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FLUIDIZED BED ELECTROWINNING OF CHROMIUM FROM VERY DILUTE SOLUTIONS

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ABSTRACT

The Fluidized Bed Electrochemical Reactor (FBER) was used to electrowin chromium from very dilute solutions, ranging in concentration from 0.52 to 3.12 g Cr/l at pH = 2. The cathode consisted of particulate chromium (450-600 μm diam.) with a current feeder made of carbon bars and a tubular lead anode in a cylindrical cell. The current efficiency was in the range of 0.08-0.22. The bed expansion, deposition rate, conversion ratio of Cr(VI) to Cr(III) and voltage - current characteristic of the cell were studied. The results indicate that the use of the FBER will make possible the removal of chromium from very dilute solutions without the introduction of other chemicals which would need to be removed or treated further downstream to satisfy environmental abatement codes.

INTRODUCTION

The conventional electrowinning cell in electrometallurgy usually operates at low space-time yield for removal or recovery of metals from dilute solutions. The fluidized bed electrochemical reactor, first proposed in the late 1960's can potentially improve

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the specific productivity in the electrodeposition of metals (1,2,3). Many studies have since been made on the application of FBER to the electrowinning of metals (4). The FBER has the following advantages when compared to conventional planar electrodes.

1) The particulate electrode has a large specific surface area, which allows electrowinning to operate at a higher current density than the conventional planar electrode cell by one or two orders of magnitude.

2) The turbulence between metal particles and catholyte is certain to improve mass transfer.

3) The continuous recovery of metal in dilute solution may be possible with the introduction of small particles at the top of the bed and extraction of the grown particles at the bottom (5).

Chromium is always included in the list of strategic and critical minerals since the United States imports all of its primary chromium ore requirements (6,7). It is used in large amounts for superalloys, metal surface coatings, and corrosion control. The recovery and removal of chromium from dilute solutions, such as mine dump ore leachates, plating effluents, printed circuit board etchants and other industrial waste streams are of interest not only for the secondary resource recovery or recycling of chromium but also from an environmental pollution abatement aspect. The electrochemical approach to chromium recovery does not introduce into the system chemicals that eventually have to be treated downtream.

Electrodialysis techniques have been examined for the regeneration of spent etchant solutions (8,9,10). Soboroff, Troyer and Cochran (11) reported a technology for the regeneration and recycling of waste chromic acid-sulfuric acid etchants using a diaphragm cell. McDonald, Soboroff and Cochran (12) reported electrolytic reduction of Cr(VI) and Cu in surface-finishing operations by using coke electrodes for the reduction of Cr(VI) to the less toxic Cr(III) form. In this report, the feasibility of recovering chromium in the concentration range of 0.52 to 3.12 g/l was carried out using a fluidized bed electrochemical reactor.

EXPERIMENTAL

A side-by-side electrode (SSE) was chosen as the cell configuration. The reactor was constructed from a plexiglass cylinder, 31.75 cm long, 10.16 cm O.D. and 7.6 cm I.D. The ends of the reactor were machined from a 10-cm- diameter Teflon rod. The cathode chamber was located in the annular space between the reactor wall and the cylindrical diaphragm. Six carbon bars projecting into the center of the fluidized bed served as current feeders. A Teflon porous plate, serving as the distributor, was positioned directly below the plexiglass cylinder and supported the particulate cathode. The distributor ensured uniform catholyte flow across the cathode chamber. The anode, a 1.14 cm O.D. and 0.53 cm I.D. lead tube, was located inside the cylindrical diaphragm and served as the inlet for the anolyte. The part above the height of the expanded bed for anode and current feeder was insulated with heat shrinkable polyolefin tubing. The membrane used to separate the cathode and anode chambers was a porous Vycor glass tube (Corning Glass Co.) 30.5 cm long, 3.5 cm O.D. and 3.0 cm I.D. The hydrogen ion selectivity of the membrane helped to maintain low resistance for the cell circuit. The -20 mesh chromium particles (Thiokol Co.) were ground and sieved, and the powder in the range of 450-600 m was used as the particulate cathode. The mean diameter was used to estimate the specific surface area with an assumed shape factor of 0.70 for the non-spherical particles.

A batch recycling FBER system was used in this work and is shown in Fig. 1. A cooling coil in the catholyte reservoir controlled the temperature fluctuations in the catholyte to less than ± 1°C. The catholyte and anolyte were recycled using peristaltic pumps. The power supply was a Raytheon Co. DCR10-170B rectifier and voltage stabilizer.

Chromium concentration was determined using a Perkin-Elmer 2380 atomic absorbtion spectrophotometer. The Cr(III) and Cr(VI) concentrations were determined using a Spectronic 700 spectrophotometer. The experimental parameters for the FBER and the operational conditions are summarized in Table 1.

RESULTS AND DISCUSSION

Bed Expansion

The bed expansion was measured under variable catholyte flowrate in the range of 40 to 110 cm^3/sec. The particulate cathode bed was pulsating under this condition. Figure 2 shows the relationship of bed expansion to catholyte flowrate. The corresponding bed voidage ε, at a specified bed expansion, E, can be calculated from the equation:

$$\varepsilon = \frac{E + \varepsilon_o}{1 + E} \qquad [1]$$

where ε_o is the bed voidage at the static bed condition. The FBER operated as a boiling bed, when the bed expansion was between 0.2-0.4.

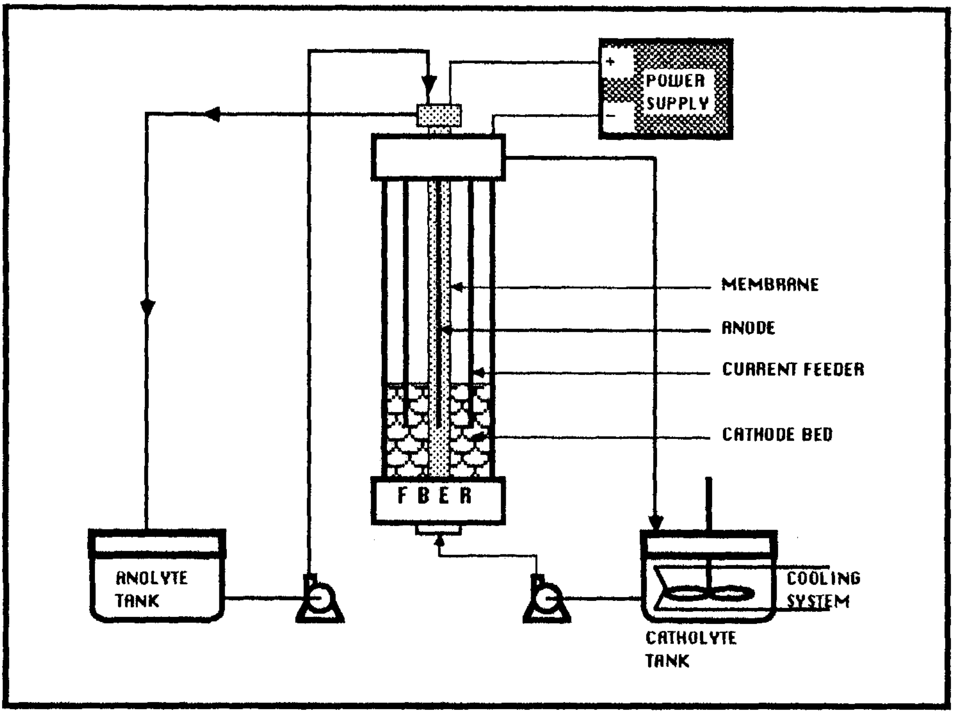

Figure 1. Schematic diagram of experimental system.

The plot of cell current versus bed expansion with cell voltage as a parameter is shown in Fig. 3. A maximum current is reached when the bed expansion is between 0.25-0.30. The results also show a linear relationship between the cell current and voltage.

The cell current increases with bed expansion to a maximum because of the increase in current loss due to the separation and intermittent contact of the particulates during the fluidization. With further bed expansion the electrical contact between the particles decreases. The increased loss of contact results in a net loss in current carrying capacity. On this basis, all subsequent experimental runs were carried out at a 0.25 bed expansion.

Cathode and Anode Reactions

The CrO_3-H_2SO_4 system was used as catholyte and no impurity components were added. The performance of the FBER in electro-

Table 1. Summary of Experimental Parameters

FLUIDIZED BED		
width	2.05 cm	
depth	4 cm	
anode	lead tube, 1.14 cm O.D.	
cathode	chromium particles, 450-600 m	
	mass = 320 g	
	surface area = $\frac{0.78m^2}{320g}$ = 0.002438 m^2/g	
current feeder	6 carbon bars	
	cross section 1.7 cm width, 4.2 cm length	
	and 0.45 cm thickness	
diaphragm	Vycor porous glass tube	
	length	30.5 cm
	O.D.	3.5 cm
bed expansion	0.25	$\left(\frac{\text{fluidized bed length}}{\text{settled bed length}} - 1\right)$
CATHOLYTE CONCENTRATION		
CrO_3	1.0-6.0 g/l (0.52-3.12 g Cr/l)	
H_2SO_4	1.84 g/l	
ANOLYTE CONCENTRATION		
H_2SO_4	1.84 g/l	
CELL VOLTAGE	5-10 V	
CURRENT	0.3-0.9 A	
SUPERFICIAL CURRENT DENSITY	0.38-1.15 A/m^2	area = $0.78m^2$
TEMPERATURE	21-23°C	

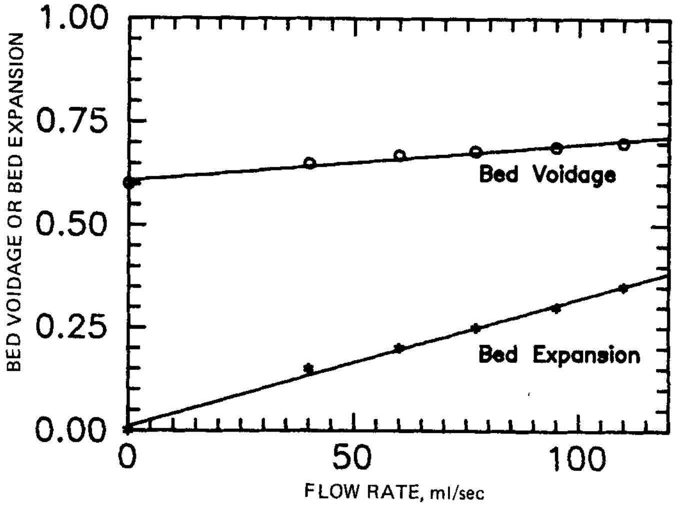

Figure 2. Plot of bed expansion and voidage vs catholyte flowrate.

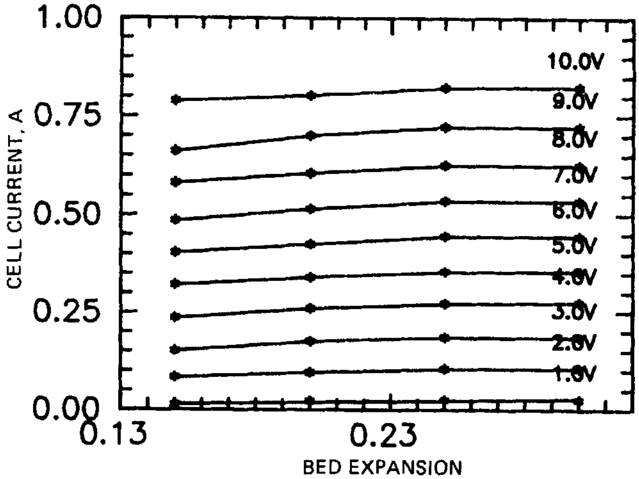

Figure 3. Plot of cell current vs bed expansion under different voltage.

winning chromium was examined at low chromium concentrations (0.52-3.12 g Cr/l) and a pH of approximately 2. This is similar to the leaching solution from a chromium ore reported by Mantell (13). The lower pH also alleviates the dissolution loss of chromium powder during the electrodeposition experiment.

The following equilibrium reactions are established in aqueous solution of CrO_3. Their corresponding equilibrium constants K are given by Hartford (14).

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \qquad K = 0.18 \qquad [2]$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^= \qquad K = 3 \times 10^{-7} \qquad [3]$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O \qquad K = 43.5 \qquad [4]$$

$$H^+ + Cr_2O_7^= \rightleftharpoons HCr_2O_7^- \qquad K = 3.0 \qquad [5]$$

The equilibrium reaction (4) is regarded as a dimerization reaction. The higher forms of chromate polymers found in high concentrations of chromate were not significant at our experimental conditions. The forms of chromate ions are dependent on the total Cr(VI) concentration and pH. According to the predominance diagram showing the relative distribution of different Cr(VI) species as a function of total Cr(VI) concentration and pH, the $Cr_2O_7^=$ with orange color should be the predominant species (15). In our electrowinning experiments, the color of the catholyte changed from orange to dark green, which is the color of $Cr(H_2O)_6^{3+}$.

Chromium ions in aqueous solution exist in various valences which can form different complexes and polymers. All these effects complicate the electrowinning process. Present thinking on the mechanism of chromium deposition is that it takes place from a cathode film and not directly from the bulk of the catholyte (16). In the film, Cr(VI) is first reduced to Cr(III). The fraction of Cr^{3+} protected by the chromic dichromate complex $[CrO_2HCr_2O_7]^=$ is further reduced to Cr(II) and Cr(0). The remaining Cr^{3+} exists in the form of $Cr(H_2O)_6^{3+}$ whose inner coordination sphere is so tightly bound that it is impossible for the Cr^{3+} to be reduced further (17). The bisulfate ion could catalyze the reduction of Cr(II) to Cr(0) and the formation of the chromic dichromate complex.

Table 2. Anode and Cathode Reactions in the Electrowinning of Chromium

In chromium powder cathode

$Cr_2O_7^{=} + 14H^+ + 6e \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E_o = 1.33V$ [6]

$Cr^{3+} + 6H_2O \rightleftharpoons Cr(H_2O)_6^{3+}$ [7]

$Cr^{3+} + e \rightleftharpoons Cr^{2+} \qquad E_o = -0.41V$ [8]

$Cr^{2+} + 2e \rightleftharpoons Cr^o \qquad E_o = -0.91V$ [9]

$2H^+ + 2e \rightleftharpoons H_2\ (g) \qquad E_o = 0$ [10]

In lead anode

$2Cr^{3+} + 7H_2O \rightleftharpoons Cr_2O_7^{=} + 14H^+ + 6e \qquad E_o = -1.33V$ [11]

$2H_2O \rightleftharpoons 4H^+ + O_2(g) + 4e \qquad E_o = 1.23V$ [12]

During the experiment it was observed that oxygen and hydrogen bubbles were evolved on the anode and the cathode. These side-reactions would increase the resistance of the cell and result in lower current efficiency.

From the preceding considerations, the expected reactions that would occur in the cathode and the anode are listed in Table 2.

The Conversion Ratio of Cr(VI) to Cr(III)

The products of Cr(VI) reduction in the bulk solution are the species, Cr(III) and Cr(0). It is obvious that:

the disappearance mass of Cr(VI), Δm_6 =
the yield of Cr(III), Δm_3 + the yield of Cr(0), Δm_o [13]

The color change of the catholyte implies that the species Cr_2O_7 is reduced to $Cr(H_2O)_6^{3+}$. Figure 4 shows the correlation

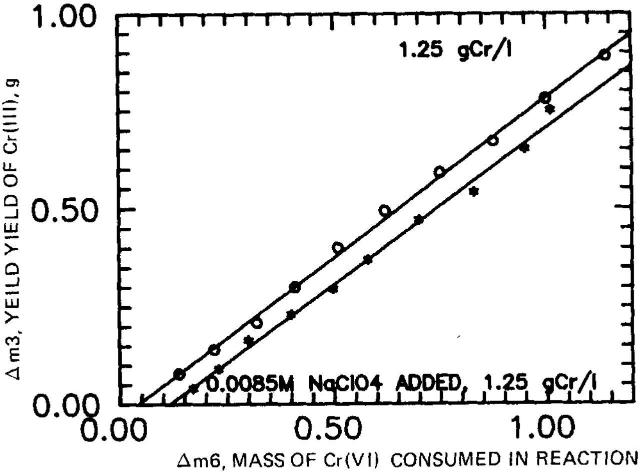

Figure 4. Mass of Cr(VI) consumed in reaction vs yield of Cr(III), with cell voltage of 10V.

between the disappearance of mass of Cr(VI), $-\Delta m_6$, and the yield of Cr(III), Δm_3 for a cell voltage of 10 V and initial Cr(VI) concentration of 1.25 g Cr/l.

The conversion ratio, $\zeta = \Delta m_3/\Delta m_6 = 0.77$, was calculated from the data given in Table 3. Under the same experimental conditions as above, an oxidant, 0.0085 M $NaClO_4$, was added to the catholyte to oxidize the Cr(III) to Cr(VI). As a result, a parallel line was obtained. This indicates that the conversion ratio is characterized by the intrinsic kinetics of the electrowinning process. The reaction on the cathode surface is not affected by the added oxidant.

Electrowinning at Constant Current

Several runs were carried out at different chromium concentrations and constant current by adjustment of the cell voltage. The current efficiency was estimated from the mass deposition and total coulombs through the cell. The current efficiency, e, is given by the expression

$$e = \frac{V_c \Delta C_c - V_a \Delta C_a}{\frac{M}{FZ}(3600)ti} \qquad [14]$$

Table 3. Current Efficiency at Various Current and Cr(VI) Concentrations

Cr(VI) Conc. g Cr/l	Cell Current ma	Current Density Cathode A/M^2	Disappearance mass m_6 g	Yield of Cr(III) m_3 g	Current Efficiency Cr(VI) to Cr(III)	Current Efficiency Cr(VI) to Cr(O)	Reduction Rate Cr(VI) to Cr(III) $g\ Cr/M^2\ hr$	Deposition Rate Cr(VI) to Cr(0) $g\ Cr/M^2\ h$
3.12	450	0.58	0.400	0.308	0.353	0.210	0.171	0.0393
	600	0.77	0.540	0.420	0.361	0.206	0.231	0.0513
	750	0.96	0.722	0.556	0.382	0.228	0.308	0.0709
	900	1.15	0.698	0.537	0.369	0.222	0.358	0.0826
1.04	300	0.38	0.168	0.129	0.222	0.134	0.072	0.0167
	450	0.58	0.274	0.211	0.242	0.144	0.117	0.0269
	600	0.77	0.388	0.299	0.257	0.153	0.166	0.0380
0.52	300	0.38	0.100	0.077	0.132	0.079	0.043	0.0098
	450	0.58	0.156	0.120	0.138	0.083	0.067	0.0154

where	V_c	catholyte volume (l)
	ΔC_c	concentration change of catholyte (g Cr/l)
	V_a	anolyte volume (l)
	ΔC_a	concentration change of anolyte (g Cr/l)
	M	atomic weight of Cr
	F	96500 coulombs
	Z	valence of Cr
	t	time (hrs)
	i	current (A)

The correction term $V_a \Delta C_a$ represents the mass due to diffusion into the catholyte through the membrane.

According to Eq. (14), the concentration of chromium in the catholyte should decrease linearly with time. As expected, the Cr(VI) concentration decreased linearly with time and is shown in Fig. 5. The initial chromium concentrations were 0.52, 1.04 and 3.12 g Cr/l. The current efficiency can be obtained from the slope of the straight lines. For the reduction process of Cr (VI) to

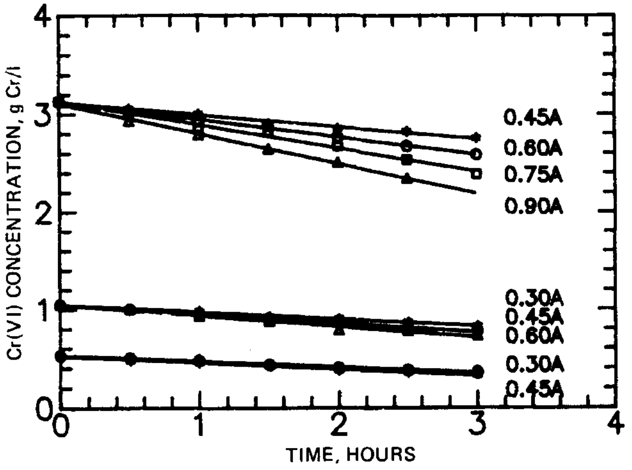

Figure 5. Cr(VI)concentration vs time, with constant current electrowinning.

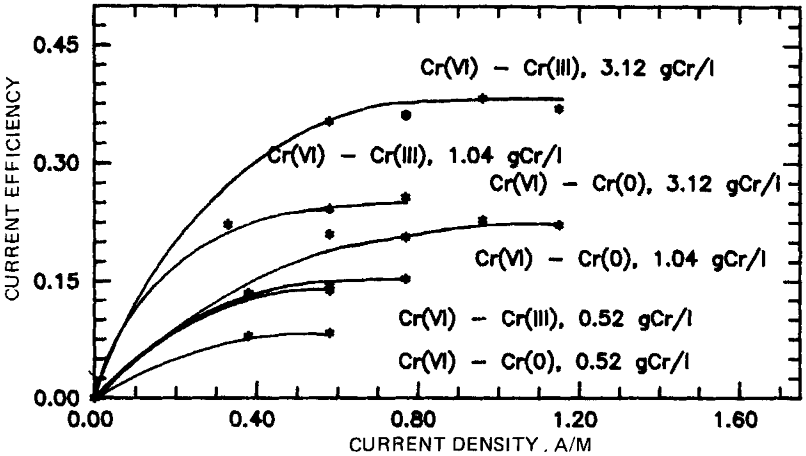

Figure 6. Current efficiency vs current density.

$Cr(H_2O)^{3+}$, Z=3 and $V_c \Delta C_c + V_a \Delta C_a$ = the yield of Cr(III). For that of Cr(VI) to Cr(0), Z=6 and $V_c \Delta C_c - V_a \Delta C_a$ = the yield of Cr(0), where the concentration increments ΔC_c and ΔC_a include the total concentration of Cr(III) and Cr(VI).

Figure 6 shows the relation of current efficiency to superficial current density at different Cr(VI) concentrations. The current efficiency increases with increasing current density and chromium concentration under these experimental conditions. The current efficiency of the reduction of Cr(VI) to Cr(0) ranged from 0.08-0.22. This value range is comparable to the current efficiency of the usual plating processes (18), even though much lower concentrations of chromium were used in this work. The typical concentration of Cr in a plating bath is 200-450 g CrO_3/l, and the current efficiency is between e = 0.08 and 0.15 (18). Figure 7 shows the deposition rate of chromium, from Cr(VI) to Cr(0), which increases with increasing current density and chromium concentration.

The plot of cell current versus cell voltage, shown in Fig. 8, indicates that the ohmic behavior of the cell is linear. This implies that the overpotential is small compared to the sum of the equilibrium potentials and the potential drops due to cell resistance.

The electrowinning data are given in Table 3 for different cell current values and the three initial concentrations of Cr(VI).

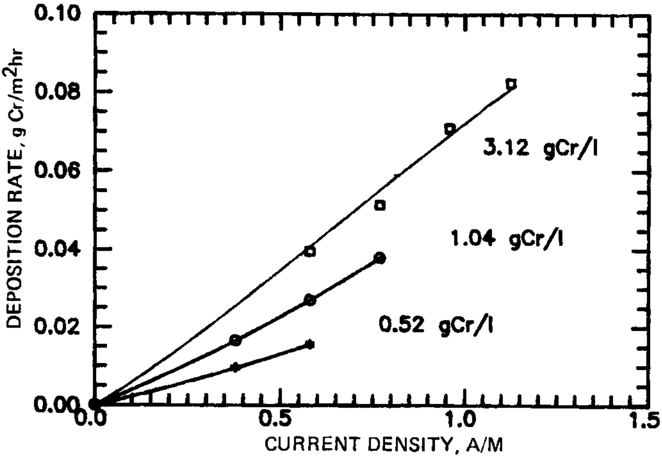

Figure 7. Deposition rate vs current density at different catholyte concentrations.

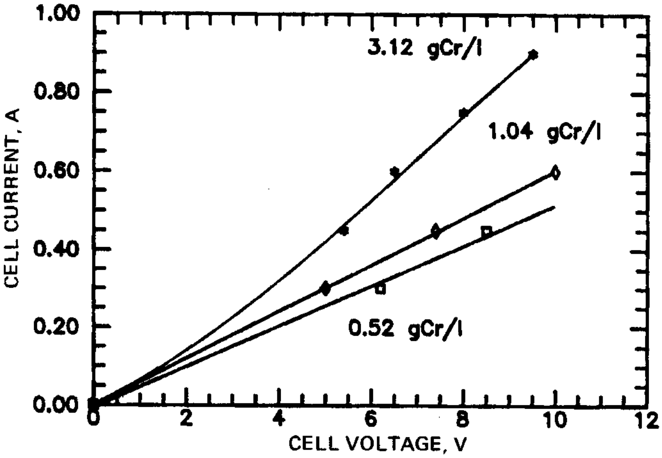

Figure 8. Cell current vs. cell voltage.

CONCLUSION

The FBER was used for the recovery and the removal of chromium from dilute solution. The chromium particulate cathode (450-600 microns diameter) with carbon bar current feeder and tubular lead anode were positioned in a cylindrical cell. Catholyte and anolyte were separated by a porous Vycor glass membrane selective to hydrogen ions.

Several runs were carried out at fixed current by adjustment of the cell voltage. The chromium concentration in the catholyte was varied from 0.52 to 3.12 g Cr/l, which is a much lower concentration than that which is found in spent conventional plating baths. The initial concentration of H_2SO_4 in the catholyte and anolyte was 1.84 g/l in order to keep the pH about 2. The superficial current density was 0.38-1.15 A/M^2. The maximum current was reached at a bed expansion between 0.25-0.30. It was observed that the deposition process of Cr(VI) is interrupted by formation of the stable complex $Cr(H_2O)_6^{3+}$. The conversion ratio of Cr(VI) to Cr(III) is about 0.77, thus helping to reduce the concentration of the toxic Cr(VI) in solution. The current efficiency of chromium deposition is between 0.08-0.22 and the removal rate of Cr(VI) is between 0.04-0.36 g Cr/M^2hr. Both current efficiency and removal rate increased with increasing chromium concentration and current density.

Based on the above results, the FBER is potentially useful in the recovery and removal of chromium from very dilute solutions at an acceptable current efficiency.

ACKNOWLEDGEMENT

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