The role of mass transfer in the electrolytic reduction of hexavalent chromium at gas evolving rotating cylinder electrodes

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The rate of electrolytic reduction of hexavalent chromium from acidic solution at a hydrogen–evolving rotating cylinder lead cathode was studied under conditions of different current densities, Cr^{6+} concentrations and rotation speeds. The rate of the reaction was found to follow a first order rate equation. The specific reaction rate constant was found to increase with increasing rotation speed until a limiting value was reached with further increase in rotation speed. Mechanistic study of the reaction has shown that at relatively low rotation speeds the reduction of Cr^{6+} is partially diffusion controlled, at higher speeds the reaction becomes chemically controlled. The limiting specific reaction rate constant was related to the operating current density by the equation $K = 0.044\, i^{1.385}$. The current efficiency of Cr^{6+}–reduction was measured as a function of current density, initial Cr^{6+} concentration and rotation speed. Possible practical applications are discussed.

Nomenclature

A	electrode area (cm^2)
a, b	constants in Equations 5 and 13, respectively
C	bulk concentration of Cr^{6+} at time t (M)
C_0	initial concentration of Cr^{6+} (M)
C_i	interfacial concentration of Cr^{6+} (M)
d	cylinder diameter (cm)
D	diffusivity of Cr^{6+} $(cm^2\,s^{-1})$
e_0	standard electrode potential (V)
F	Faraday's constant (96 487 C)
I_{H_2}	current consumed in hydrogen discharge (A)
i	current density $(A\,cm^{-2})$
I	cell current (A)
K_1	mass transfer coefficient $(cm\,s^{-1})$
K_r	mass transfer coefficient due to cylinder rotation $(cm\,s^{-1})$
K_0	natural convection mass transfer coefficient $(cm\,s^{-1})$
K_g	mass transfer coefficient due to hydrogen stir-

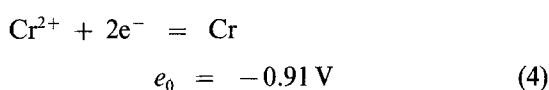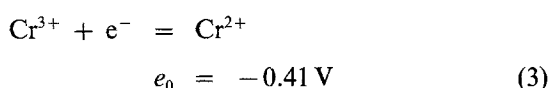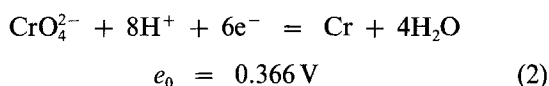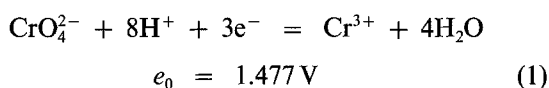|	
	ring $(cm\,s^{-1})$
K_2	specific reaction rate constant $(cm\,s^{-1})$
K	overall rate constant $(cm\,s^{-1})$
m	theoretical amount of Cr^{6+} reduced during electrolysis (g)
P	gas pressure (atm)
R	gas constant $(atm\,cm^3\,mol^{-1}\,K^{-1})$
T	temperature (K)
t	time (s)
V	linear speed of the rotating cylinder $(cm\,s^{-1})$
V_{H_2}	hydrogen discharge rate $(cm^3\,cm^{-2}\,s^{-1})$
V_s	solution volume (cm^3)
z	electrochemical equivalent $(g\,C^{-1})$
Z	number of electrons involved in the reaction
Re	Reynolds number (Vd/v)
Sh	Sherwood number $(K_r d/D)$
Sc	Schmidt number (v/D)
ω	rotation speed (r.p.m.)
v	kinematic viscosity $(cm^2\,s^{-1})$

1. Introduction

Hexavalent chromium reduction is receiving increasing industrial attention for many reasons, the most important of which is that Cr^{6+} is an environmental hazard. Waste waters polluted with toxic hexavalent chromium results from sources such as textile mills, the pigment industry, metal finishing industries (for example chromium plating and chromate conversion coating of metals), drug and organic chemical industries (where hexavalent chromium is used as oxidizing agent) and plant cooling systems where chromate is used as a corrosion inhibitor. So far, removal of hexavalent chromium from industrial waste solutions is carried out by chemical reduction, using reducing agents such as SO_2 or $FeSO_4$ [1]. Results of electrochemical removal of hexavalent chromium using three–dimensional electrodes such as reticulated carbon [2] or porous carbon [3] were not encouraging because of the simultaneous evolution of hydrogen bubbles which reduced the effective area of the reactor and increased the ohmic drop. Additionally, hydrogen evolution increases the local pH of the solution with a consequent precipitation of $Cr(OH)_3$ which plugs the

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pores of the three-dimensional electrode and decreases its effective area.

During the electrochemical reduction of hexavalent chromium the following reactions are thermodynamically possible:

$$CrO_4^{2-} + 8H^+ + 3e^- = Cr^{3+} + 4H_2O$$

$$e_0 = 1.477\,V \qquad (1)$$

$$CrO_4^{2-} + 8H^+ + 6e^- = Cr + 4H_2O$$

$$e_0 = 0.366\,V \qquad (2)$$

$$Cr^{3+} + e^- = Cr^{2+}$$

$$e_0 = -0.41\,V \qquad (3)$$

$$Cr^{2+} + 2e^- = Cr$$

$$e_0 = -0.91\,V \qquad (4)$$

$$Cr^{3+} + 3e^- = Cr$$

$$e_0 = -0.74\,V \qquad (5)$$

$$2H^+ + 2e^- = H_2$$

$$e_0 = 0 \qquad (6)$$
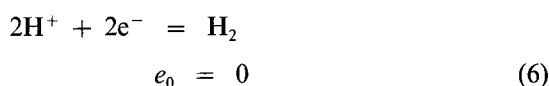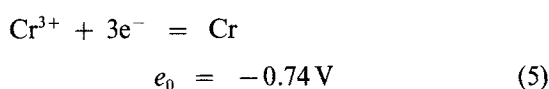
Previous studies using cyclic voltametry (CV) on the kinetics of the electrochemical reduction of hexavalent chromium revealed that the reduction products depend on the acidity of the solution. Golub and Oren [3] who used a porous carbon cathode and a solution having the composition $2\,mg\,dm^{-3}$ CrO_3, $0.5\,N$ Na_2SO_4 and $0.006\,M$ H_2SO_4, found the final product was only $Cr(OH)_3$.

The authors checked that no chromium metal was deposited on the cathode by X-ray diffraction. Diaz and Schermer [4], who used a platinum microelectrode and a solution having the composition $0.01\,M$ Cr^{6+} and $0.19\,M$ H_2SO_4 found that the final reduction product was Cr^{3+}. Electrolysis of solutions concentrated in Cr^{6+} led to the formation of insoluble Cr^{3+} salts on the cathode. Lee and Sekine [5] studied the electrochemical reduction of Cr^{6+} using different cathode materials and a solution of composition $3\,mM$ $K_2Cr_2O_7$ and $0.05\,M$ H_2SO_4, these authors found two reactions, namely, the reduction of Cr^{6+} to Cr^{3+} and hydrogen evolution. The absence of Reaction 3 in strong acidic solution is attributed to the instability of Cr^{2+} in strong acidic solutions [6, 14] where it is oxidized by H^+ and the excess Cr^{6+}. Previous studies [7, 8] on the electrodeposition of chromium metal from divalent and trivalent chromium salts have shown that it is not possible to deposit the metal from strongly acidic solutions below pH 1.8. Deposition of chromium metal from Cr^{6+} solutions is possible only within certain limits of the CrO_3/SO_4^{2-} ratio which ranges from 18.2 to 127.5; beyond these limits, deposition of chromium is not possible [9].

The object of the present work was to explore the possibility of using the rotating cylinder electrode for Cr^{6+} reduction from strongly acidic solution under hydrogen evolving conditions. These are likely to occur in practice where acidic dilute solution are dealt with. The rotating cylinder electrode has proved to be
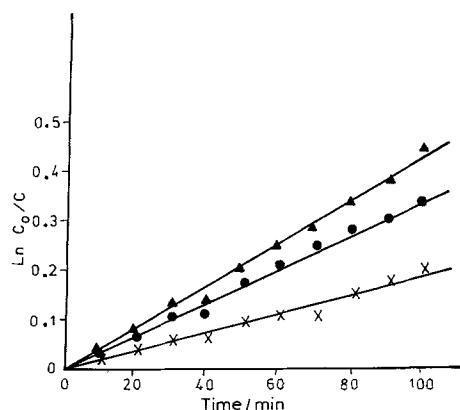

Fig. 1. Typical $\ln C_0/C$ against t for different rotation speeds. $[Cr^{6+}] = 10\,g\,dm^{-3}$; c.d. $= 0.075\,A\,cm^{-2}$. Rotation speed/r.p.m.: (x) 0, (●) 50 and (▲) 950.

efficient in waste water treatment [10–13]. Besides its ability to enhance the rate of reduction under partial or complete diffusion control, the use of this electrode in Cr^{6+} reduction would have the following specific advantages as a result of the favourable mixing conditions: (i) it would alleviate the problem of $Cr(OH)_3$ precipitation at the cathode surface caused by the local increase in solution pH as a result of simultaneous hydrogen evolution at the cathode; and (ii) it would prevent crystallization of the low solubility violet chromium sulphate produced during electrolysis on the cathode surface when processing relatively high chromium concentrations. Apart from the environmental importance of the present work, electrochemical reduction of hexavalent chromium is of special importance for the production of trivalent chromium chemicals which are traditionally produced in industry by chemical reduction of chromate obtained by roasting chromite ore with Na_2CO_3 [14, 15].

The present study used an experimental apparatus consisting of a rotating lead cathode surrounded by a set of graphite rod anodes in a single compartment cell. Lead was selected in view of its high hydrogen overpotential which favours high current efficiencies for hexavalent chromium reduction. Graphite was chosen as anode material in view of the fact that trivalent chromium is not reoxidized at graphite anodes [16]. Highly acidic Cr^{6+} solutions were used to avoid Reactions 2–5.

2. Experimental techniques

The cell was a $2\,dm^3$ glass container of 15 cm diameter and 23 cm height. A rotating lead cylinder of 2.9 cm diameter and 15 cm height, placed in the centre of the container, was used as a cathode. The cathode bottom was isolated with epoxy resin. The anode consisted of ten high grade graphite rods uiformly distributed at the container wall around the cathode, each rod being 1 cm in diameter and 25 cm high. The ten rods were fixed to a circular copper holder placed outside the solution; this holder also acted as a current feeder. The rotating cylinder cathode was driven by a variable speed motor connected to the rotating cylinder
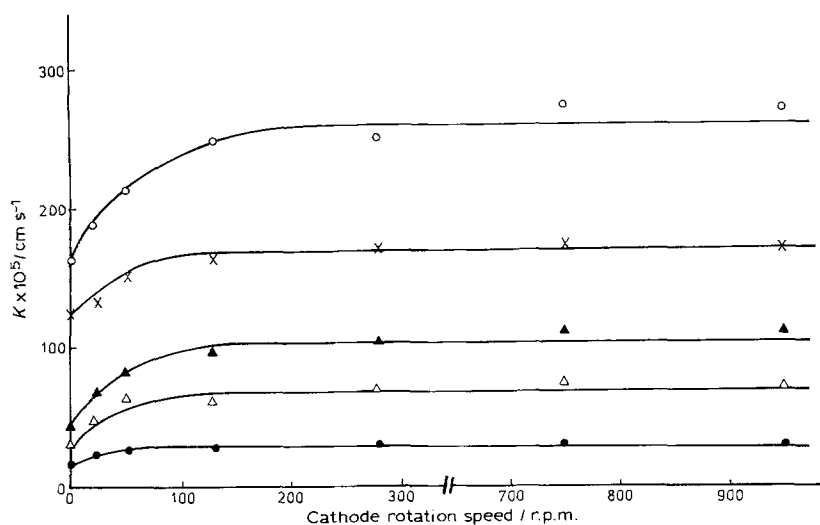
Fig. 2. Effect of cathode rotation speed on the rate constant of the reaction at different current densities. $[Cr^{6+}] = 10\,g\,dm^{-3}$. C.d./$A\,cm^{-2}$: (●) 0.025, (△) 0.05, (▲) 0.075, (x) 0.1 and (○) 0.125.

through a plastic sleeve to avoid current leakage. The motor was fixed firmly against a wall to avoid vibrations. The electrical circuit consisted of a 12 V d.c. power supply with a voltage regulator connected in series with a multi range ammeter and the cell.

Before each run the cell was filled with 12 dm³ of acidified chromate solution, the cathode rotation speed, which was adjusted by means of a variac connected to the motor, was measured by an optical tachometer. Care was taken to isolate the upper part of the rotating cathode with a Teflon tape to make sure that active part of the cathode lay below the solution vortex caused by cylinder rotation. Electrolysis was conducted at a constant current for 100 min at 25 ± 1° C. A 2 cm³ sample was taken every 10 min for hexavalent chromium analysis by adding a known excess of a standard ferrous ammonium sulphate solution and titrating it against standard $K_2Cr_2O_7$ using diphenylamine as indicator [6].

Electrolysis was conducted using different hexavalent chromium concentrations, namely: 1, 2.5, 5, 7.5 and 10 g dm⁻³ (as chromium): in all cases 1 M H_2SO_4 was used as a supporting electrolyte. CrO_3 was used as a source of hexavalent chromium. In preparing all solutions, distilled water and AR chemicals were used.
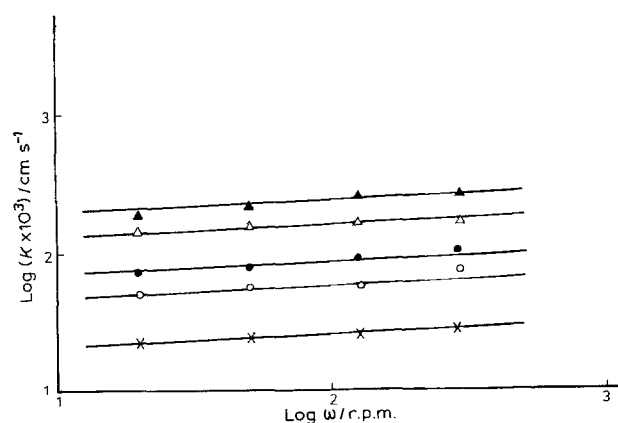
The current efficiency (c.e.) of Cr^{6+} reduction to Cr^{3+} was calculated under different conditions from the equation

$$c.e. = \frac{\text{Actual amount of } Cr^{6+} \text{ reduced to } Cr^{3+}}{\text{Theoretical amount of } Cr^{6+} \text{ reduced to } Cr^{3+}}$$

(1)

The theoretical amount (m) was calculated from Faraday's law of electrolysis:

$$m = zIt$$

(2)

The hydrogen discharge rate V_{H_2} was calculated from the current consumed in hydrogen discharge I_{H_2} using Faraday's law and the gas law

$$V_{H_2} = I_{H_2}\frac{RT}{2FPA}$$

(3)

The quantity I_{H_2} was obtained by subtracting the current consumed in Cr^{6+} reduction from the total cell current. The current consumed in Cr^{6+} reduction is the product of the total cell current and the current efficiency of Cr^{6+} reduction. The viscosity and density of the solution needed for data analysis were determined by an Ostwald viscometer and a density bottle respectively [17]. The diffusivity of Cr^{6+} was
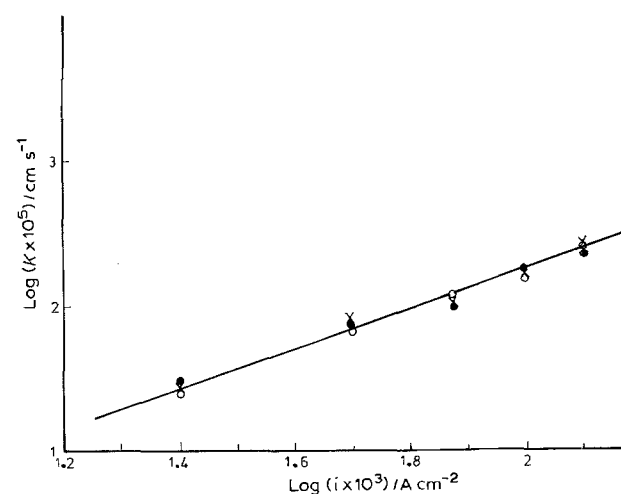

Fig. 3. Log K against log ω for the increasing rate region at different current densities. $[Cr^{6+}] = 10\,g\,dm^{-3}$. C.d./$A\,cm^{-2}$: (x) 0.025, (○) 0.05, (●) 0.075, (△) 0.1 and (▲) 0.125.

Fig. 4. Effect of current density on the limiting rate constant of the reaction. $[Cr^{6+}] = 10\,g\,dm^{-3}$. Rotation speed/r.p.m.: (●) 280 ($Re = 13\,800$), (x) 760 ($Re = 37\,400$) and (○) 950 ($Re = 46\,700$).
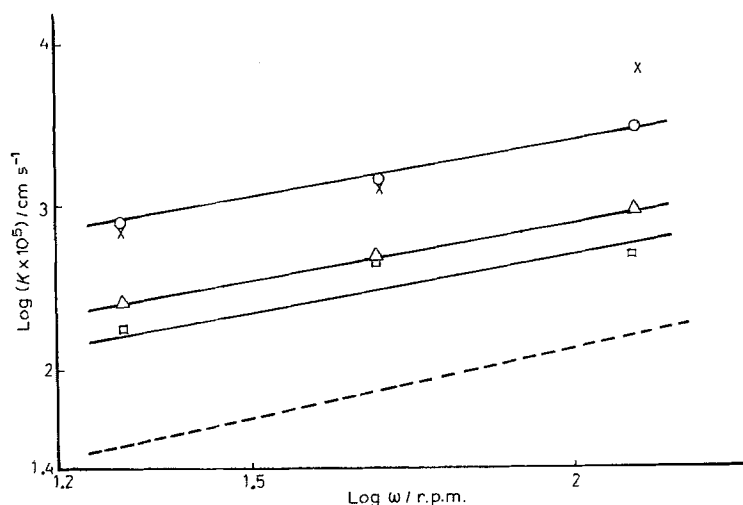
Fig. 5. Log K_1 against log ω for different current densities. C.d./A cm^{-2}: (x) 0.125, (O) 0.1, ($\triangle$) 0.075 and ($\square$) 0.05. (- - -) Mass transfer coefficient calculated from Equation 12.

obtained from the literature [4] and corrected for the change in viscosity and temperature.

To ensure that no chromium metal was deposited on the cathode during electrolysis under the present conditions residual Cr^{6+} and Cr^{3+} were analyzed after 100 min of electrolysis at different current densities as mentioned elsewhere [6]. In all cases the sum of the residual Cr^{6+} and Cr^{3+} was equal to the original Cr^{6+}. Additionally visual inspection of the cathode showed no chromium deposit.

3. Results and discussion

Figure 1 shows that the rate of Cr^{6+} reduction to Cr^{3+} fits the equation.

$$\ln \frac{C_0}{C} = \frac{KAt}{V_s} \qquad (4)$$

The specific reaction rate constant K was calculated from the slope of the ln C_0/C against t plot. Figure 2 shows the effect of cylinder rotation speed on the rate constant K at different current densities. The value of K increases with increasing cylinder rotation speed up to a certain value and then remains almost constant with further increase in rotation speed. Figure 3 shows that, for relatively low rotation speeds up to 280 r.p.m. ($Re = 13\,800$), K can be related to the rotation speed (ω) by the equation

$$K = a\omega^{0.1} \qquad (5)$$

The constant a in the above equation is a function of the operating current density. Figure 4 shows that the limiting specific reaction rate can be related to the operating current density by the equation.

$$K = 0.044\ i^{1.385} \qquad (6)$$

The rotation speed exponent 0.1 of Equation 5 is at variance with the value 0.7 obtained for fully diffusion controlled reactions [18]. The slight dependance of K on rotation speed as shown by Equation 5, before reaching the limiting value, suggests that the reaction is partially diffusion controlled at relatively low rotation speeds. With increasing rotation speed the reaction becomes fully chemically controlled. To substantiate this mechanism the reaction kinetics were

expressed mathematically as follows to calculate the hypothetical mass transfer coefficient due to cylinder rotation and compare it with the value calculated from the established rotating cylinder mass transfer equation [18].

Since reduction of Cr^{6+} involves two consecutive steps, namely a mass transfer step and a charge transfer step, the reaction rate can be written in terms of both steps. The rate of mass transfer is given by

$$-\frac{V_s}{A}\frac{dC}{dt} = K_1(C - C_i) \qquad (7)$$

Assuming a first order reaction, the rate of the chemical step is given by

$$-\frac{V_s}{A}\frac{dC}{dt} = K_2 C_i \qquad (8)$$

Eliminating C_i between Equations 7 and 8 gives

$$-\frac{V_s}{A}\frac{dC}{dt} = \frac{K_1 K_2}{K_1 + K_2} C \qquad (9)$$

Equation 9 can be written in the form

$$-\frac{V_s}{A}\frac{dC}{dt} = KC \qquad (10)$$

which integrates to Equation 4. From Equations 9 and 10

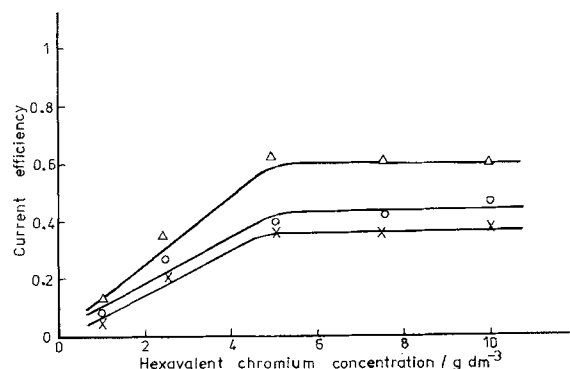$$K = \frac{K_1 K_2}{K_1 + K_2} \qquad (11)$$

Fig. 6. Effect of hexavalent chromium concentration on the current efficiency. Current density = 0.075 A cm^{-2}. Rotation speed/r.p.m.: (x) 0, (O) 50 and ($\triangle$) 280.
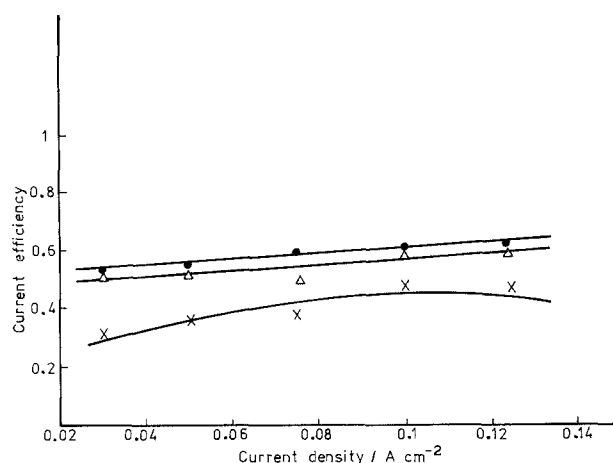
Fig. 7. Effect of current density on the current efficiency at different cathode rotation speeds. $[Cr^{6+}] = 10\,g\,dm^{-3}$. Rotation speed/r.p.m.: (x) 0, (△) 50 and (●) 280.

The hypothetical mass transfer coefficient K_1 was calculated for three different rotation speeds (20, 50 and 130 r.p.m.) and different current densities using Equation 11. The value of K_2 at different current densities used in calculating K_1 was taken as the limiting value shown in Fig. 2. Figure 5 shows the effect of rotation speed on the mass transfer coefficient K_1 in comparison with the value calculated from the established rotating cylinder equation 18

$$Sh = 0.079\,Sc^{0.356}\,Re^{0.7} \qquad (12)$$

Most of the data fit the equation

$$K_1 = b\omega^{0.68} \qquad (13)$$

The rotation speed exponent 0.68 is in agreement with the value given by Equation 12. This agreement lends support to the suggested partially diffusion controlled mechanism of the reaction at relatively low rotation speeds. Figure 5 shows that the present mass transfer coefficient K_1 is higher than the value calculated from Equation 12; generally, the higher the current density the higher the mass transfer coefficient K_1. This discrepancy may be attributed to the fact that K_1 is a composite mass transfer coefficient whose value is affected by cylinder rotation and H_2 stirring [19]. Additionally, it is probable that natural convection is operating under the present conditions where low rotation speeds and low hydrogen discharge rates, which ranged from 3.6×10^{-3} to $7.9 \times 10^{-3}\,cm^3\,cm^{-2}\,s^{-1}$, were used. Accordingly K_1 can be expressed

by the equation

$$K_1 = K_r + K_g + K_0 \qquad (14)$$

The increase in K_1 with increasing current density can be ascribed in part to the increase in the hydrogen discharge rate and the subsequent increase in the mass transfer coefficient due to hydrogen evolution K_g [19]. The direction and magnitude of natural convection and its variation with current density is difficult to assess owing to the lack of information on the density change in relation to the transport properties of some of the ionic species involved in the reaction at the cathode. Apart from the enhancing effect of cylinder rotation on the mass transfer coefficient K_1 at relatively low speeds, cylinder rotation increases the rate of Cr^{6+} reduction through decreasing the degree of cathode coverage by hydrogen bubbles and the consequent increase in the effective cathode area [20, 21]. However, it seems that this effect is modest; according to Leistra and Sides [22] who measured the degree of surface coverage by hydrogen bubbles in 1 M H_2SO_4 at cylindrical electrodes the degree of surface coverage does not exceed 3%.

Figure 6 shows the effect of Cr^{6+} concentration on the current efficiency of Cr^{6+} reduction at different cathode rotation speeds. The current efficiency increases with increasing Cr^{6+} concentration up to about $5\,g\,dm^{-3}$ and then remains almost constant with further increase in Cr^{6+} concentration. The increase in current efficiency with rotation speeds as shown in Fig. 6 is consistent with the effect of rotation speed on the reaction rate constant. Figure 7 shows that the current efficiency increases slightly with increasing current density at different rotation speeds. This study suggests that the rotating cylinder electrode can be used with advantage in the industrial production of trivalent chromium chemicals from concentrated chromate solution (obtained by roasting chromite ore with sodium carbonate). To assist in assessing the economic feasibility of using such a process in comparison with the traditional chemical reduction, power consumption was calculated for the reduction of $10\,g\,dm^{-3}\,Cr^{6+}$ at different current densities. Figure 8 shows that under the present conditions power consumption, which ranged from 6 to $17\,KW\,h\,kg^{-1}$ of reduced Cr^{6+}, increases with increasing current density and decreases with increasing cylinder rotation speed. The saving in power caused by cylinder rotation
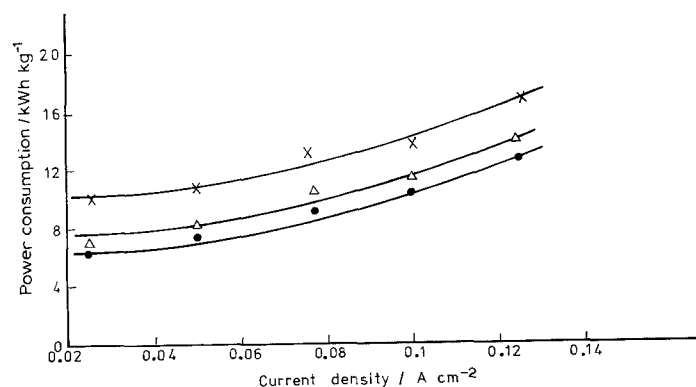

Fig. 8. Effect of current density on power consumption at different cathode rotation speed. $[Cr^{6+}] = 10\,g\,dm^{-3}$. Rotation speed/r.p.m.: (x) 0, (△) 50 ($Re = 2460$) and (●) 280 ($Re = 13\,800$).

is much higher than the mechanical power consumed in rotating the cylinder cathode. For rotation speeds of 50 and 280 r.p.m, the mechanical power required to rotate the cylinder was calculated as mentioned elsewhere [23] and found to be 2.7×10^{-5} and 2.9×10^{-3} W, respectively.

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