})_3$; and when the pH is higher than 11.8, Cr(III) exists as anionic $\text{Cr}(\text{OH})_4^-$. Thus, under normal soil pH conditions, Cr(VI) exists as either as HCrO_4^- , CrO_4^{2-} or combination of these two species, whereas Cr(III) exists as Cr^{3+} , $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_3$ or a combination of these species.

Since clay surfaces are generally negatively charged, Cr(VI) species are weakly adsorbed to the clays and they exist in aqueous form over a wide pH range. Batch experiments on kaolin revealed that Cr(VI) adsorption varies from 20% at soil pH of 2 to negligible adsorption at soil pH of 8 (Reddy et al., 1997). On the other hand, Cr(III) species are cationic; therefore, they tend to adsorb to clay surfaces. This adsorption increases with increasing soil pH, and at a soil pH greater than 6, most Cr(III) precipitates as $\text{Cr}(\text{OH})_3$. Batch experiments on kaolin revealed that Cr(III) adsorption varies from less than 5% at the soil pH of 3 to 100% at the soil pH of 6 (Griffin et al., 1977). Therefore, under normal soil pH conditions, Cr(III) is adsorbed significantly to soil surfaces, while Cr(VI) mostly remains in the pore water.

The amount of aqueous Cr(III) in soils depends on the solubility of the Cr(III) species that are present at different soil pH values. $\text{Cr}(\text{OH})^{2+}$ solubility decreases with an increase in the soil pH up to 6. When the soil pH exceeds 6, $\text{Cr}(\text{OH})_3$ is formed which severely limits the aqueous Cr(III) present in the soil. When the soil pH is greater than 12, the solubility of Cr(III) increases due to the existence of $\text{Cr}(\text{OH})_4^-$ (Pourbaix, 1974). For normal soil pH conditions, the solubility of Cr(III) species is very limited; therefore, Cr(III) species are considered less mobile within the subsurface environment.

3. GEOCHEMISTRY OF CHROMIUM UNDER ELECTRIC POTENTIAL

A comprehensive research program was undertaken at the University of Illinois at Chicago (UIC) in 1993 to understand the geochemistry of chromium during electrokinetic remediation. This understanding was deemed necessary in order to develop enhancements to increase the remedial efficiency of the electrokinetic process. Several bench-scale electrokinetic experiments were conducted to systematically investigate the effects of: the initial form of chromium, the soil type, the presence of naturally occurring reducing agents, and the presence of naturally occurring oxidizing agents, on the migration of chromium under induced electric potential. A summary of the experimental methodology and the results is presented and discussed in this section.

Materials and Methods

Two different soils, kaolin and glacial till, were used for this study. Kaolin consists of kaolinite mineral and it does not contain any organic matter, while the glacial till consists of different types of minerals including about 35% carbonates and it also contains 2.8% organic matter. These soils were spiked with selected heavy metals, particularly Cr(VI) or Cr(III), Ni(II), and Cd(II) in concentrations of 1000 mg/kg, 500 mg/kg, and 250 mg/kg, respectively. When investigating the effects of reducing agents or oxidizing agents, the soils were first spiked with these agents and then they were spiked with the heavy metals. Each of the spiked soil was packed into the electrokinetic cell and subjected to an electric potential of 1 VDC/cm for 120-260 hours. A detailed explanation of the materials used, the electrokinetic test set-up, and the testing procedures is provided elsewhere (Reddy and Parupudi, 1997; Reddy et al., 1997; Reddy and Chinthamreddy, 1999; Chinthamreddy and Reddy, 1999; Chinthamreddy, 1999). The test results with respect to chromium are presented and discussed in the following sections to demonstrate the complex geochemistry during the electrokinetic remediation.

Effect of Initial Form of Chromium

Figure 1 shows the chromium profiles for two tests performed on kaolin with different initial forms of chromium. The first test was performed with Cr(III) concentration of 1000 mg/kg and the second test was performed with Cr(VI) concentration of 1000 mg/kg. Solid symbols show the total chromium, (Cr(total)), Cr(VI) and Cr(III) profiles for the first test where the initial form of chromium was Cr(III). The Cr(total) profile shows that the migration is towards the cathode. Low concentrations were observed near the anode and then concentrations increased towards the cathode. From the geochemistry of chromium it is known that under low pH and moderate oxidizing conditions, Cr(III) exists in Cr³⁺ form and moves towards the cathode due to its positive charge. However, when it encounters high pH conditions near the cathode, it precipitates in the form of Cr(OH)₃. After the electric field is applied, the chromium that was introduced into the soil exists in Cr³⁺ form due low pH conditions developed by electrolysis near the anode. Thus the Cr³⁺ migrates towards the cathode and this can clearly be seen in Figure 1. Near the cathode, electrolysis produces high pH conditions and this causes the Cr(III) that migrated from anode to precipitate. The initially introduced Cr(III) remained mainly in the form of Cr(III) throughout the soil specimen as seen from the Cr(VI) and Cr(III) profiles for this test (Cr(VI) concentrations were negligible throughout the specimen). From this test, it could be concluded that when

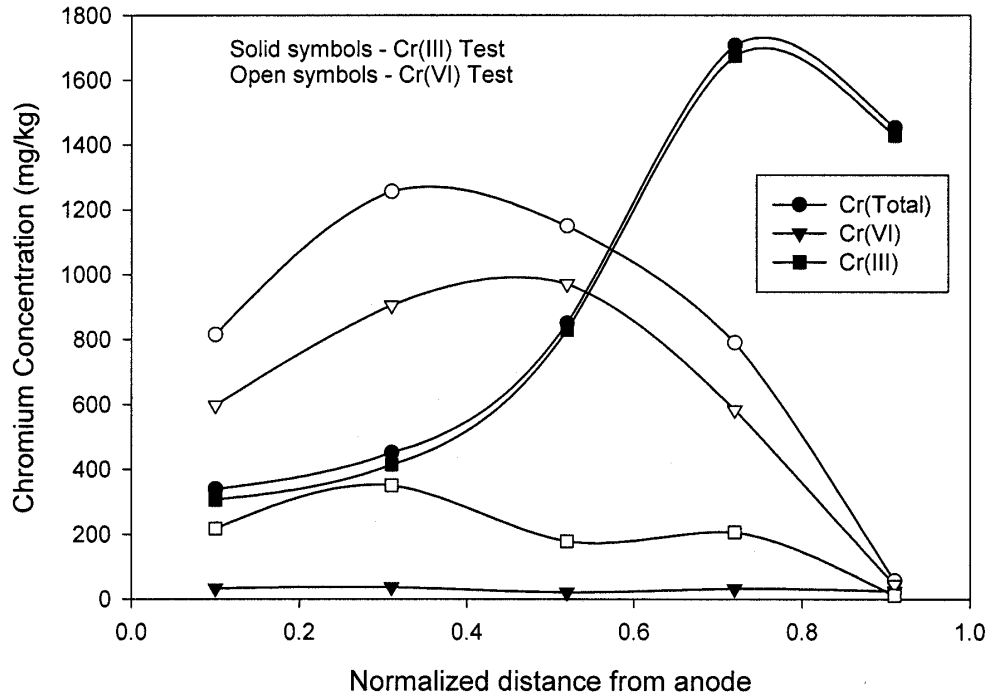


Figure 1. Effect of initial form of chromium in kaolin under induced electric potential of 1 VDC/cm

the initial form of chromium is Cr(III), the migration is towards cathode. The Cr(III) precipitates and accumulates near the cathode because of the high pH conditions that were developed during electrolysis.

Open symbols in Figure 1 show the Cr(total), Cr(VI) and Cr(III) profiles for the test where the initial form of chromium was Cr(VI). In this test, it can be seen that the migration of Cr(VI) is towards the anode due to its anionic nature. Cr(VI) mostly exists in soluble form in high pH conditions; however, in low pH conditions, it tends to adsorb to the soil. This can be clearly seen from the results shown in Figure 1. All of the Cr(VI) moved away from the cathode where high pH conditions existed and migrated towards the anode. High Cr(VI) concentrations were found near the anode due to low pH conditions. It also can be seen that most of the Cr(VI) remained in Cr(VI) form, however, some Cr(VI) was reduced to Cr(III). The reduction of Cr(VI) into Cr(III) near the anode was also observed in previous investigations, and this was mainly attributed to the anodic reactions that take place during electrokinetics. From this test, it could be concluded that when the initial form of chromium is Cr(VI), migration is towards the anode and the accumulation near the anode regions is due to low pH (2-4) conditions where adsorption of Cr(VI) takes place (low pH conditions exist in about 2/3 of the soil specimen from the anode).

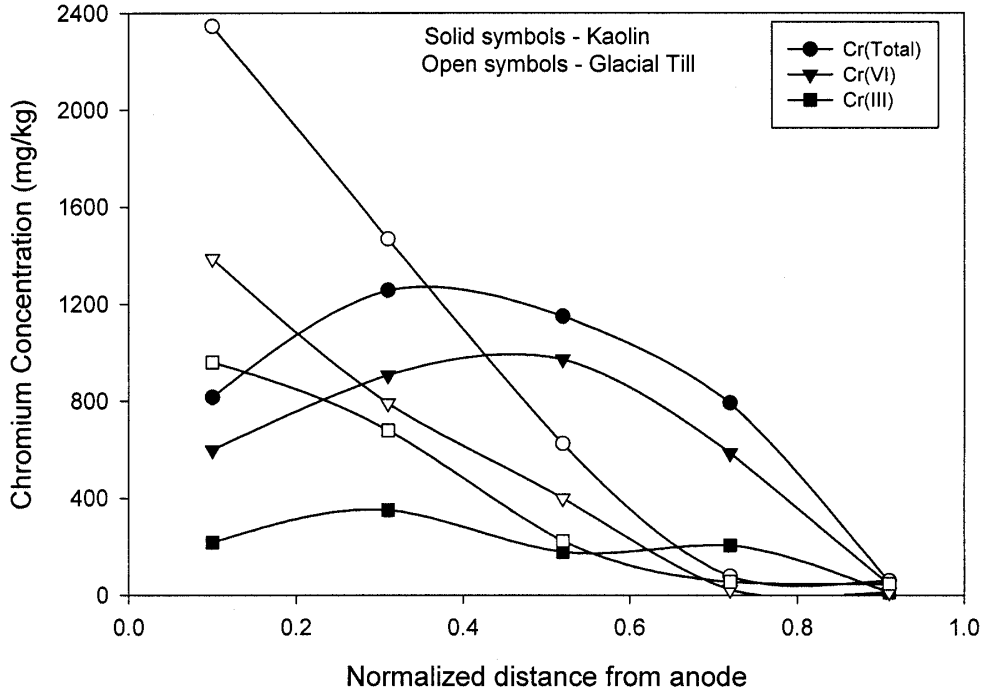


Figure 2. Effect of soil type on Cr(VI) migration under induced electric potential of 1 VDC/cm

Effect of Soil Type

Figure 2 shows the effect of soil type on Cr(VI) migration under induced electric potential. Kaolin and glacial till were the soils used and they were contaminated with 1000 mg/kg of Cr(VI). Kaolin represents a low buffering soil, while the glacial till represents a high buffering soil (Reddy et al., 1997). The results for kaolin are shown with solid symbols and the results for the glacial till are shown with open symbols. The Cr(VI) migration in kaolin was described in the previous section where the effect of initial form of chromium was discussed. The migration of Cr(VI) in glacial till also occurred towards the anode as it was observed in kaolin. However, because of high buffering capacity of glacial till, high pH (>6) conditions existed throughout this soil which caused Cr(VI) to remain in aqueous phase. Cr(VI) and Cr(III) profiles show that even though chromium was initially introduced in Cr(VI) form, a significant amount of Cr(VI) was reduced into Cr(III) in glacial till. This higher reduction of Cr(VI) into Cr(III) in glacial till as compared to that observed in kaolin may be attributed to the naturally occurring reducing agents present in the glacial till. From these tests, it can be concluded that the type of soil plays a major role in Cr(VI) migration.

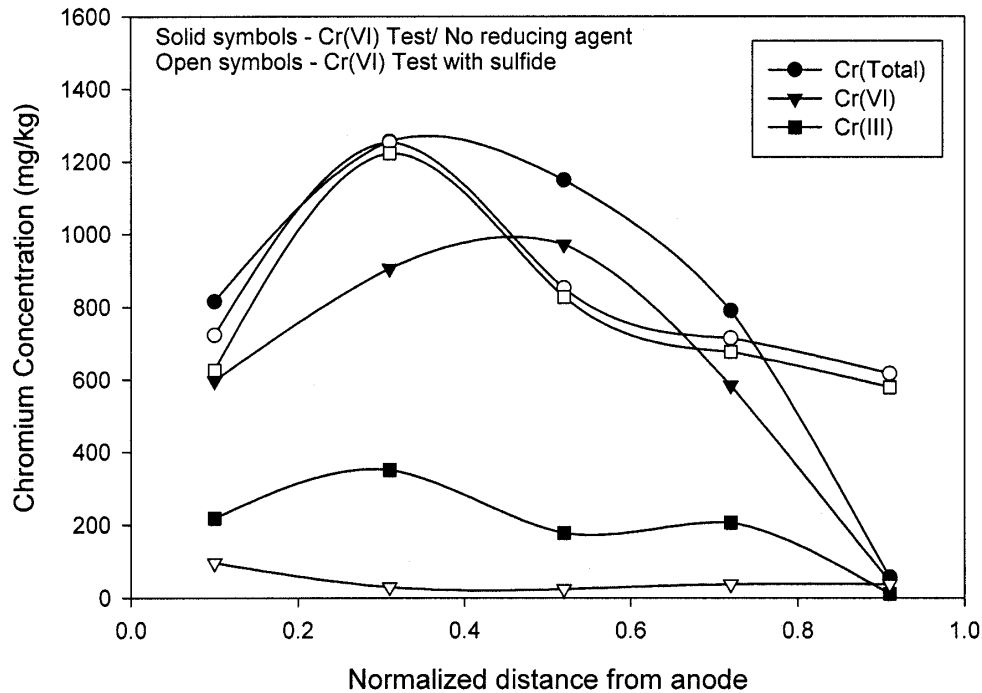


Figure 3. Effect of reducing agents in kaolin on Cr(VI) migration under induced electric potential of 1 VDC/cm

Effect of Reducing Agents

Figure 3 shows the effect of reducing agents on electrokinetic remediation of Cr(VI) contaminated clays. Two tests were performed on kaolin contaminated with Cr(VI) concentration of 1000 mg/kg. In the first test, reducing agents were not present in the soil, and in the second test, sulfide in a concentration of 1000 mg/kg (using sodium sulfide) was introduced as a representative reducing agent in the soil. Solid symbols in Figure 3 show the results for the first test, whereas the open symbols show the results for the second test. The description of the results of the first test was given in the section on effect of initial form of chromium. The results of the test with sulfides show that the chromium migration pattern is significantly different from the test performed without reducing agents. The total chromium profile shows that chromium, being initially in Cr(VI) form, attempted to migrate towards the anode; however, the Cr(VI) and Cr(III) profiles show that most of the Cr(VI) was reduced into Cr(III) (a negligible amount of Cr(VI) was observed throughout the soil specimen). The results showed that high pH (5-12) conditions existed throughout the soil except near the anode region. The high pH conditions caused Cr(III) to precipitate as hydroxide/sulfates and

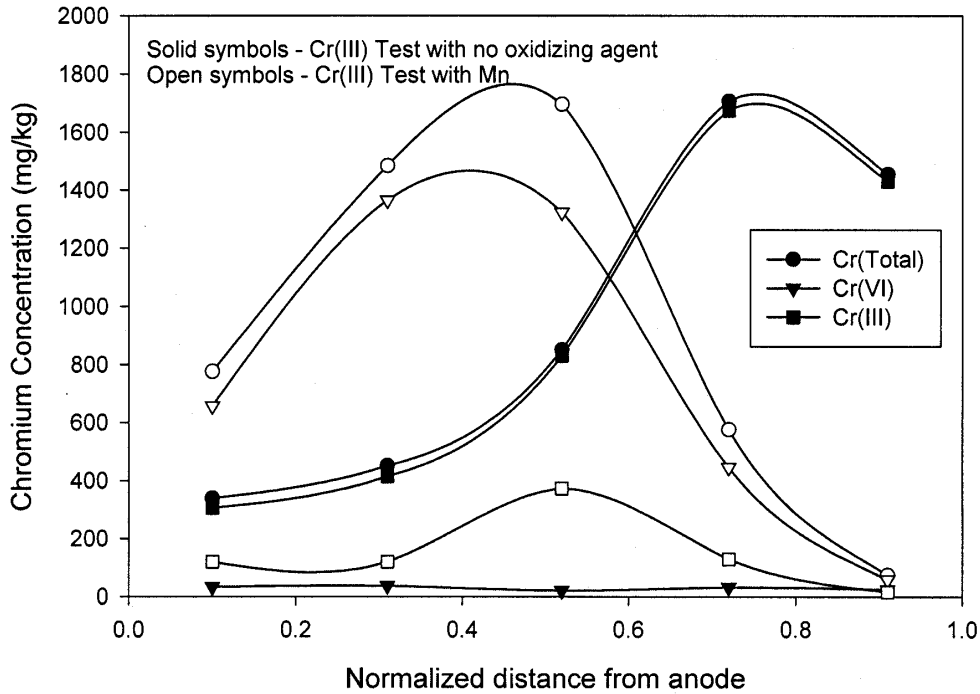


Figure 4. Effect of oxidizing agents in kaolin on Cr(III) migration under induced electric potential of 1 VDC/cm

hence retarded migration. The test results show that the reduction of Cr(VI) into Cr(III) may occur in the presence of reducing agents which may significantly affect the chromium migration under induced electric potential.

Effect of Oxidizing Agents

Figure 4 shows the results of tests that were performed to determine the effect of oxidizing agents on the remediation of Cr(III) contaminated clays using electrokinetics. Two tests were performed on kaolin contaminated with 1000 mg/kg of Cr(III). The soil in the first test did not contain any oxidizing agent, but in the second test manganese Mn(IV) (using potassium permanganate) was introduced at a concentration of 1000 mg/kg as a representative oxidizing agent in the soil. Solid symbols show the results of the first test and open symbols show the results of the second test. The results from the first test have been described in the section on effect of initial form of chromium. In the presence of oxidizing agent, concentration profiles show that the chromium migration occurred towards the anode. Cr(VI) and Cr(III) profiles show that most of Cr(III) that was introduced initially into the soil oxidized into Cr(VI). Small amounts of Cr(III) were found in the soil. Thus, the test results

show that in the presence of oxidizing agents, Cr(III) oxidizes into Cr(VI) and as a result the direction of chromium migration reverses.

4. CONCLUSION

The speciation of chromium significantly effects the direction and the overall removal of chromium in soils. If chromium is present in the form of Cr(III), it migrates towards the cathode and precipitates near the cathode, and when chromium is in the form of Cr(VI), it migrates towards the anode and adsorbs to the soil near the anode region. The buffering capacity of the soil affects the soil pH and dictates the amount of aqueous chromium present in the soil. High buffering capacity soils contain most of Cr(VI) in aqueous phase, while the low buffering capacity soils act as an adsorbate for Cr(VI). Oxidizing agents and reducing agents also can change the form of chromium that, in turn, can affect the direction and extent of chromium migration. This study showed that the form in which chromium is present in the soil, the soil type, and the presence of reducing and oxidizing agents in the soil can significantly influence the chromium chemistry; therefore, it is of paramount importance to properly characterize the geochemistry of chromium in the design of electrokinetic remediation systems.

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