



Electrochemically enhanced reduction of hexavalent chromium in contaminated clay: Kinetics, energy consumption, and application of pulse current



Tian R. Sun^{a,b,*}, Sibel Pamukcu^a, Lisbeth M. Ottosen^b, Fei Wang^a

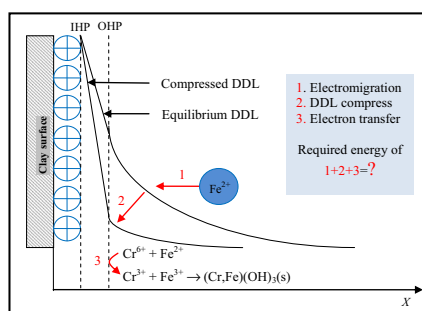
^a Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, PA 18015, United States

^b Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

HIGHLIGHTS

- Direct current significantly increased the reduction rate of Cr(VI) in clay.
- Mass transport process of Fe(II) in clay pore fluid was the rate controlling step.
- [(Cr,Fe)(OH)₃] formation was responsible for the non-productive energy consumption.
- Application of pulse current could decrease the non-productive energy consumption.
- Effect of pulse current was found more significant in lower pulse frequency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 July 2014

Received in revised form 18 October 2014

Accepted 22 October 2014

Available online 29 October 2014

Keywords:

Cr(VI) reduction
Contaminated clay
Kinetics
Energy consumption
Pulse current

ABSTRACT

Electrochemically enhanced reduction of Cr(VI) in clay medium is a technique based on inputting extra energy into the clay to drive the favorable redox reaction. In this study, the reducing reagent Fe(II) was transported into Cr(VI) spiked kaolinite clay by direct current to investigate the dependency of reaction rate on energy consumption. A modified electrophoresis cell with platinum wires as working electrodes was used to run experiments. Results showed that the reduction rate of Cr(VI) was significantly increased by application of current with the pseudo-first-order rate constant k_{pse} from 0.002 min^{-1} at current density of 0 mA/cm^2 to 0.016 min^{-1} at current density of 0.6 mA/cm^2 , and the corresponding reduction efficiency after 60 min experimental time was increased from 8.5% to 57.5%. Mass transport process of Fe(II) in clay pore fluid was determined as the rate controlling step. With the increasing rate of Cr(VI) reduction, both of the productive and non-productive energy consumption increased, from 0.53 and 0.15 mW h at current density of 0.1 mA/cm^2 to 18.9 and 12.6 mW h at current density of 0.6 mA/cm^2 , respectively. The non-productive energy consumption was caused by the formation of [(Cr,Fe)(OH)₃] precipitates. XRD analysis suggested that the [(Cr,Fe)(OH)₃] formed at the clay surface and grew into the pore fluid. SEM-EDX results indicated that the overall Fe(III):Cr(III) ratio of the precipitates was approximately 1.26:1. Application of pulse current decreased the non-productive energy consumption by decreasing the polarization potential drop of each cycle. This effect was more significant in lower pulse frequency due to the better restoration of equilibrium state of clay medium during relaxation period.

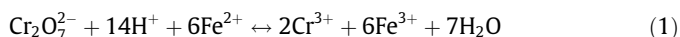
© 2014 Elsevier B.V. All rights reserved.

* Corresponding author at: Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark. Tel.: +45 45255029; fax: +45 45883282.
E-mail address: tiran@byg.dtu.dk (T.R. Sun).

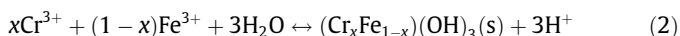
1. Introduction

Chromium contamination widely exists in soils at industrial areas, e.g., electroplating, pigment production, tanning, ore and petroleum refining, manufacture and usage of alloys, and ceramic industries. Improper storage and disposal during these industrial processes caused the release of chromium compounds to the environment. Of great concern is the hexavalent chromium, Cr(VI), which is toxic and potentially carcinogenic [1,2]. Various techniques have been developed to reduce the impact of chromium and to remediate the contaminated site. Reduction of Cr(VI) to less toxic and less mobile Cr(III) is recognized as an important and widely accepted remedial strategy [3–5]. The successful removal of Cr(VI) depends on the formation and stability of Cr(III) precipitates. Ferrous iron [Fe(II)], as a strong reducing agent, has been used to reduce Cr(VI) over a wide range of pH [6–8]. The desired reduction is enhanced by injection of excess Fe(II) into a Cr(VI) contaminated soil. However, it is often difficult for a reagent to achieve uniform distribution in tight clay soils by injection due to their low hydraulic permeability.

It has been demonstrated that the electrokinetically induced mass transport could facilitate the transport of ionic species in tight clay soils [9,10]. The ionic migration takes place in the water phase through the pore structure and is most efficient when the clay is water saturated. More importantly, when electrical energy is applied across the saturated clay, similar to an electrolytic cell, it is possible to force the non-spontaneous oxidation–reduction reactions to move forward by rendering more products than what the Nernst equation predicts. The laboratory evidence of electrically enhanced Cr(VI) reduction to Cr(III) was given in previous studies [11–13]. During the reduction of Cr(VI) at clay surface, the energy consumption is highly related to its kinetics like other heterogeneous chemical reactions. Similar to an electrode surface [14], the reduction process at the vicinity of clay surface could be divided into three steps including mass transport of Fe(II) from the pore fluid to clay surface, the electron transfer, and the formation of new products. The reaction between Fe(II) and Cr(VI) under anoxic conditions and acidic environments is as follows:



The formation of new product after reaction is known as:



where x varies from 0 to 1. For example, it was reported $x = 0.75$ when Cr(VI) was reduced at FeS surface [15], whereas $x = 0.25$ when Cr(VI) was reduced by aqueous Fe(II) [16,17]. The formation of this new solid phase is desirable for remediation since it has rapid precipitation and dissolution kinetics and yields lower solubility than that of Cr(OH)₃. Among these three steps, the step with the lowest rate becomes the rate controlling step, in other words, the most energy will be consumed at the controlling step if a constant current is applied to the system. The first objective of the present work has been to investigate the kinetics of the reduction process at clay surface and determine the energy consumption in each step.

The pulse mode of current has been widely used in analytical electrochemistry and conventional electrolysis, e.g., pulse voltammetry and electrodeposition [14,18,19], to examine the kinetics of processes on electrode surfaces. Similar application was reported in soil electro-remediation [20–23], where it was found that the pulse current could increase the ionic conductivity in soil pore fluid and decrease the energy consumption for transport. The energy consumption of electrochemically based remediation techniques is an important factor influencing costs and thus the applicability of these techniques beyond bench and pilot scale setups [24,25]. Hence, the second objective of this study has been to investigate

the effect of pulse current on energy consumption during the Cr(VI) reduction process and discuss its mechanism from the viewpoints of transport, surface reaction, and re-equilibrium process at relaxation period.

2. Materials and methods

2.1. Preparation of clay samples

High-purity kaolinite clay (china grade, Ward's Earth Science) was used as the test clay medium in this study. The kaolinite clay has low swelling property and low impurity content which could minimize possible influence of background iron. The nominal particle size of the clay is 2 μm. The spiked clay samples were prepared by adding 20 mL freshly mixed potassium dichromate (1200 mg/L K₂Cr₂O₇) stock solution to 10 g dry kaolinite clay. The mixture was allowed to equilibrate under agitation for 24 h. Afterwards the mixture was dried at low temperature of 30 °C to avoid the loss of lattice water in kaolinite and damaging its structure. The dry clay sample was fully wetted by distilled water before experiment. The resulting clay sample was a soft, smooth paste which allows for full liquid saturation and uniform distribution of chromium. The measured initial concentration of Cr(VI) after spike was 800 mg/kg dry clay. The initial pH of the mixture was 4.9.

2.2. Experimental setup

A schematic diagram of the experimental setup is given in Fig. 1. The experimental setup was modified from an electrophoresis (EP) cell supplied by C.B.S Scientific (San Diego, CA). The cell is a rectangular transparent box with a sample tray. Two liquid chambers sit on each side of the sample tray. A lid was used to cover the whole apparatus. Two internal working electrodes were separately equipped in each liquid chamber. The oxidation–reduction potential (ORP) could be directly measured in the clay by use of 0.25 mm diameter platinum wire electrode (E2) embedded in the base plate of the sample tray. An Ag–AgCl reference electrode (electrode potential = +0.200 V vs. SHE, Fisher Scientific, Pittsburgh, PA) was located in the anode chamber. The ORP was measured at platinum wire electrode E2 with reference to the Ag–AgCl electrode when the current was switched off. The potential drop across the clay matrix (between platinum wire electrodes E1 and E3) was

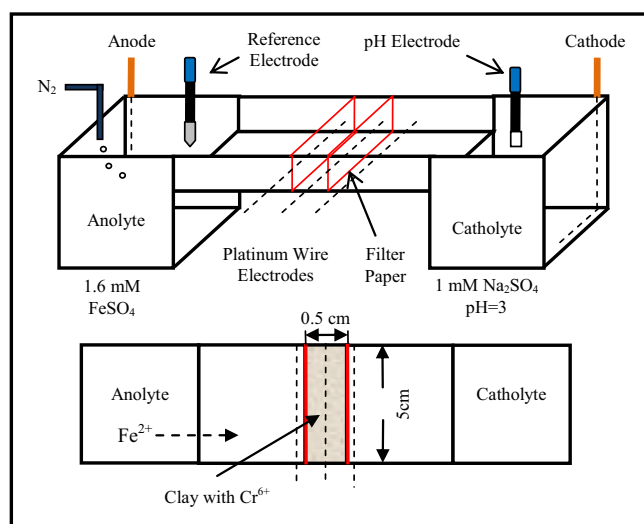


Fig. 1. Schematic diagram of the experimental setup. The length and width of the used electrophoresis cell is 18 and 5 cm, respectively. The clay sample in the middle of the cell is 0.5 cm thick.

Download English Version:

<https://daneshyari.com/en/article/6585611>

Download Persian Version:

<https://daneshyari.com/article/6585611>

[Daneshyari.com](https://daneshyari.com)