Electrokinetically enhanced reduction of [Cr(VI)] in contaminated soils

Amélioration de la réduction de [Cr(VI)] à l'aide de l'électrocinétique

Antoinette Weeks & Dr. Sibel Pamukcu – *Lehigh University, Bethlehem, Pennsylvania*

ABSTRACT: A study demonstrating the in-situ stabilization of hexavalent chromium, [Cr(VI)], to trivalent chromium, [Cr(III)], by electrokinetically introducing a reducing agent such as ferrous iron, [Fe(II)], using both laboratory-controlled and field-spiked contaminated samples are presented herein. The experimental results obtained from this study will be applied to an existing electrochemical model using the Nernst Equation to estimate the chromium concentrations remaining in the contaminated soils. Within the range of this study, reasonable estimates for the concentration of the remaining chromium species in the contaminated samples were obtained as a function of varying soil potentials using the Nernst Equation. The results also showed that [Cr(VI)] can effectively be reduced to [Cr(III)] in soils via electrokinetic applications. Overall, the results obtained showed that electrochemical stabilization of [Cr(VI)] might be a promising in-situ alternative for the remediation of [Cr(VI)] in contaminated soils and that the Nernst Equation may be applicable to composite soil-water systems to estimate post electrokinetic treatment concentrations of the [Cr(VI)] species.

Résumé : Cette étude fait part de la stabilisation in-situ de chromate hexavalent [Cr(VI)] en sa trivalente forme [Cr(III)] par électrocinétique ceci a l'aide de l'introduction d'un agent réducteur tel que l'ion ferrique [Fe(II)]. Parmi les échantillons étudiés, une partie a été recrée en laboratoire le reste provenant d'un site contaminé. Les résultats expérimentaux issus de cette étude sont comparés à un modèle électrochimique existant basé sur l'équation de Nernst ceci affin d'estimer les concentrations finales de chromate dans. Les échantillons contaminés. Dans le cadre de cette étude, raisonnables estimations des concentrations résiduelles de chromate sont obtenues ceci en fonction du potentiel électrique des sols étudiés. Les résultats montrent qu la réduction via électrocinétique de [Cr(VI)] en [Cr(III)] est effectif. Principalement, les résultats expérimentaux montrent que la stabilisation électrochimique de [Cr(VI)] peut être une alternative in-situ prometteuse pour les sols contamines et que l'équation de Nernst peut être appliquée au système biphasique, ici fluide et sol dans le but d'estimer les concentrations résiduelles de [Cr(VI)] après traitement par éctrocinétique.

1 INTRODUCTION

1.1 *Overview*

Hazardous materials including heavy metals, may pose a treat to the environment when present in the soil and groundwater system. [Cr(VI)] may enter the subsurface environment through a variety of industrial processes such as electroplating, pulp producing, tanning, the production of stainless steel, and ore and petroleum refining processes (Eary & Rai, 1988, Fendorf & Li, 1996). In some instances, chromium has been released to the environment via leaking underground containers, poor storage, or improper disposal practices.

Hexavalent chromium, [Cr(VI)], is of interest because of its toxic and potentially carcinogenic nature (Bartlett & Kimble, 1976, Eary & Rai, 1988, Fendorf and Li, 1996). Another problem associated with [Cr(VI)] is its high mobility in soil and groundwater systems. Past studies have reported that the U.S. effluent water standard for [Cr(VI)] concentration is 1.7 ppm (Bartlett & Kimble, 1976). In addition, [Cr(VI)] concentrations as low as 0.5 ppm in groundwater and 5.0 ppm in soil are suggested as being toxic to plants (Fendorf & Li, 1996). These findings and others have necessitated much of the on-going research concentrated on developing alternative methods to remediate [Cr(VI)] in the subsurface environment. Despite much of these efforts, the increasing evidence of chromium contamination would suggest that more suitable techniques for estimating and predicting chromium concentrations in soils, as well as, its ultimate treatment and removal are still needed (Lingren et al., 1998).

1.2 *Background: Chromium in Soils*

In soils, two of the more common oxidation states for chromium are trivalent chromium, [Cr(III)], and [Cr(VI)] (Kouh et al., 2000). One of the primary reasons for reducing [Cr(VI)] to [Cr(III)] in soils is the measurable reduction in both toxicity and mobility (Bartlett & Kimble, 1976, Eary & Rai, 1988, Hug et al, 1997). Additionally, [Cr(III)] has also been reported an essential trace element for glucose metabolism in both humans and animals (Hug et al., 1997). Past researchers have also indicated that the reduction of [Cr(VI)] to [Cr(III)] in both the aqueous and mixed environments may constitute a favorable remediation alternative to existing pump-and-treat technology (Eary & Rai, 1988, Fendorf & Li, 1996, Hug et al., 1997, Pamukcu et al., 1997).

The present study has concentrated on reducing [Cr(VI)] to [Cr(III)] by electrokinetically introducing a reducing agent such as ferrous ion, [Fe(II)], to the contaminated soil medium. Several laboratory experiments of electrokinetically enhanced chromium reduction treatment were performed on laboratory-controlled kaolinite-clay and chromium-spiked field samples. The samples were analyzed at constant chromium concentrations; while, the concentrations of [Fe(II)] were varied to obtain the optimum treatment conditions. The reduction of [Cr(VI)] using [Fe(II)] was observed indirectly as the difference in the concentration of total chromium [Cr] remaining in the soil and the amount [Cr(VI)] removed.

2 EXPERIMENTAL METODOLOGY

2.1 *The Lehigh Electrophoretic (EP) Treatment Apparatus*

The treatment cell used to perform the [Cr(VI)] reduction study is a modified version of a standard electrophoretic apparatus. This modified cell incorporates some of the features of another apparatus called the electrokinetic (EK) treatment cell. The EK cell is well defined in literature and various versions of the apparatus has been utilized in the treatment of other heavy metals including chromium (Acar et al., 1995, Lingren et al., 1998, Pamukcu et al., 1997). One of the primary reasons for using the modified electrophoretic (EP) treatment cell during this study was the ability to obtain direct potential, E, measurements in a uniform electric field throughout the soil medium. Figure 1 shows a schematic of the Lehigh Electrophoretic (EP) treatment cell. The EP cell allows for a flat, thin, homogeneous layer of contaminated soil to be analyzed between the two electrode chambers. The electrode chambers are designated as the anode and cathode chambers or the positive and negative electrodes, respectively. Depending on the selected experiment, the electrode chambers were used to house the stock solutions of [Cr(VI)], [Fe(II)], and deionized water to be introduced to the soil.

In the EP cell, there are seven evenly spaced inert platinum wires, which are installed onto the sample tray located in its middle section. This sample tray is used to house the contaminated soil layer. These platinum wires are installed approximately one inch apart beneath the soil layer and are designated as the soil electrodes. The soil electrodes were used to monitor the electrical potential drop or variation occurring throughout the contaminated soil medium as a function of time.

2.2 *Procedures and Analysis*

During the experiment, predetermined amounts of potassium dichromate, $K_2Cr_2O_7$, and ferrous sulfate, FeSO4.9H_2O, were dissolved in deionized water to prepare the stock solutions to be used as the sources of [Cr(VI)] and [Fe(II)], respectively. The [Fe(II)] stock solution was purged with 99.999% ultra purified grade nitrogen gas (N_2) to prevent the oxidation of [Fe(II)] to ferric oxide, [Fe(III)], prior to placement in the EP cell.

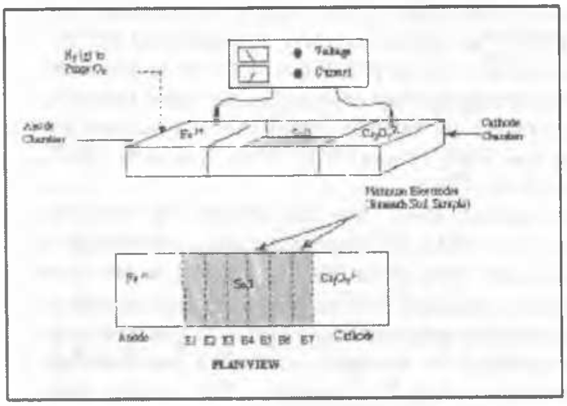

Figure 1: Lehigh Electrophoretic (EP) Treatment Cell

Aqueous [Fe(II)] stock solution concentrations of 0.5, 1.0, 2.0, 4.0, 6.0, and 12.0 times the constant [Cr(VI)] concentrations of 300, 500, and 1000 ppm used to precontaminate the kaolinite-clay and field-spiked samples, were placed in the anode chamber of the EP cell. Constant voltage gradients up to 5.0 volts were applied to the electrode chambers during the testing program. During each test, voltage readings were taken at the soil electrodes, designated as E1 through E7, located beneath soil cake on the sample tray of the EP Treatment cell.

At regular time intervals, measurements for current, soil electrode potential, and solution pH were obtained for each sample tested. At the completion of each test, soil samples were obtained within the vicinity of each soil electrode to determine the concentrations of iron and chromium at various locations along the soil layer. Post experimental measurements for pH and moisture content were obtained for applicable samples.

The preparation, preservation, collection, extraction, and dilution of all soil and liquid samples were performed in accordance to the standard U.S. EPA and water and wastewater treatment guidelines (U.S. EPA, 1986, Standard Methods, 1992). All samples were analyzed using a Perkin Elmer AAnalyst 100 Flame Atomic Absorption Spectroscopy (AA) and a Hach DR/4000U Spectrophotometer (UV) to generate the chromium and iron concentration distributions in soil and water; as well as, the speciated concentrations of iron [Fe] and chromium [Cr].

3 RESULTS AND DISCUSSION

3.1 *Chromium Reduction Results*

Figure 2 shows the mass fraction distributions of total chromium obtained for several laboratory-controlled samples spiked with 300 ppm of [Cr] as the [Fe] concentrations were varied. These results show that for all samples tested, the net chromium decrease as a result of possible ionic migration in the soil was less than 20% for all [Fe]/[Cr] ratios used. This indicated that little of the [Cr] was free to electromigrate in presence of [Fe]. However,

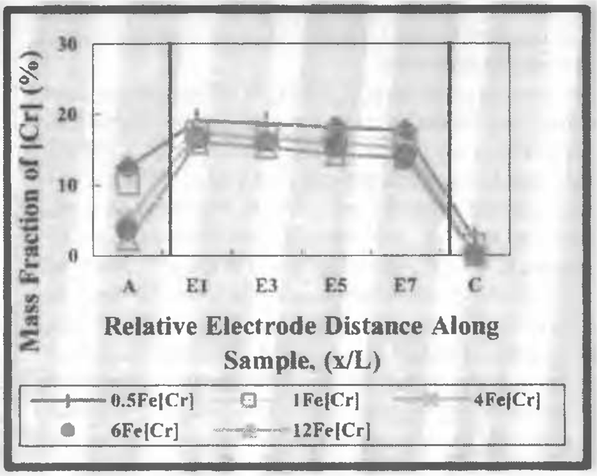

Figure 2: Mass Fraction Distribution in Soil and Liquid Samples Spiked with 300 ppm of Total Chromium, [Cr]

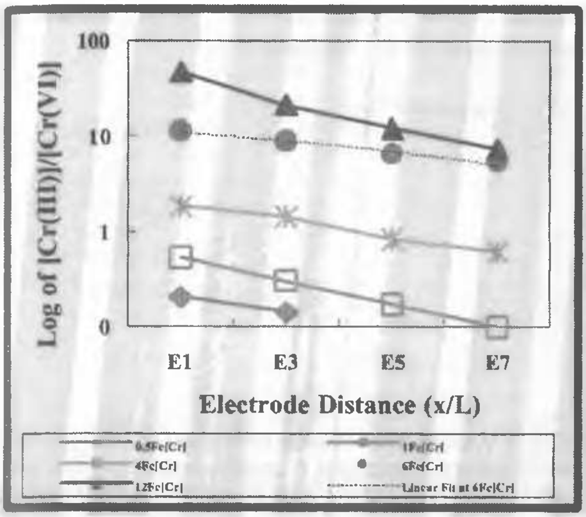

Figure 3: Mass Ratio of [Cr(III)]/[Cr(VI)] Remaining in Kaolinite-Clay Samples Tested in the EP Cell

the mass of [Cr] remaining in soil decreased with increasing proportions of [Fe], and there was an apparent accumulation of [Cr] towards the positive electrode. These observations indicated possible formation of soluble complex species iron and chromium free to electromigrate.

Figure 3 shows the mass ratio of [Cr(III)]/[Cr(VI)] in kaolinite-clay samples tested with varying concentrations of [Fe]. These results show a marked reduction in the concentration of [Cr(VI)], while [Cr(III)] increased with higher concentrations of [Fe] added. Nearly fifty times the amount of [Cr(III)] was observed at the higher ratios of [Fe(II)] then at the lower concentrations. An average soil pH of 3.0 would suggest that the form of chromium remaining in the soil is likely not the [Cr(VI)] species, but the less mobile form, [Cr(III)]. The resulting [Cr(III)] species exists primarily because of the on-going reaction occurring between the [Cr(VI)] spiked-soil samples and the electrokinetically introduced reducing agent, [Fe(II)].

4 The Chromium Reduction Model

The results obtained during this study showed that [Cr(VI)] was electrokinetically reduced to [Cr(III)] by the [Fe(II)] introduced at the anode. Using these results, a model to estimate the chromium species remaining in the soil as a function of the ratio of the initial [Cr(VI)] added and the reducing agent, [Fe(II)], is proposed using the Nernst Equation. Equation 1 shows the general form of the Nernst Equation model commonly used to define the relationship existing between the electrode potential, E, and the concentration ratio, C_R, of the reactants and products in an electrochemical process.

$$E = E^{o} - \frac{RT}{nF} \ln \frac{[C_{OX}]}{[C_{RED}]} \qquad (1)$$

E^{o} is the standard potential, R, T, and F are reaction constants, and *n* is the number of moles of electrons transferred during the reaction. As shown, the Nernst Equation is commonly used to analyze the reactions occurring in aqueous systems. For the case of this study, comprising various composite soil-water samples, we expect that the response obtained for E and C_R in the contaminated porous media will deviate from the predictable linear fit of the Nernst Equation.

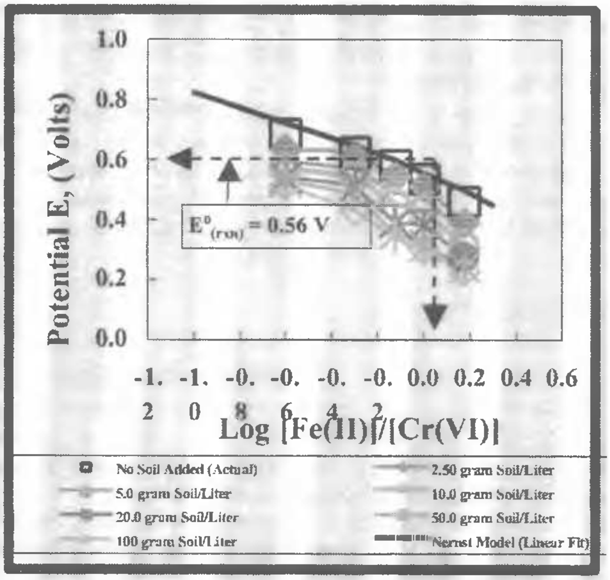

Figure 4: Reaction Potential Variations in Kaolinite-Clay for Aqueous and Composite Soil-Water Systems With Increasing Soil-Water Ratios

Figure 4 shows the relationships between E and C_R as demonstrated by the ratio of [Fe(II)] to [Cr(VI)] obtained for a typical kaolinite-clay sample. These results suggest that the pure aqueous or the "no soil added" system showed a nearly linear and parallel approximation to the Nernst Equation; while, the composite soil-water systems showed slightly non-linear profiles occurring with a shift away from the ideal linear behavior. Both the deviation and the shift for the composite systems, was lessened beyond a mass of about 50 grams of soil per liter of solution, as the soil-to-water ratios were increased. Based on this observation, it is predicted that the Nernst Equation model may be applicable to systems containing higher soil-to-water ratios.

Although some of the inherent restrictions of the bench-scale laboratory set-up may be used to interpret the shift away from linearity in the composite systems, the data presented in Figure 4 indicate that the form of the Nernst relation defined by Equation 1 may have to be modified to more adequately represent denser soil-water systems. Further analysis and interpretations are currently underway to validate this assumption and a Nernst type relationship to predict C_R from direct readings of cell potential in large-scale electrokinetically enhanced treatment of chromium-contaminated soils.

5.1 Managing Contaminated Sites

As previously discussed in Part 4, the Nernst model is applicable to soils contaminated with heavy metals; including, those containing hexavalent chromium. In the case of this study, the Nernst model can be used to quantify the metal ratio in soils by applying the relationship

existing between the reduced and oxidized species in the contaminated medium. For a given value of E, a corresponding [Fe(II)] concentration can be used to estimate the remaining amount of chromium in the soil. When combined with the results previously discussed for Figure 3, we can derive a direct correlation between the metal (chromium) mass ratio and the amount of the reducing agent (in this case, [Fe(II)]), which is electrokinetically added to the soil medium.

Given these initial results, we are hopeful that the Nernst model can be expanded to estimate other metal concentrations in contaminated soils. Thereafter, appropriate methods can be applied to remediate soils contaminated with heavy metals and similar other hazardous materials.

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