

Removal of Hexavalent Chromium from Effluents by Indirect Reduction in a Redox Flow Galvanic Cell with Mesh Electrodes

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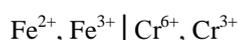
Abstract- Indirect reduction of hexavalent chromium to trivalent chromium by ferrous sulphate in the redox flow galvanic cell: $\text{Fe}^{3+}, \text{Fe}^{2+} | \text{Cr}^{6+}, \text{Cr}^{3+}$ with mesh electrodes was studied by measuring the polarization behaviour of the cell under different solution flow rates and different reactant concentrations. It was found that the rate of Cr^{6+} reduction as indicated by the cell current increases with increasing solution flow rate and reactant concentration. Within the present range of conditions, indirect Cr^{6+} reduction by FeSO_4 was found to be under mixed mass and charge transfer control. The advantages of the present technique over direct hexavalent chromium reduction by iron scrap were highlighted. Possible practical applications of the technique in treating industrial effluents containing Cr^{6+} were noted.

Keywords- Water Pollution; Hexavalent Chromium Removal; Redox Flow Galvanic Cell

I. INTRODUCTION

The high toxicity of hexavalent chromium and the necessity of its removal before biological treatment of wastewater have recently made its removal from industrial effluents a highly active research area especially with the increasingly stringent enforcement of pollution standards by governments. Waste solutions containing hexavalent chromium are produced by industries such as printed circuit etching, chromium plating, anodizing of Al, chromate conversion coating of Zn and Al, production of pigments, textile dyeing, wood preservation, passivation of steel, organic synthesis and pharmaceutical industry where hexavalent chromium is used as an oxidizing agent. Although several removal techniques have been studied such as ion exchange, adsorption, solvent extraction, membrane separation, direct reduction with scrap iron, photocatalytic reduction and electrolytic reduction^[1-8], the traditional method of direct chemical reduction by a suitable reducing agent such as SO_2 and FeSO_4 is still the most popular method on the commercial scale despite the inherent shortcomings such as air pollution in the case of using SO_2 and sludge formation in the case of using FeSO_4 ^[4].

The present work represents an attempt to explore the possibility of indirect reduction of hexavalent chromium by ferrous sulfate in the redox flow galvanic cell:



by using screen electrodes in view of their turbulence promoting ability under flow conditions^[9, 10].

The main aim of the present study is to shed some light on the kinetics of indirect galvanic reduction of Cr^{6+} along with the performance characteristics of the galvanic cell which serves simultaneously as a reactor and electrical energy generator. The present work was motivated by the fact that indirect Cr^{6+} reduction would offer the following advantages over direct reduction:

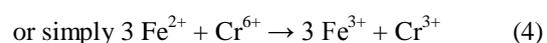
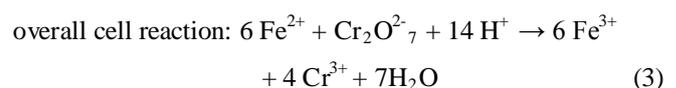
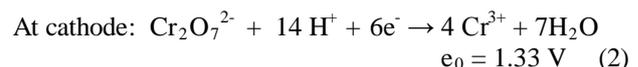
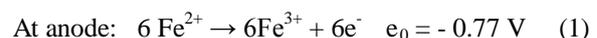
(i) A trivalent chromium salt free of iron salt is obtained, the resulting trivalent chromium salt can be treated with alkali to obtain pure $\text{Cr}(\text{OH})_3$ which can be utilized in pigment production (Cr_2O_3) or trivalent salt production.

(ii) The process does not need external energy or expensive chemicals. The resulting Fe^{3+} can be reduced back to Fe^{2+} by iron scrap in a separate reactor. Galvanic reduction of Cr^{6+} generates direct current electrical energy which can be stored in an accumulator and exploited beneficially, e.g., in the cathodic reduction of more Cr^{6+} in an electrolytic cell^[7].

(iii) Cr^{6+} galvanic reduction would produce far less sludge than direct chemical reduction^[4].

In a previous related study^[8], indirect Cr^{6+} reduction using iron electrode in the galvanic cell $\text{Fe}, \text{Fe}^{2+} | \text{Cr}^{6+}, \text{Cr}^{3+}$ was studied. Although the results show that the above cell is promising, it has some drawbacks such as (i) Fe dissolution is relatively slow, i.e., accompanied with high activation polarization^[11] and (ii) Fe tends to passivate especially at high current density and low acidity^[11].

The present study seeks to eliminate the above drawbacks by using the redox system $\text{Fe}^{2+}, \text{Fe}^{3+}$ instead of the iron electrode. The present cell involves the reactions:



The free energy, ΔG , of the above reaction is given by^[11]:

$$\Delta G = \Delta G_o + R_T \ln \frac{[\text{Fe}^{3+}]^3 [\text{Cr}^{3+}]}{[\text{Fe}^{2+}]^3 [\text{Cr}^{6+}]} \quad (5)$$

At equilibrium, $\Delta G = 0$ and

$$\frac{[\text{Fe}^{3+}]^3 [\text{Cr}^{3+}]}{[\text{Fe}^{2+}]^3 [\text{Cr}^{6+}]} = K \quad (6)$$

Accordingly, at equilibrium the standard free energy change, ΔG_0 , is related to the equilibrium constant K by the equation:

$$\Delta G_0 = -RT \ln K \quad (7)$$

Eliminating ΔG_0 between the above equation and $\Delta G_0 = -ZE_0F$ leads to:

$$E_0 = \frac{RT}{ZF} \ln K \quad (8)$$

For the present cell, $E_0 = -0.77 + 1.33 = 0.56$ V

i.e.,

$$0.56 = \frac{0.059}{3} \log K$$

From which $K = 2.63 \times 10^{28}$

The high equilibrium constant of the present cell reaction shows that Cr^{6+} concentration could be reduced to a very low level if the operating conditions of the cell are optimized. Although redox flow cells are usually used for converting chemical energy into electrical energy [12], their use in conducting spontaneous reactions which leads to an important product or pollutant removal was pioneered by Langer and Anderson [13]. The rate of Cr^{6+} reduction was determined in the present work from polarization data [14-16].

II. EXPERIMENTAL TECHNIQUE

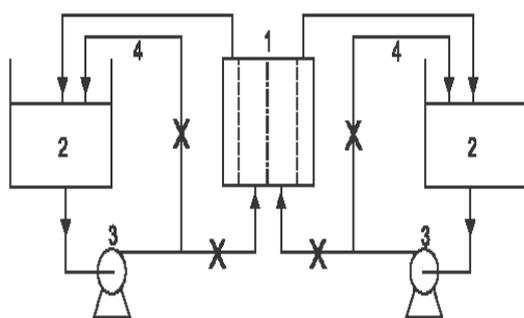


Figure 1 The Apparatus

1. Cell; 2. Storage tank; 3. Centrifugal pump; 4. Bypass

Figure 1 shows the apparatus used in the present study, the apparatus consists of two 5 L Plexiglass storage tanks for storing acidified dichromate and acidified ferrous sulfate solutions and a Plexiglass galvanic cell.

The cell (Fig. 2) consisted of two compartments separated by an anion exchange membrane, each compartment containing a vertical platinized titanium screen electrode of 12 mm active height and 15 mm width, wire diameter = 0.07 mm, mesh number = 154 wire/inch and porosity = 0.72. The two electrodes were separated by a

distance of 3.6 cm, each electrode was separated from the membrane by a distance of 1.8 cm. The cell contained four openings, two at the lower side and two at the upper side, for the inlet and outlet of the electrolyte, respectively.

The cell was fitted with two reference saturated calomel electrodes ($\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{Cl}$) one in the cathode compartment and the other in the anode compartment to measure the cathode and the anode potentials, respectively. Before each run, five litre of acidified potassium dichromate and five litre of acidified ferrous sulfate solutions were prepared in the anolyte and the catholyte storage tanks, respectively.

In preparing the potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) solution and FeSO_4 solution, 1 M sulfuric acid was used as supporting electrolyte. The high concentration of H_2SO_4 compared to FeSO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ concentration not only improves solution conductivity but also eliminates electrical migration of $\text{Cr}_2\text{O}_7^{2-}$ ions across the anion exchange membrane [11]. In all cases the concentration of FeSO_4 was equal to that of $\text{K}_2\text{Cr}_2\text{O}_7$. All solutions were prepared using A.R. chemicals and distilled water.

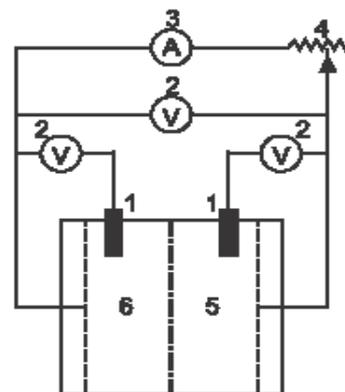


Figure 2 Electrical Circuit

1. Reference electrode; 2. Voltmeter; 3. Multirange ammeter; 4. Variable resistance; 5. Cathode compartment; 6. Anode compartment

Catholyte and anolyte were recirculated from their respective storage tanks to the cell by two plastic (glass-reinforced epoxy) centrifugal pumps. Flow rate of the solution was controlled by means of a bypass and was measured by a graduated cylinder and a stopwatch. In all cases the catholyte flow rate was equal to the anolyte flow rate. All valves and connecting pipes were made of Plexiglass. During solution circulation the cell voltage, and the cathode and anode potentials were measured at different cell currents which were controlled by a variable resistance connected in series with the cell. The total cell voltage was measured by a high impedance digital voltmeter connected in parallel with the cell while anode and cathode potentials were measured against saturated calomel electrode by high impedance digital voltmeter, cell current was measured by an ammeter connected in series with the cell (see Fig. 2). The temperature was maintained at $25 \pm 1^\circ\text{C}$.

III. RESULTS AND DISCUSSION

Figure 3 shows typical polarization curves for the cathodic and anodic reactions at three different solution flow rates. The intersection of the anodic and cathodic polarization curves gives the maximum cell current which reflects the maximum rate of chromate reduction under the prevailing conditions.

Figures 3 and 4 show that the maximum cell current and the maximum rate of chromate reduction increase with increasing catholyte and anolyte solution flow rates. The increase in the maximum cell current and the maximum rate of chromate reduction with increasing solution flow rate is ascribed to the decrease in concentration polarization at the anode and the cathode as a result of mass transfer enhancement. The absence of limiting current plateau from cathodic and anodic polarization curves rules out the possibility that the process is under complete diffusion control.

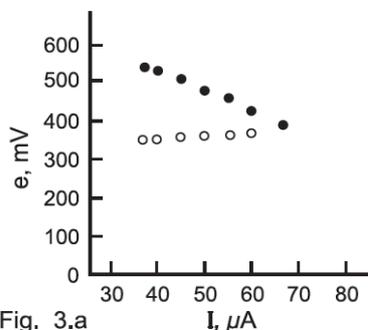


Fig. 3.a

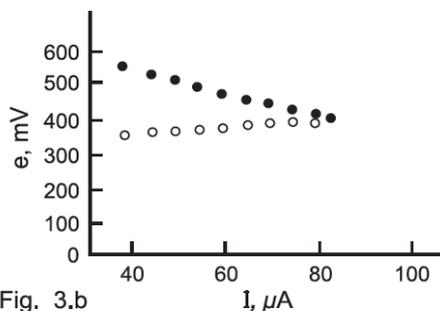


Fig. 3.b

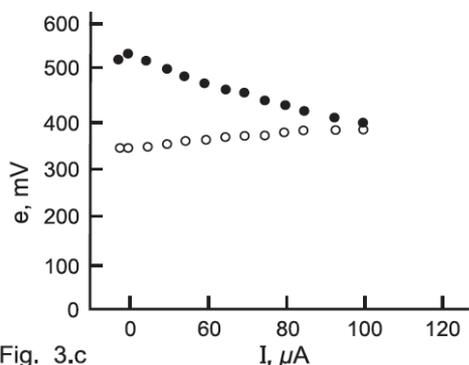


Fig. 3.c

Figure 3 Polarization Curves at three different solution flow rates

3a. $Q = 1.67 \text{ cm}^3/\text{s}$; 3b. $Q = 5.1 \text{ cm}^3/\text{s}$; 3c. $Q = 10.7 \text{ cm}^3/\text{s}$

However the response of the polarization data to solution flow rate suggests that the process is under mixed

charge transfer and mass transfer control. Figure 4 shows the effect of solution flow rate on the maximum cell current I . The rate of Cr^{6+} reduction can be approximated by the equation:

$$I = a Q^{0.25} \tag{9}$$

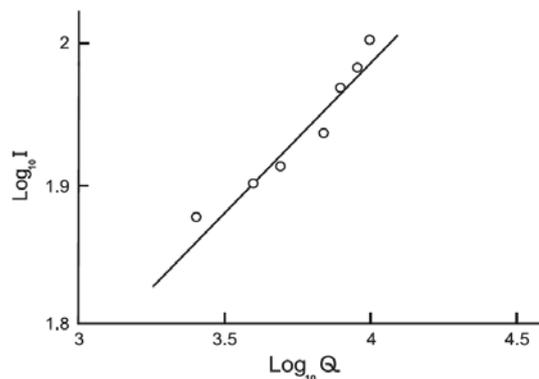


Figure 4 Effect of solution flow rate on the maximum current

Previous mass transfer studies on the effect of solution flow rate on the rate of diffusion controlled reactions at screen electrodes found that the reaction rate increases with Q raised to a power ranging from 0.33 to 0.37^[17-22].

The fact that hexavalent chromium reduction by the present technique is under mixed mass and charge transfer control is consistent with the fact that the system $\text{Fe}^{2+}, \text{Fe}^{3+}$ is fast (reversible)^[23] while the system $\text{Cr}^{6+}, \text{Cr}^{3+}$ is slow (irreversible) on platinum^[24].

The performance of the cell as energy generator was characterized in terms of the current vs. cell voltage relation, the voltage efficiency and the output energy in kWh/kg of $\text{Na}_2\text{Cr}_2\text{O}_7$ in the cell. Figure 5 shows the current-cell voltage relationship at different solution flow rates, the current corresponding to a certain voltage increases with increasing solution flow rate owing to the decrease in concentration polarization at the anode and the cathode as a result of decreasing the diffusion layer thickness at the two electrodes and the subsequent increase in the rate of diffusion of electroactive ions to the electrodes. Figure 6 shows the current-cell voltage relation at different electrolyte concentrations, the current corresponding to certain cell voltage increases with increasing electroactive ion concentration owing to the decrease in concentration polarization as a result of the increase in the rate of diffusion of the electroactive ions to the electrode surface.

The voltage efficiency ($V.E.$) of the cell was calculated from the equation:

$$V.E. = \frac{E}{E_{eq}} \times 100 \tag{10}$$

where E is the actual cell voltage and is given by

$$E = E_{eq} - (\eta_a + \eta_c + IR) \tag{11}$$

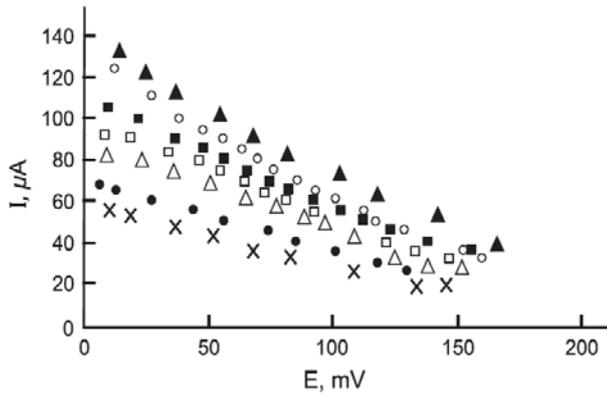


Figure 5 Current vs. Cell Voltage at different solution flow rates
 FeSO₄ Conc.= 0.08 M; Na₂Cr₂O₇ Conc. = 0.08 M
 Q, cm³/s: X—0.54; Δ— 3.9; ●— 2.8; □— 6.2;
 ■— 7.3; ○—8.4; ▲— 10.7

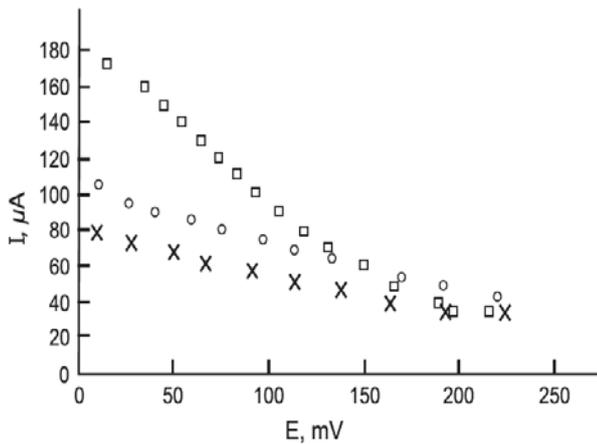


Figure 6 Current vs. Total Cell Voltage at different electrolyte concentrations.

FeSO₄ and Na₂Cr₂O₇ Conc. (M)
 X— 0.01; ○— 0.02 □— 0.1

The equilibrium cell voltage (E_{eq}) is given by:

$$E_{eq} = e_{anode} + e_{cathode} \tag{12}$$

$$e_{anode} = e_o - \frac{RT}{ZF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \tag{13}$$

$$e_{cathode} = e_o - \frac{RT}{ZF} \ln \frac{[C_r^{3+}]^4}{[C_{r2}O_7^{2-}][H^+]^{14}} \tag{14}$$

η_a = Concentration and activation polarization at the anode
 η_c = Concentration and activation polarization at the cathode

IR = Ohmic drop due to the internal cell resistance.

The equilibrium voltage (open circuit voltage) of the cell measured by a high impedance digital voltmeter was 0.37 V under the present conditions.

The output energy ($O.E.$) from the cell was calculated from the equation:

$$O.E. = \frac{I \times E}{1000 \times m} \tag{15}$$

where m is the amount of Na₂Cr₂O₇ reduced in the cell in kg/h, calculated from the Faraday's law.

Table 1 shows the cell voltage, voltage efficiency and output energy at different cell currents. As the current withdrawn from the cell increases, the cell voltage, voltage efficiency and output energy decrease because of the increase in activation polarization, concentration polarization and Ohmic drop (IR). This finding is consistent with the results of previous studies conducted on other galvanic cells [8, 15, 16].

TABLE I EFFECT OF CURRENT ON CELL VOLTAGE, VOLTAGE EFFICIENCY AND OUTPUT ENERGY

Current (μA)	Total Cell Voltage (mV)	Voltage Efficiency	Output Energy kWh/kg of reduced Na ₂ Cr ₂ O ₇
22	250	67.6	0.154
30	200	54	0.123
42	150	40.5	0.093
52	100	27	0.062
62	50	13.5	0.031

Concentration of Na₂Cr₂O₇ = 0.01 M

Concentration of FeSO₄ = 0.01 M

Solution Flow Rate = 0.54 cm³/s

IV. PRACTICAL APPLICATION

Although this preliminary study has shown that indirect galvanic reduction of hexavalent chromium with FeSO₄ is thermodynamically and kinetically promising, the process needs to be improved by increasing the cell space time yield via using three dimensional electrodes such as a closely packed screen stack or fixed bed of carbon particles for the cathode and the anode. The high surface area of such electrodes would reduce the current density with a consequent reduction in activation polarization at the two electrodes while the turbulence promoting ability of such electrodes [9] would enhance the rate of mass transfer and reduce concentration polarization at the two electrodes. To further increase the capacity of the process, a multimodular stack in which the cells are electrically connected in series can be used. The resulting output electrical energy can be stored in an accumulator to be used in further Cr⁶⁺ reduction via electrolytic reduction [7]. Oxidized ferric sulfate from the cathode compartment can be reduced back to ferrous sulfate by iron scrap in a separate chemical reactor according to the equation:



Alternatively, other sources of inexpensive FeSO₄ can

be used such as pickling effluents of steel mills. The resulting Cr^{3+} can be precipitated by an alkali where it can be used in pigment manufacture and leather tanning.

The proposed redox flow galvanic electrochemical reactor can be operated as a batch recirculating or continuous reactor. To assess the economic feasibility and potential problems of the present technique compared to other techniques of hexavalent chromium reduction, such as direct reduction by chemicals (e.g. SO_2 , NaS_2O_4 , NaHSO_3 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_5$), electrolytic reduction, ion exchange and adsorption, a pilot plant study is needed.

V. CONCLUSIONS

This preliminary study has shown that indirect reduction of hexavalent chromium in the redox flow galvanic cell: $\text{Fe}^{2+}, \text{Fe}^{3+} | \text{Cr}^{6+}, \text{Cr}^{3+}$ can be used advantageously to remove the highly toxic hexavalent chromium from the effluents of a wide array of industries. Besides generating low voltage d.c. electrical energy, the technique has also the advantages of producing pure chemicals such as trivalent chromium salts and iron salts. The technique consumes only iron scrap and produces less sludge than direct reduction. Further refinement of the cell design and operation with favourable electroactive ion concentration, flow rates and the use of three dimensional electrodes would make the present technique more attractive for practical applications, especially for treating effluents with relatively high Cr^{6+} content.

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NOMENCLATURE

a	constant
e	Electrode potential, V
E	Cell Voltage, V
F	Faraday's Constant, 96487 Coulombs/equivalent
I	Current, A
I_m	maximum cell current, A
K	Equilibrium constant
m	Rate of $\text{Na}_2\text{Cr}_2\text{O}_7$ reduction, kg/h
R	Cell resistance, Ohms
Q	Catholyte and anolyte solution flow rate, cm^3/s
η_a	Activation polarization, V
η_c	Concentration polarization, V

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