Simulation of Reduction of Cr(VI) by Fe(II) Produced Electrochemically in a Parallel-Plate Electrochemical Reactor

Sean Rayman
University of South Carolina - Columbia, rayman@cec.sc.edu

Ralph E. White
University of South Carolina - Columbia, white@cec.sc.edu

Follow this and additional works at: https://scholarcommons.sc.edu/eche_facpub

Publication Info
© The Electrochemical Society, Inc. 2009. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in Rayman, S. & White, R.E. (2009). Simulation of Reduction of Cr(VI) by Fe (II) Produced Electrochemically in a Parallel-Plate Electrochemical Reactor. Journal of the Electrochemical Society, 156(6): E96-E104.
Publisher's Version: http://dx.doi.org/10.1149/1.3098476

This Article is brought to you by the Chemical Engineering, Department of at Scholar Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of Scholar Commons. For more information, please contact digres@mailbox.sc.edu.
Hexavalent chromate, Cr(VI), widely used for the production of stainless steel, textile dyes, wood preservation, and as anticorrosion coating, is highly toxic to both animals and plants. Concentrations of Cr(VI) as low as 0.5 ppm in solution and 5 ppm in soil can be toxic for plants; in contrast, the trivalent chromium is generally only toxic to plants at high concentrations and is a necessary micronutrient for animals. Currently, there are many industrial sites in the world that have been contaminated with Cr(VI) due to inefficient containment of process solutions containing Cr(VI). In the U.S. there has been an ongoing effort to clean up these sites by treating the ground water on site. There are three ways to remove Cr(VI) from the aqueous solution: electroreduction, chemical reduction, and electrochemical reduction (electrococagulation). Compared with chemical reduction, where an extra reducing agent (such as ferrous salts) is supplied from outside the system to reduce an ion, and electroreduction, where the ion is reduced directly at the cathode, electrodissolution uses electricity to produce a reducing agent (ferrous ions from an iron anode) from a sacrificial anode, and then the reducing agent is oxidized via a homogeneous reaction. Several works have studied Cr(VI) reduction. Fendt dorf and Li developed the chemical reduction of Cr(VI) in a batch reactor where the hexavalent chromate (Na₂CrO₄) was reduced by ferrous ion (FeCl₂) rapidly at room temperature. Rodriguez-Valdez et al.5 experimentally studied the electrochemical reduction of Cr(VI) on a reticulated vitreous carbon cathode. They experimentally show that conversion of Cr(VI) to Cr(III) increases at lower flowrates, lower initial concentrations, and higher potentials. Legrand, et al. determined that the formation of Cr(III) monolayers on green rust limits the reduction of Cr(VI) by permeable reactive barriers. Gheju and Lovi reported that the reduction of Cr(VI) by iron metal occurs more rapidly at lower pH; however, as time progresses, the iron metal surface becomes passivated. Parrish and Newman developed a two-dimensional (2D) model of a parallel-plate electrochemical reactor (PPER) assuming that there was a diffusion boundary layer at each electrode and a well-mixed region between the two electrodes. White et al. developed a 2D mathematical description of a PPER for the electrowinning of copper on a cathode, relaxing Parrish and Newman’s assumption of a well-mixed region. Alkire and Lisius developed a PPER model assuming a well-mixed region like Parrish and Newman that included multiple homogeneous reactions in which water was reduced to form OH⁻ and Br⁻ was oxidized, and both electrochemically generated species were reactants in some of the homogeneous reactions. Mader et al. simplified the PPER model by assuming that the axial rate of change of the concentration of every species was constant, the “one-step approximation.” The one-step approximation greatly reduced computational time. Mader and White in a later paper modeled a PPER with a separator and a single homogeneous equilibrium reaction using the previously developed one-step approximation for the Zn/Br₂ cell. Nguyen et al. showed that when the distance between the electrodes is small compared to the length of the electrodes, mass transport in the axial direction is dominated by convection, allowing the axial diffusion and migration terms to be neglected while maintaining the accuracy of the model. Nguyen et al. modeled a process in which a continuously stirred tank reactor and PPER were coupled, allowing a homogeneous reaction to take place outside of the PPER. Coleman et al. modeled a PPER with a separator accounting for gas evolution and multiple electrochemical reactions taking place at both electrodes. Prasad et al. present a PPER model for the electrochemical reduction of nitrates and nitrites, which is based on the boundary-layer model of Parrish and Newman. Georgiadou, using finite-difference formulas, showed that at high Reynolds numbers, Re = 1200, the convection in the axial direction limited the concentration gradients normal to the electrodes to small distances from the electrodes. Hicks and Fedkiw studied experimentally and theoretically the electrolysis of acetate to ethane using a PPER with bulk turbulent flow with diffusion boundary layers at each electrode. Drake et al.20-23 present a steady-state and a transient two-phase PPER model for the Simmons process, assuming that there is a no-slip boundary condition between the liquid and vapor phases. Jha et al.24-26 expand Drake’s PPER model of the Simmons process to include both potentiostatic and galvanostatic operation, nonsteady-state operation, and slip between the liquid-vapor boundary layer. Neither Drake nor Jha provide concentration distributions normal to the bulk fluid flow in the liquid or vapor phases. This paper presents a mathematical model for a PPER that combines diffusion and migration throughout the entire subdomain, multiple homogeneous reactions, and the oxidation of the anode to form one of the homogeneous reactants for the first time. The chemistry presented in this paper is the reduction of Cr(VI) to Cr(III) by Fe(II) as given by Fendt dorf.

A model is presented for the reduction of hexavalent chromium in a parallel-plane electrochemical reactor via a homogenous reaction between Cr(VI) and Fe(II) generated at the iron anode. The effects of the space velocity of the feed solution, the concentration of supporting electrolyte, the distance between the electrodes, and the cell potential on conversion of Cr(VI) to Cr(III), are discussed. This study indicates that for reduction of Cr(VI) using Fe(II), the space velocity must be maintained below 0.02 m/s or the system becomes limited by the rate of reduction of Cr(VI) by Fe(II). Increasing the current density by increasing the amount of supporting electrolyte, and decreasing the distance between the electrodes increases the single pass conversion of Cr(VI) to Cr(III); however, increasing the current density also increases the specific energy required by the system.

Manuscript submitted July 18, 2008; revised manuscript received November 25, 2008. Published April 3, 2009.
5. Constant physical and transport parameters exist.
6. The Butler–Volmer equation adequately describes the current density of the electrochemical reactions.
7. The Nernst–Einstein equation, \( u_i = D_i/RT \), applies.
8. The fluid is an incompressible Newtonian fluid in well-developed laminar flow.
9. A small aspect ratio \((S/L)\) exists between the width and length of the reactor \((S/L \ll 1)\). The material balance equation of the \(i\)th species is expressed as

\[
\nabla \cdot \mathbf{N}_i = R_i
\]

where the flux vector consists of diffusion, migration, and convection terms, respectively

\[
\mathbf{N}_i = -D_i \nabla c_i - z_i \mu_i c_i \mathbf{F} \nabla \psi + c_i \mathbf{v}_i
\]

For a system with a total number of \(N\) species, there are \(N\) material balance equations but \(N + 1\) variables (the concentration of each species \(c_i\) plus the solution potential \(\psi\)). The electroneutrality condition is used as the extra required equation

\[
\sum_{i=1}^{N} z_i c_i = 0
\]

As mentioned above in assumption 8, the velocity distribution within the reactor is a well-developed laminar flow and is given as

\[
v_x = 6 \nu \frac{\gamma}{S} \left( \frac{y}{S} \right)^2
\]

and

\[
v_y = 0
\]

In order for the Reynolds number to be greater than 2300, the average velocity of the solution phase in a reactor with a width of 91 cm given in this paper and an electrode gap of 3 cm, would be greater than 2 cm/s, \(\tau > 0.14\) s\(^{-1}\). If the electrode gap was 0.3 cm, the average velocity would be less than 40 cm/s, \(\tau > 1.3\) s\(^{-1}\), to ensure laminar flow.

In a 2D Cartesian coordinate system, the material balance is derived by substituting Eqs. 4 and 2 into Eq. 1:

\[
\begin{align*}
- z_i D_i \frac{\partial^2 c_i}{\partial x^2} - z_i D_i \frac{\partial}{\partial x} \left( \frac{c_i \partial \psi}{\partial x} \right) + 6 \nu \frac{\gamma}{S} \left( \frac{y}{S} \right)^2 \frac{\partial c_i}{\partial y} - D_i \frac{\partial^2 c_i}{\partial y^2} \\
- z_i D_i \frac{\partial}{\partial y} \left( \frac{c_i \partial \psi}{\partial y} \right) = R_i
\end{align*}
\]

Next, the following characteristic quantities are defined

\[
\gamma = \frac{S}{L}, \quad \xi = \frac{\chi}{L}, \quad \eta = \frac{y}{S}, \quad \theta_i = \frac{c_i}{c_{i,ref}}.
\]

and substituted into Eq. 6 to obtain a material balance with dimensionless dependent and independent variables for the \(i\)th species

\[
\begin{align*}
- \gamma^2 D_i \frac{\partial^2 \theta_i}{\partial \xi^2} - \gamma^2 \xi D_i \frac{\partial}{\partial \xi} \left( \frac{\partial \psi}{\partial \xi} \right) + 6 \nu \frac{\gamma}{S} \theta_i \frac{\partial \theta_i}{\partial \eta} - D_i \frac{\partial^2 \theta_i}{\partial \eta^2} \\
- \xi D_i \frac{\partial}{\partial \eta} \left( \frac{\partial \psi}{\partial \eta} \right) = \frac{S^2}{c_{i,ref} R_i}
\end{align*}
\]

Using assumption 9, the terms with the coefficient of \(\gamma^2\) can be eliminated, which is equivalent to assuming that convection dominates migration and diffusion in the axial direction.\(^{19}\) Applying the one-step approximation\(^{13}\) for the concentration gradient in the axial convection term yields

\[
6 \tau (\eta - \eta^2) (\theta_i - \theta_i,ref) = \frac{S^2}{c_{i,ref} R_i}
\]

The one-step approximation approximates \(\partial \psi/\partial \xi\) as \(\theta_i(\xi = 1, \eta) - \theta_i(\xi = 0, \eta)/1 - 0\) simplified as \(\theta_i/\theta_i,ref = 0 - \theta_i,ref\). In essence, there is only one computational element in the axial direction when the one-step approximation is applied. Mader\(^{15}\) uses the one-step approximation for a PPER that contains a homogenous equilibrium reaction. By doing so, he is able to eliminate the source terms from the material balance equations. As shown later in this work, the first homogenous reaction is considered to go to completion, and thus not all the source terms can be eliminated from the set of material balances. Because the equilibrium condition cannot be assumed for the present work, the one-step approximation will need to be relaxed in future work. The length of the reactor, \(L\), used in this work is 30.5 cm. In order to remain within the limits of assumption 9, the maximum distance between the electrodes, \(S\), should be no more than 3 cm. Equation 8 is now a simplified material balance for the \(i\)th species in one spatial dimension with the following boundary conditions: at \(\eta = 0\) (anode)

\[
N_{ai} = \frac{\partial \theta_i}{\partial \eta} + z_i \frac{\partial \psi}{\partial \eta} = \frac{S}{c_{i,ref} R_i} \sum_j s_j \phi_{aij}, \quad \text{for Fe}^{2+}
\]

at \(\eta = 1\) (cathode)

\[
N_{ai} = -\frac{\partial \theta_i}{\partial \eta} - z_i \frac{\partial \psi}{\partial \eta} = \frac{S}{c_{i,ref} R_i} \sum_j s_j \phi_{aij}, \quad \text{for OH}^{-}
\]

and at both \(\eta = 0\) and \(\eta = 1\) the electroneutrality condition is satisfied

\[
\sum_i z_i \theta_i c_{i,ref} = 0
\]

The current that flows through the reactor is a result of the electrochemical reactions that take place at the anode and cathode. At the anode, the only electrochemical reaction considered is the oxidation of \(	ext{Fe}^{0}\) to \(	ext{Fe}^{2+}\), described by

\[
\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2 e^{-}
\]

At the cathode, the only electrochemical reaction considered is the reduction of \(	ext{H}_2\text{O}\) to \(	ext{OH}^{-}\) and \(	ext{H}_2\), described by
Table I. Transport properties and reference concentration.

<table>
<thead>
<tr>
<th>Species</th>
<th>(10^3D_i) (cm²/sec)</th>
<th>(z_i)</th>
<th>(10^3c_{i,ref}) (mol/cm³)</th>
<th>(c_{i,ref}) (mol/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.334</td>
<td>+1</td>
<td>1.0</td>
<td>Adjusted to maintain electroneutrality of the feed</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.032</td>
<td>−1</td>
<td>1.0</td>
<td>0.5 × 10⁻³</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.719</td>
<td>+2</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>H⁺</td>
<td>9.311</td>
<td>+1</td>
<td>1.0</td>
<td>1.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>OH⁻</td>
<td>5.273</td>
<td>−1</td>
<td>1.0</td>
<td>1.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>CrO₄²⁻</td>
<td>1.132</td>
<td>+3</td>
<td>1.0</td>
<td>6.17 × 10⁻⁹</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>0.604</td>
<td>+3</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>0.595</td>
<td>+3</td>
<td>1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\[2H₂O + 2e⁻ \rightarrow H₂ + 2OH⁻\]

In Eq. 10 and 11, the normal component of the current density of the electrochemical reaction \(j\) can be determined using the Butler-Volmer equation:

\[i_{n,j} = i_{0,j,ref} \left( \prod \theta_i^{\alpha_i} \exp \left( \frac{F}{RT} \phi_{i,0} - \frac{F}{RT} U_{j,ref} \right) \right) - \left( \prod \theta_i^{\alpha_i} \exp \left( \frac{F}{RT} \phi_{i,0} - \frac{F}{RT} U_{j,ref} \right) \right) \]  \[\text{(12)}\]

and at the cathode

\[i_{n,j} = i_{0,j,ref} \left( \prod \theta_i^{\alpha_i} \exp \left( \frac{F}{RT} \phi_{i,0} - \frac{F}{RT} U_{j,ref} \right) \right) - \left( \prod \theta_i^{\alpha_i} \exp \left( \frac{F}{RT} \phi_{i,0} - \frac{F}{RT} U_{j,ref} \right) \right) \]  \[\text{(13)}\]

where

\[U_{j,ref} = U_j^{\phi} - \frac{RT}{n_iF} \sum_i \theta_i \ln \left( \frac{c_{i,ref}}{p_i} \right) \]  \[\text{(14)}\]

Tables I-IV provide the values of the constants and the range of values used for the parameters investigated in this paper. A base case, represented in Fig. 2-5 as a bold gray line, was established with the following parameters: \(v_{avg} = 0.50\) cm/s, \(V_{avg} = 0.60\) V, \(S = 0.3175\) cm, and \(ConcSE = 1.00E-7\) mol/cm³. In the case of these simulations, the concentration of the supporting electrolyte, ConcSE, was changed by changing the concentration of Cl⁻ in the feed solution. The Na⁺ concentration was calculated by assuming that the electroneutrality held in the feed solution. The concentration of most species remained below 10⁻³ mol/cm³ even at the electrodes, which indicates that the solution is dilute, assumption 4, and that the mobility of the ions is proportional to the diffusion coefficient, assumption 7.

**Source Terms in the Material Balance Equation**

In the considered system, nine ionic species are included: Na⁺, Cl⁻, Fe²⁺, Fe³⁺, H⁺, OH⁻, CrO₄²⁻, Cr³⁺, and Cr⁴⁺. All the ionic species except Na⁺ and Cl⁻ are involved in the homogeneous reactions expressed as Eq. 17-19 below.

\[CrO₄²⁻ + 3Fe²⁺ + 4H₂O \rightarrow 3Fe³⁺ + Cr³⁺ + 8OH⁻\]  \[\text{(15)}\]
\[H⁺ + OH⁻ \rightarrow H₂O\]  \[\text{(16)}\]
\[Cr³⁺ + 3OH⁻ \rightarrow Cr(OH)₃\]  \[\text{(17)}\]
\[Fe³⁺ + 3OH⁻ \rightarrow Fe(OH)₃\]  \[\text{(18)}\]
\[Fe²⁺ + 2OH⁻ \rightarrow Fe(OH)₂\]  \[\text{(19)}\]

Fendorf and Li determined that Cr(VI) is reduced by Fe(II) according to the kinetic rate expression

\[r_1 = k_{Cr} [Fe²⁺]^{0.6} [CrO₄²⁻]^{-1}\]  \[\text{(20)}\]

where \(k_{Cr} = 56.3 (± 3.7) \text{ mmol}^{-0.6} \text{ min}^{-1} \text{ L}^{0.6}\). The products of Reaction 1, Cr⁵⁺ and Fe³⁺, react with OH⁻ to form Cr(OH)₃, Fe(OH)₃, and Fe(OH)₂ as described by Eq. 17-19, respectively.

For Eq. 16-19, the kinetic rate expressions are as fast equilibrium reactions

\[r_2 = k_{2,2} Fe²⁺ OH⁻ \rightarrow k_{2,2} FeH₂O\]  \[\text{(21)}\]
\[r_3 = k_{3,4} Fe²⁺ CrO₄²⁻ \rightarrow k_{3,4} Fe(CrO₄)³⁻\]  \[\text{(22)}\]
\[r_4 = k_{3,4} Fe²⁺ CrO₄²⁻ \rightarrow k_{4,3} Fe(CrO₄)³⁻\]  \[\text{(23)}\]
\[r_5 = k_{3,4} Fe²⁺ CrO₄²⁻ \rightarrow k_{5,3} Fe(CrO₄)³⁻\]  \[\text{(24)}\]

where the backward and forward rate constants are related by the following dissociation constants

\[K_a = \frac{k_{3,4}}{k_{3,4}} \quad K_{Cr(OH)₃} = \frac{k_{3,4}}{k_{3,4}} \quad K_{Fe(OH)₃} = \frac{k_{4,3}}{k_{4,3}} \quad K_{Fe(OH)₂} = \frac{k_{5,3}}{k_{5,3}}\]  \[\text{(25)}\]

For the purpose of this work, the authors assumed that the dissolution of the solid products is extremely slow compared to the formation of the solid products, i.e., the forward reactions progressed much faster than the backward reactions. Equations 16-19 allow for the formation of solids in the solution phase; however, it is assumed

Table II. Kinetic and thermodynamic properties of electrochemical reactions.

<table>
<thead>
<tr>
<th>Reaction (j)</th>
<th>(10^3b_i,j/RT) (A/cm²)</th>
<th>(\alpha_{a,j})</th>
<th>(\alpha_{c,j})</th>
<th>(n_j)</th>
<th>(U_j) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>−0.440</td>
</tr>
<tr>
<td>2</td>
<td>300.0</td>
<td>0.5</td>
<td>0.5</td>
<td>1.0</td>
<td>−0.828</td>
</tr>
</tbody>
</table>

Table III. Stoichiometry of the electrochemical reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Species</th>
<th>(x_j)</th>
<th>(p_j)</th>
<th>(q_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe²⁺</td>
<td>−0.5</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>OH⁻</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Chosen arbitrarily.
that none of the solid particles coagulate inside of the reactor (assumption 3).

By taking into account the homogenous reactions, the source term in the material balance equation for each species is specified as

\[ R_{Na^+} = 0 \]  \hspace{1cm} \text{[21]}  \\
\[ R_{Cl^-} = 0 \]  \hspace{1cm} \text{[22]}  \\
\[ R_{Fe^{2+}} = -3r_1 - r_5 \]  \hspace{1cm} \text{[23]}  \\

\[ R_{H^+} = -r_2 \]  \hspace{1cm} \text{[24]}  \\
\[ R_{CrO_4^{2-}} = 8r_1 - r_2 - 3r_3 - 3r_4 - 2r_5 \]  \hspace{1cm} \text{[25]}  \\
\[ R_{Cr^{3+}} = -r_1 \]  \hspace{1cm} \text{[26]}  \\
\[ R_{Fe^{3+}} = -r_4 \]  \hspace{1cm} \text{[27]}  \\
\[ R_{Cr^{4+}} = -r_3 \]  \hspace{1cm} \text{[28]}  

Figure 2. Dimensionless concentration profile of Cr(VI) as current density increases.

Figure 3. Dimensionless concentration profile of Cr(VI) as concentration of supporting electrolyte increases.
Results and Discussion

The effects of the cell potential, concentration of supporting electrolyte in the feed solution, distance between the electrodes, space velocity of the feed solution on the current density, conversion of Cr(VI) to Cr(III), and specific energy required were investigated by numerically solving Eqs. 8-11 at different $V_a$, $C_{Cl^{-},feed}$, $S$, and $v_{avg}$.

As the current density is increased in the reactor by an increase in applied potential from 0.11 to 6.0 V, more Fe(II) is generated at the anode, favoring the progression of Reaction 15, Fig. 2. In addition, as the current density increases, the flux due to migration of chromate toward the anode increases. The migration of chromate toward the anode and the consumption of chromate by Fe(II) migrating away from the anode allows for the maximum concentration of chromate to be found close to the center of the reactor, as shown in Fig. 2. Figure 2 also indicates that as the current density is increased, the overall concentration of Cr(VI) exiting the reactor decreases. Using Fig. 2, it is clear that for all but the highest applied voltage, the power density of the reactor is less than $10^{-2}$ W/cm$^2$, thus validating the assumption of isothermal operating conditions.

Also, at an applied cell potential of 5.8 V, the current density is 2.15 mA/cm$^2$. If all of the H$_2$ exited the reactor in the gas phase, the volumetric flowrate of gas exiting the reactor would be 0.35 cm$^3$/s; thus, the first part of assumption 3 is reasonable. The current density...
of the reactor can also be increased while maintaining a constant applied potential by adding supporting electrolyte to increase the conductivity of the feed solution, Fig. 3. The results shown in Figure 3 indicate that as more supporting electrolyte is added to the feed solution, the peak concentration of chromate in the reactor moves from the anode toward that cathode, because more of the current in the solution is carried by the more-mobile chloride ion. Yet another way to increase the current density is to decrease the distance between the electrodes, Fig. 4. While actively changing the distance between the electrodes while the cell is in operation is not currently practical, the distance between the electrodes should be considered a design parameter. The results shown in Fig. 4 indicate that at distances between electrodes greater than 1 cm at the base space velocity of 0.017 s⁻¹, there is a well-mixed region that exists in the reactor. Figures 2-4 illustrate that when the current density increases, as a result of increasing the applied potential, increasing the

Figure 6. Conversion of Cr(VI) as a function of space velocity as electrode gap increases.

Figure 7. Current density as a function of concentration of supporting electrolyte as the electrode gap increases.
concentration of the supporting electrolyte, or decreasing the distance between the electrodes, the bulk concentration of chromate is decreased. By increasing the distance between the electrodes, \( S \), or by increasing the space velocity, \( \tau \), the convection term in Eq. 8 begins to dominate the diffusion and migration terms over much of the reactor, giving rise to the sharp increases in chromate concentration near the anode seen in Fig. 4 and 5. As the space velocity increases, Fig. 5, diffusion- and migration-dominated transport regions move toward the electrodes, where the convection term becomes small. As the region where diffusion- and migration-dominated transport becomes thinner, the rate of diffusion in that region becomes much greater due to an increase of the concentration gradient near the electrodes, decreasing the concentration of Fe(II) at the anode. Further, the rate of diffusion of OH\(^-\) toward the anode is much greater than that of CrO\(_4^{2-}\), resulting in favorable conditions for homogeneous Reaction 5, Eq. 19, to consume most of the available Fe(II). Once enough of the OH\(^-\) ions have been consumed to slow down Reaction 5, Eq. 19, some Fe(II) ions become available to react with...
CrO$_4^{2-}$, decreasing the concentration of CrO$_4^{2-}$ near the anode. The same trend of an abrupt increase in chromate concentration near the anode with a much broader peak in the center of the reactor occurring at large distances between electrodes is illustrated in Fig. 4. Figure 6 further illustrates that as the distance between electrodes is increased for a given space velocity, the conversion of Cr(VI) to Cr(III) (the ratio of the feed concentration minus outlet concentration to the feed concentration) decreases. Likewise, for a given distance between electrodes, as the space velocity decreases, the conversion of Cr(VI) to Cr(III) increases. Figures 2–5 also illustrate that there are practical space velocities, less than 0.1 s$^{-1}$, and electrode gaps, less than 1 cm, for which the reactor is not well-mixed.

While maintaining a constant applied cell potential, the concentration of supporting electrolyte was varied with different electrode gaps to determine the effect on current density. Based on the results illustrated in Fig. 7, the reduction of distance between electrodes by a factor of 5 has a much greater effect on current density than increasing the concentration of supporting electrolyte by 4 orders of magnitude. While it was not studied in this work, there is a practical limitation to how close together the electrodes can be placed.

There is also a practical design limitation in the space velocity of the reactor no matter how much supporting electrolyte is added to the system. Fig. 8 or how much the applied potential is practically increased. Fig. 9. In order to maintain high single-pass conversion, the space velocity of the reactor must be less than 0.02 s$^{-1}$. Otherwise, at space velocities greater than 0.02 s$^{-1}$, the conversion of Cr(VI) to Cr(III) becomes reaction-rate-limited using the kinetic expression for the reduction of Cr(VI) by Fe(II), as suggested by Fendorf.  

The specific energy required by the reactor to reduce one mole of Cr(VI) to Cr(III), given by

$$E = \frac{(V_F - V_j)IL}{C_{CrO_4^{2-}, feed} - C_{CrO_4^{2-}, outlet}SV_{avg}}$$

was calculated as a function of applied cell potential at different supporting electrolyte concentrations. The results displayed in Fig. 10 indicate that between 0 and 3 V, the specific energy requirements increase with increasing amount of supporting electrolyte, with the lowest energy requirement being 57.5 J/mol of Cr(VI) reduced. However, at cell potentials greater than 4 V, the concentration of supporting electrolyte has little effect on the specific energy requirements.

Conclusions

A model where diffusion and migration are allowed to occur over the entire subdomain has been developed, showing that there are variations in concentration profiles in the entire laminar subdomain. The current density of the reactor can be increased by increasing the electrical potential of the cell, increasing the amount of supporting electrolyte, or decreasing the distance between the electrodes. By increasing the current density, more Fe(II) is produced from the anode. The conversion of Cr(VI) to Cr(III) can be increased by increasing the current density as long as the conversion is not reaction-limited or by reducing the space velocity of process fluid as long as there is enough Fe(II) being produced to reduce all the Cr(VI) to Cr(III). Increasing the amount of supporting electrolyte increases the amount of Fe(II) produced at the anode, which increases conversion of chromate. Further, by increasing the amount of supporting electrolyte, the specific energy of the system to convert a mole of Cr(VI) to Cr(III) also increases. Thus, it is necessary to balance the gains of adding supporting electrolyte on conversion with the increased energy requirements that result in increased supporting electrolyte concentration.

Acknowledgment

This work was supported in part by Flour Hanford, Inc.

University of South Carolina assisted in meeting the publication costs of this article.

List of Symbols

- $c_i$: concentration of species $i$, mol/cm$^3$
- $c_{i,ref}$: reference concentration of species $i$, mol/cm$^3$
- $c_{sup}$: concentration of the supporting electrolyte (NaCl), mol/cm$^3$
- $D_i$: diffusion coefficient of species $i$, cm$^2$/cm
- $E_{cell}$: potential, (V$_F$ - V$_j$) V
- $F$: Faraday’s constant, 96487 C/mol
- $I_{norm}$: normal component current density due to electrochemical reaction $j$, A/cm$^2$
- $I_{exch,j}$: exchange current density of reaction $j$ at reference concentration, A/cm$^2$
Greek

α_{ai} anodic transfer coefficient for reaction j
α_{ci} cathodic transfer coefficient for reaction j
ϕ solution potential, V
γ ratio of the gap between the electrodes to the electrode length
η dimensionless normal coordinate
θ_i dimensionless concentration of species i
Φ dimensionless solution potential
ρ_0 solvent density, g/L
τ ratio of the average solution velocity in the axial direction to the electrode length, s^{-1}
ξ dimensionless axial coordinate

References