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Reduction of ferric ions in dilute solution in a semi-technical scale GBC reactor*

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The performance of a semitechnical gas diffusion electrode packed bed electrode cell (GBC) for the reduction of metal ions is investigated. Reduction of Fe^{3+} in sulphuric acid solution is described by first order kinetics and is found to be significantly influenced by temperature, H_2SO_4 concentration and the inlet concentration of Fe^{3+}. The condition of packing has a major influence on the overall conversion in the cell. It is shown that a slight decrease in the amount of bed particles can cause a significant drop in the overall degree of conversion. The mass transfer coefficient k_m is found to be proportional to $u_s^{0.48}$ at low flow velocities and $u_s^{0.80}$ at high flow velocities, where u_s is the mean flow velocity. Partitioning of the overall reaction rate, $k_{o,av}$, into an overall mass transfer coefficient $k_{m,av}$ and an apparent overall electrochemical rate constant, $k_{r,av}$, shows that, for H_2SO_4 concentration less than 1 M, $k_{r,av}$, can be described by an empirical relationship involving the effects of the inlet Fe^{3+} concentration, the solution conductivity and temperature.

Keywords: *Gas diffusion electrode*, *Packed bed electrode*, *Metal ion reduction*, *Mass transfer*

List of symbols

A_e	specific bed electrode area ($m^2\,m^{-3}$)
A_p	geometrical particle surface area (m^2)
C_{in}	inlet Fe^{3+} concentration ($mol\,m^{-3}$)
C_{out}	outlet Fe^{3+} concentration ($mol\,m^{-3}$)
D	diffusion coefficient ($m^2\,s^{-1}$)
d_p	average particle diameter (m); $d_p = \sqrt{(A_p/\pi)}$
E_D	diffusion activation energy ($kJ\,mol^{-1}$)
$k_{m,av}$	overall mass transfer coefficient ($m\,s^{-1}$)
$k_{o,av}$	apparent overall rate constant ($m\,s^{-1}$)
$k_{r,av}$	overall reaction rate constant ($m\,s^{-1}$)
N_A	Avogadro's number (mol^{-1})
Q_s	volumetric flow rate of solution ($m^3\,s^{-1}$)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
Re	Reynolds number, $Re = u_s d_p/v$
Sc	Schmidt number, $Sc = v/D$
Sh	Sherwood number, $Sh = k_m d_p/D$
r	molecular radius (m)
T	temperature (K)
u_s	mean velocity of solution ($m\,s^{-1}$)
V_r	volume of reactor (m^3)
X	degree of conversion, $X = (C_{in} - C_{\alpha t})/C_{in}$

Greek letters

α	constant in Equation 2
β	constant in Equation 3
γ	constant in Equation 5
ϵ_b	bed porosity
η	dynamic viscosity (Pa s)
κ_{eff}	effective solution conductivity ($S\,m^{-1}$)
κ_{sol}	solution conductivity ($S\,m^{-1}$)
v	kinematic viscosity ($m^2\,s^{-1}$)
τ	residence time (s), $\tau = \epsilon_b V_r/Q_s$

1. Introduction

The electrochemical reduction of metal ions in dilute solution is of much interest in the purification of waste waters and in the design of zero effluent systems. Conventional methods of addition of reductants into an effluent stream [1] are becoming less useful as environmental requirements become more stringent and requirements for even cleaner technologies for effluent treatment become necessary. Electrochemical methods are gaining popularity due to their versatility in the sense that both direct and indirect oxidations or reductions can be carried out, reactions may involve phase separations and quite varied levels of concentrations and quantities of waste may be handled. Electrochemical processes are usually conducted at low temperatures, thus ensuring low energy requirements. Electrochemical cells may be designed to minimize power losses, voltage drops and side reactions. In most cases, electrochemical processes offer environmental compatibility by providing a clean reagent [2].

The GBC (*g*as diffusion electrode packed *b*ed electrode *c*ell) process provides an alternative cleaner technology which utilizes hydrogen gas to reduce metal ions. The coupling of a gas diffusion electrode

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and a packed bed provides a means of treating metal ions in dilute solutions. The gas diffusion electrode (GDE) consists of carbon black bonded with Teflon on a Toray paper carrier. The reaction layer within the GDE consists of platinum on Vulcan XC-72. Hydrogen gas dissolved in the liquid phase within the GDE diffuses to the reaction layer catalytic sites near the liquid-gas interface where it reacts. The electrons generated are transferred via the gas diffusion electrode solid matrix to the reaction sites on the electrically conducting bed particles, where they are picked up by the metal ions to be reduced. The hydrogen ions diffuse from the GDE reaction layer through the liquid phase into the bed.

The processes involved are:

(i) Dissolution of H_2 gas in the liquid within the pores of the GDE
(ii) Diffusion of H_2 molecules to the reaction sites
(iii) Oxidation of H_2 according to

$$H_2(aq) \longrightarrow 2H^+(aq) + 2e^-$$

(iv) Transport of H^+ to the bulk of the liquid
(v) Transport of Fe^{3+} ions to the surface of the bed particles
(vi) Reduction of Fe^{3+} according to

$$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$$

(vii) Transport of Fe^{2+} ions into the bulk of the liquid.

In this arrangement, practically no hydrogen oxidation occurs on the packed bed/GDE interface and because of diffusion limitations, practically no metal ion reduction occurs within the GDE. More details of the process are reported elsewhere [3].

Electrochemical processes are usually accompanied by side reactions which affect process efficiency. Cathodic reduction of metal ions is normally accompanied by hydrogen evolution reaction as the main side reaction although oxygen reduction is also possible. The operation of GBC in undivided mode with no external power source can be applied to systems which are more electropositive than hydrogen. In such situations, the electrochemical reaction is spontaneous. Fe^{3+}/Fe^{2+} and CrO_4^{2-}/Cr^{3+} systems are examples of spontaneous reduction by hydrogen. Although no power source is used in this case, the reactions occurring are electrochemical in nature and the configuration is considered as a two electrode system.

Metal ion concentration in waste water streams can be as high as 10^5 ppm, while the maximum permissible levels are between 0.05 and 5 ppm. As the concentration of the metal ion becomes smaller, mass transport enhancement becomes increasingly important. The use of packed-bed electrodes is appropriate for mass transport enhancement. The overall reaction rate also depends on the potential distribution in the bed. The current distribution depends on the local concentration of the electroactive species, as well as the potential distribution. Potential distribution over the bed depends on the solution conductivity, applied voltage, cell geometry and transport properties. A major drawback of a porous electrode is the excessive potential drop in the solution due to its small effective conductivity. Because of the ohmic potential drop, the electrode reaction poorly penetrates the electrode matrix. The operation of packed-bed electrodes requires a careful selection of electrolytic conditions. One possibility is to operate the cell under diffusion control, thus giving maximum duty [2, 4–6], however the operation of an undivided GBC gives no possibility of externally fixing the cell potential, since potentials in the system are determined by the system itself. Due to plug flow characteristics in the GBC, the concentration of reactant in the bed varies from the maximum at the entrance to the minimum at the outlet. This fact may influence the reaction regime within the bed, where one part of the bed may be more influenced by diffusion, while the other part is influenced by an electrochemical reaction on the bed surface.

Experimental results for a laboratory scale GBC operated in a batch recycle mode are reported in [3, 7–9]. This paper evaluates the behaviour of a semi-technical scale undivided GBC operated in a single pass mode. The effects of temperature, supporting electrolyte concentration, solution flow rate and inlet concentration of the electroactive species are reported.

2. Experimental details

2.1. *The setup*

The experimental setup consisted of a cell, two vessels of 60 dm^3 each as feed and receiving vessels, a pump, a flow meter and a heat exchanger. A schematic representation of the setup is shown in Fig. 1. The cell consisted of an activated carbon (NORIT-RB1) bed in direct contact with a gas diffusion electrode (GDE). The bed had a thickness of 1 cm and a height of 20 cm and contained 234 g of activated carbon rods. The carbon rods had a diameter of 1 mm and length of between 1–4 mm. The average length of the rods was 1.8 mm. A 20 cm × 20 cm fuel cell grade gas diffusion electrode (GDE) on Toray paper purchased (E-TEK, USA) was used. The GDE had a platinum loading of 0.50 mg cm^{-2}. A schematic representation of the cell is shown in Fig. 2. To support the GDE against the pressure exerted on the bed side, a titanium mesh plate was placed against the GDE gas side. Moreover, excess pressure on the GDE against the bed was obtained by introducing a water column at the gas outlet. Pressure measurements were made using U-tube water manometers. The tapping for the U-tubes was located at the cell entrance and outlet.

2.2. *Solution, procedure and analysis*

Tracer studies were done using an aqueous 0.5 M K_2SO_4 solution. A constant volume of tracer of 2 cm^3 was injected as a pulse input. The solution conductivity at the inlet and the outlet of the GBC

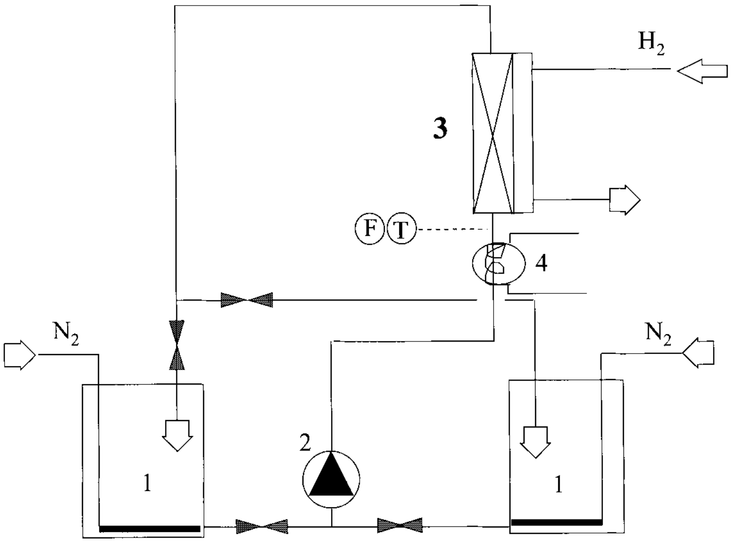

Fig. 1. Schematic representation of the setup: (1) containers, (2) solution pump, (3) GBC, (4) heater.

cell was monitored as a function of time by measuring the conductivity with cells (type Philips PR 9511) with cell constants of 1.46 and 1.49 cm^{-1}, respectively. Data were recorded on an X–t recorder (Kipp $ zonen BD8). All tracer experiments were conducted at 298 K.

A system of Fe^{3+}/Fe^{2+} in sulphuric acid solution was used as a model to study the GBC behaviour. Experiments were conducted in a flow-by single pass mode with inlet ferric concentrations varying between 0.1 and 50 mM. Solutions of 60 dm^3 were made using $Fe_2(SO_4)_3.5H_2O$ in sulphuric acid of 0.1 to 1 M strength. Millipore water was used to make the solutions. The acid used was of technical grade. Bypassing the cell, the solution was recirculated for 1 h to reach the experimental temperature, while nitrogen gas was purged through the solution in the feed vessel and through the gas compartment of the cell. The solution was passed through the cell after reaching the required temperature, and the nitrogen gas flow was replaced by a pure hydrogen flow through the gas compartment of the cell. A nitrogen purge in the vessel was maintained during the experiments. The inlet concentration of Fe^{3+} was determined before each run. The outlet concentration of Fe^{3+} was measured first after 30 min and thereafter at 10 min intervals until a constant value was obtained, indicating steady state. The temperature was varied between 25 and 50 °C; Flow through the reactor was varied between 3 and 20 cm^3 s^{-1}. After each run, the solution in the receiving vessel was regenerated by the addition of 54 cm^3 of 30 wt% hydrogen peroxide where Fe^{2+} ions were oxidized to Fe^{3+}. The regeneration was carried out for 15 h to ensure that there was no hydrogen peroxide in the solution.

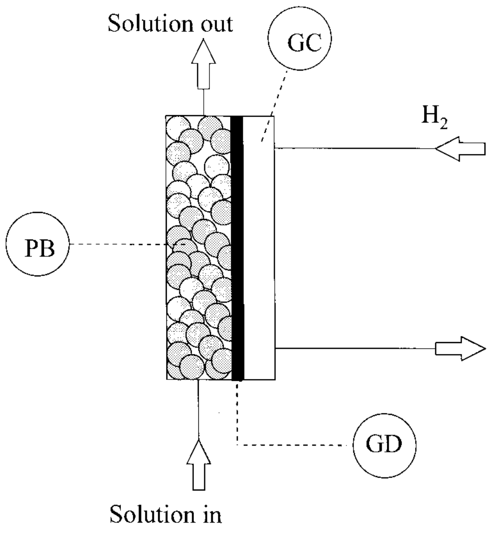

Fig. 2. Schematic representation of the cell: (GC) gas chamber, (PB) packed bed electrode, (GD) gas diffusion electrode.

3. Results

3.1. *Bed characteristics*

3.1.1. Tracer studies. Tracer studies were carried out to assess the flow pattern in the bed and to detect dead space and bypassing. The conductivity of the inlet and outlet solution was determined for various volumetric flow rates of solution between 3 and 20 cm^3 s^{-1} as a function of time. Typical exit response curves for plug flow characteristics were obtained. No serious bypassing or dead space in the cell were found.

3.1.2. Bed packing. The operation of an undivided GBC requires good contact between the gas diffusion electrode and the bed. Poor contact is known to give a poor potential distribution. Increased gas compartment pressure of the cell improves the bed–GDE contact. The reduction of Fe^{3+} was determined as a function of the gas pressure in the gas compartment for a 1 M H_2SO_4 solution containing 20 mM Fe^{3+}. It was observed that the degree of conversion increases with pressure. After this series of experiments, the cell was opened and about 1 wt% extra carbon particles were added. The series of experiments was repeated and it was found that for the same residence time,

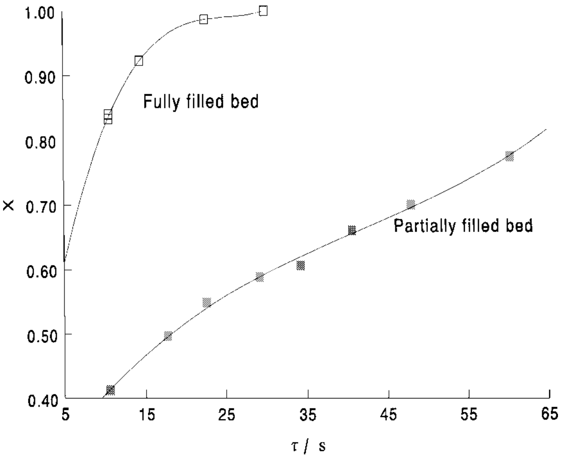

Fig. 3. Importance of compactness within the cell: the partially filled bed has 1% wt/wt less particles than the fully filled bed. Supporting electrolyte = 1 M H_2SO_4, temperature = 25 °C and C_{in} = 20 mM. (■) Partially filled bed, (□) fully filled bed.

higher Fe^{3+} conversions were obtained and there was no effect of gas pressure on the Fe^{3+} conversion.

Figure 3 shows the importance of a properly filled bed in the reduction process. It can be seen that the degree of conversion X, as well the relation between the degree of conversion and the residence time τ, depend strongly on the compactness of the bed.

In the Sections that follow, results exclusively for a fully-filled bed are presented.

3.2. *Overall rate constant*

3.2.1. Temperature. To determine the overall rate constant and the behaviour of a packed-bed electrode, the degree of conversion was measured as a function of the solution flow rate at different temperatures. The inlet Fe^{3+} concentration was maintained at 20 mM and the supporting electrolyte was 0.2 M H_2SO_4. Figure 4 shows the dependence of $\log(1 - X)$ on the residence time τ at different temperatures, where $V_r = 400\,\text{cm}^3$ and $\epsilon_b = 0.4$. (The bed porosity is estimated from the void space between the carbon particles outer surface.) Figure 4 shows that $\log(1 - X)$ decreases linearly with increasing τ. From this it follows that the experimental results from Fig. 4 can be described by the performance expression for a plug flow reactor (PFR) with no axial dispersion and for first order reaction kinetics.

For an ideal PFR and first order kinetics [5, 10]

$$-2.3\log(1 - X) = A_e k_{o,av} \tau \qquad (1)$$

Using this relation, the overall rate constant, $k_{o,av}$, was obtained from the slope of the $\log(1 - X)$ against τ curve. Assuming that the inner surface of the carbon particles of the bed does not contribute to the reduction process, the specific electrode surface A_e calculated from the geometric surface area of one particle and the bed voidage is then $2800\,\text{m}^{-1}$. It is likely that it does not depend on temperature. From Fig. 4, it can be concluded that $k_{o,av}$ increases strongly with increasing temperature.

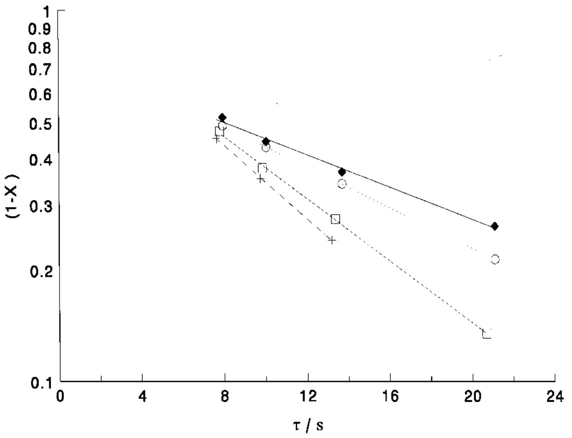

Fig. 4. Influence of temperature on the overall conversion at various residence times: supporting electrolyte = 0.2 M H_2SO_4, C_{in} = 20 mM. Key: (◆) 25 °C, (○) 30 °C, (□) 40 °C and (+) 50 °C.

3.2.2. Concentration of supporting electrolyte. The effect of acid concentration on the degree of conversion, X, was investigated at 25 °C with ferric inlet concentration of 20 mM. The results are shown in Fig. 5. The results were correlated by Equation 1, and $k_{o,av}$ values were calculated from the slopes of the $\log(1 - X)/\tau$ curves. The plot of $k_{o,av}$ against the sulphuric acid concentration is shown in Fig. 6. The overall rate constant $k_{o,av}$ was found to increase rapidly from 1.3×10^{-5} to $6.5 \times 10^{-5}\,\text{m}\,\text{s}^{-1}$ with increase in sulphuric acid concentration from 0.1 to 1 M.

3.2.3. Effect of inlet Fe^{3+} concentration. The inlet Fe^{3+} concentration, C_{in}, was varied between 0.15 to 50 mM. Experiments were conducted at 25 °C using a constant solution flow rate of $17.5\,\text{cm}^3\,\text{s}^{-1}$ corresponding to a residence time of 10 s. Supporting electrolytes were 0.5 and 1 M H_2SO_4. The outlet Fe^{3+} concentration was measured under steady state conditions. From the degree of conversion and using Equation (1) and $A_e = 2800\,\text{m}^{-1}$, the overall rate constant $k_{o,av}$ was obtained.

Results for 1 M H_2SO_4 are shown in Fig. 7. From this Figure, it follows that $k_{o,av}$ approaches a limiting value for a decreasing inlet Fe^{3+} concentration. The

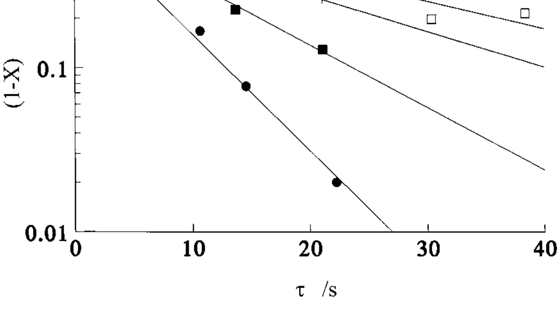

Fig. 5. Effect of H_2SO_4 concentration on the overall conversion at various τ, 25 °C and C_{in} = 20 mM. Key: (□) 0.1 M, (+) 0.2 M, (■) 0.5 M and (●) 1 M.

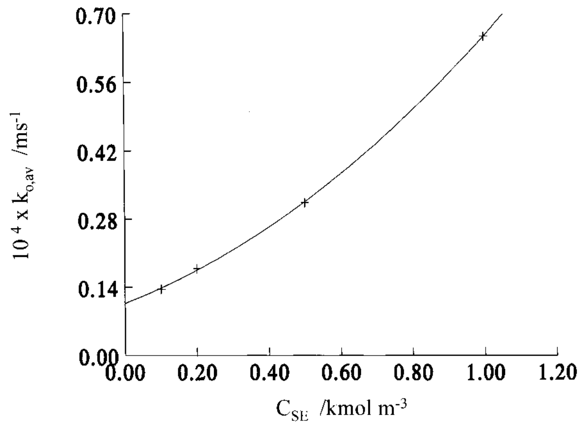

Fig. 6. Dependence of $k_{o,av}$ on H_2SO_4 concentration. $T = 25\,°C$ and $C_{in} = 20$ mM.

limiting $k_{o,av}$ is about $7.5 \times 10^{-5}\,m\,s^{-1}$. A series of experiments done for 0.5 M H_2SO_4 produced similar results. In this case a limiting $k_{o,av}$ of $8.9 \times 10^{-5}\,m\,s^{-1}$ was obtained. It is likely that $k_{m,av}$ is equal to $k_{o,av,lim}$.

The effect of the flow rate on $k_{o,av}$ was determined separately at $C_{in} = 4$ mM, where $k_{o,av}$ was practically equal to $k_{o,av,lim}$ and so to $k_{m,av}$. The mass transfer coefficient is known to vary with solution flow rate according to [5]:

$$k_{m,av} = \alpha u_s^{\beta} \tag{2}$$

Figure 8 shows the plot of $\log k_{o,av}$ against $\log u_s$. Two distinct regions were obtained, in both of which $k_{o,av}$ increased with the flow rate. It was found that at low flow rates, namely $< 0.025\,m\,s^{-1}$, $k_{o,av} = 2.4 \times 10^{-4}\ u_s^{0.48}\,m\,s^{-1}$, and at high flow rates namely $> 0.05\,m\,s^{-1}$, $k_{o,av} = 8.5 \times 10^{-4}\ u_s^{0.80}\,m\,s^{-1}$ was obtained.

4. Discussion

The results of this work have shown that GBC may provide a useful tool for the reduction of Fe^{3+} ions in dilute solutions. Due to the importance of bed/GDE contact it is necessary for the bed to be properly packed. Improper packing may result from either the rearrangement of particles to form a closely packed configuration after randomly filling the bed or from the wear of the particles due to long term use. Reduction involving chromate on a bed of carbon particles is also known to involve a chemical reaction between chromate and carbon particles [7]. This would imply that the amount of particles in the bed will continually diminish, giving rise to bad contact within the GBC.

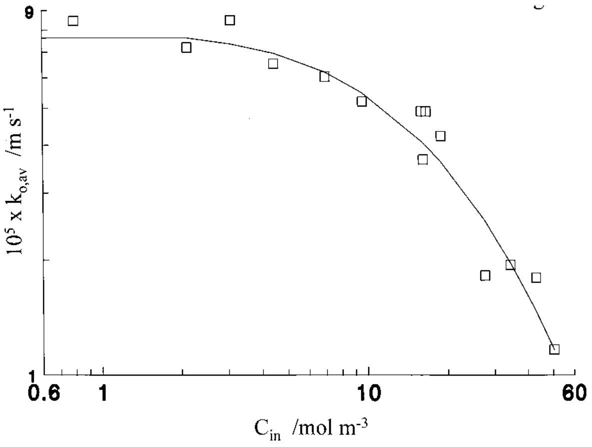

Fig. 7. Effect of inlet Fe^{3+} concentration on $k_{o,av}$: supporting electrolyte: 1 M H_2SO_4, $T = 25\,°C$.

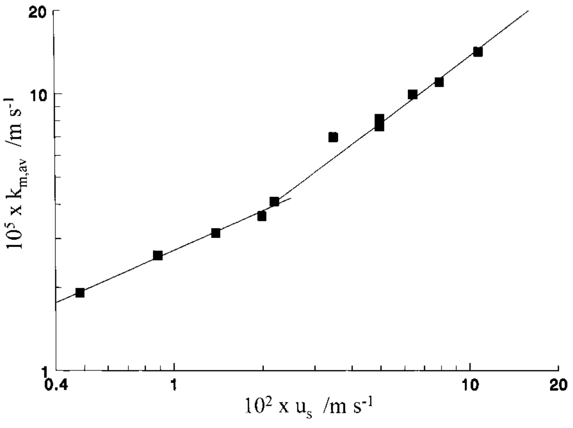

Fig. 8. Dependence of mass transfer coefficient k_m on mean flow velocity u_s. $T = 25\,°C$, $C_{in} = 20$ mM and supporting electrolyte: 1 M H_2SO_4.

In the reduction of Fe^{3+}, the packed bed electrode behaves as a plug flow reactor (PFR). The rate determining step depends on the inlet Fe^{3+} concentration. At inlet Fe^{3+} concentrations smaller than 4 mM for 1 M H_2SO_4 at 25 °C, $k_{o,av}$ is practically constant and equal to the overall mass coefficient $k_{m,av}$. It can be concluded that at $C_{in} < 5$ mM, the degree of conversion X is determined by mass transfer of Fe^{3+} for the whole applied range of flow velocity. At a high inlet Fe^{3+} concentration, for instance 50 mM, $k_{o,av}$ is about seven times smaller than $k_{m,av}$ (Fig. 7). This means that the apparent overall electrochemical reaction rate constant $k_{r,av}$ predominantly determines the degree of conversion. Moreover, it was found that for $C_{in} = 4$ mM, $\beta = 0.48$ at a low solution flow rate, indicating a laminar flow pattern within the reactor. At a high flow rate, $\beta = 0.80$ was obtained, indicating a turbulent flow pattern within the reactor. Literature value of $0.3 < \beta < 0.50$ for laminar and $0.45 < \beta < 0.80$ for turbulent solution flow has been found [5].

The overall rate constant $k_{o,av}$ can be partitioned into the overall mass transfer coefficient, $k_{m,av}$, and the apparent overall electrochemical reaction rate constant, $k_{r,av}$, as follows [10]:

$$\frac{1}{k_{o,av}} = \frac{1}{k_{m,av}} + \frac{1}{k_{r,av}} \tag{3}$$

The average electrochemical reaction rate constant $k_{r,av}$ was calculated at 25 °C and a residence time $\tau = 10\,s$ corresponding to $17.5\,cm^3\,s^{-1}$ for various inlet Fe^{3+} concentrations and 1 M H_2SO_4 as supporting electrolyte where $k_{m,av}$ was obtained from Fig. 8. The results are shown in Fig. 9 for the con-

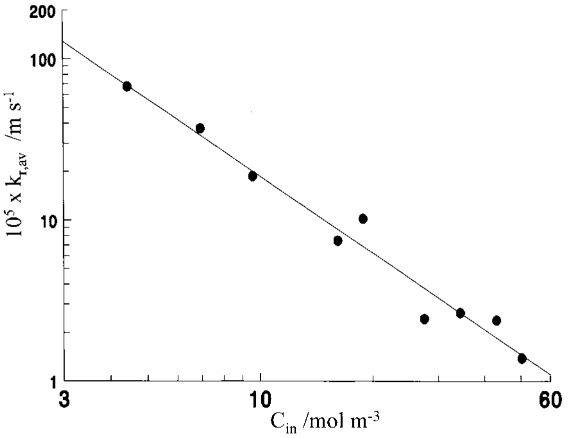

Fig. 9. Dependence of $k_{r,av}$ on inlet Fe^{3+} concentration: supporting electrolyte: 1 M H_2SO_4, $T = 25\,°C$ and residence time $\tau = 10$ s.

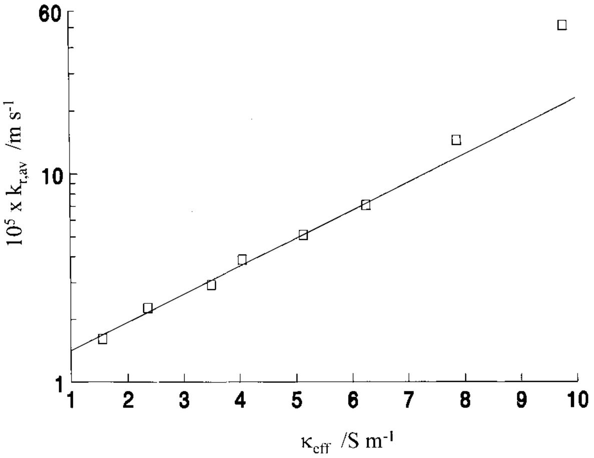

Fig. 10. Dependence of $k_{r,av}$ on effective conductivity of solution. $T = 25\,°C$, $C_{in} = 20$ mM and residence time $\tau = 10$ s.

centration ranges where the charge transfer step plays a significant role. From Fig. 9, it follows that $k_{r,av}$ depends on C_{in} according to

$$k_{r,av} = \gamma C_{in}^{-1.59} \tag{4}$$

The value of γ was found to be 0.0073 mol$^{1.59}$ m$^{-3.77}$ s^{-1} for 1 M H_2SO_4.

Increasing the supporting electrolyte concentration leads to larger degrees of conversion. This is due to higher conductivity which improves the potential and current distribution due to decreased ohmic losses in the solution. When the ohmic potential drop decreases, the electrode potential within the bed becomes more uniform and thus increases the driving force for the electrochemical reaction which leads to increased conversion. At the same time, however, increased supporting electrolyte concentration lowers the diffusion coefficient of the Fe^{3+} ions, but its impact is of less importance. The effective conductivity of the solution is known to depend on the specific conductivity of the solution and the porosity of the bed according to the Bruggemann equation [16]:

$$\kappa_{eff} = \kappa_{sol}\epsilon_b^{1.5} \tag{5}$$

This implies that κ_{eff} can be improved by increasing the conductivity of the bulk solution κ_{sol} and using a cathode of a high porosity, such as reticulated vitreous carbon (RVC), or a stack of expanded metal gauze or graphite felts which ensures porosities of the order of 97%.

The dependence of $k_{r,av}$ on the effective conductivity of the solution was evaluated at a residence time, τ, of 10 s corresponding to 17.5 cm^3 s^{-1}, $T = 25\,°C$ and an inlet Fe^{3+} concentration of 20 mM. This can be used to calculate the mass transfer coefficient at different H_2SO_4 concentrations from that at 1 M H_2SO_4, using a dimensionless number correlation for the bed. At $\tau = 10$ s

$$Sh = 1.32\, Re^{0.48}\, Sc^{1/3} \tag{6}$$

On substitution of the average particle size $d_p = 1.8 \times 10^{-3}$ m and the flow velocity at $\tau = 10$ s namely $u_s = 0.05$ m s^{-1}, Equation 6 can be rewritten as

$$k_m = 15.4\, D^{2/3}\, \nu^{-0.15} \tag{7}$$

For most spherical ions, the diffusion coefficient can be calculated with reasonable accuracy from the available data at 25 °C and the Stokes–Einstein equation [12, 13].

$$D\eta = \frac{RT}{N_A}\frac{1}{6\pi r} = \text{constant} \tag{8}$$

The diffusion coefficient for Fe^{3+} in 0.5 M sulphuric acid at 25 °C is 5.5×10^{-10} m^2 s^{-1} [14]. Equations 7 and 8 were used to calculate k_m at different supporting electrolyte concentrations and at 25 °C. Viscosities were extracted from [15]. These results were used to calculate $k_{r,av}$ from $k_{o,av}$, using Equation 3.

The dependence of $k_{r,av}$ on the effective conductivity κ_{eff} was evaluated and the results are shown in Fig. 10. It was found that for $\kappa_{eff} < 7.8$ S m^{-1} corresponding to a 0.8 M H_2SO_4 solution, $C_{in} = 20$ mM, and at 25 °C, $k_{r,av}$ varies with κ_{eff} as follows:

$$k_{r,av} = 1.04 \times 10^{-5} \exp(0.31\, \kappa_{eff}) \tag{9}$$

The temperature dependence of $k_{r,av}$ was evaluated for a supporting electrolyte concentration of 0.2 M

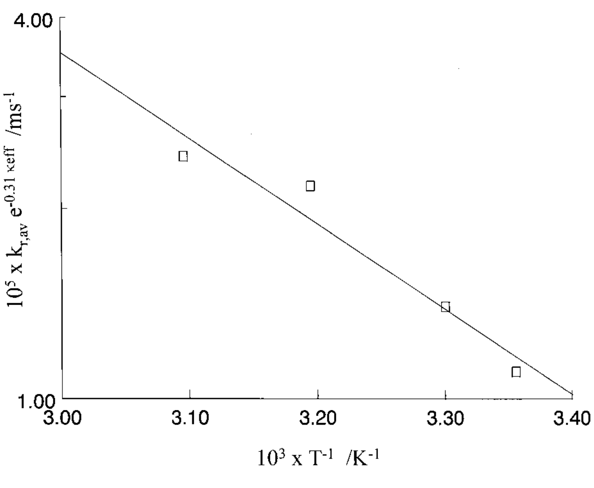

Fig. 11. $k_{r,av}\exp(-0.31\kappa_{eff})$ dependence on temperature. Supporting electrolyte: 0.2 M, H_2SO_4, $C_{in} = 20$ mM and residence time $\tau = 10$ s.

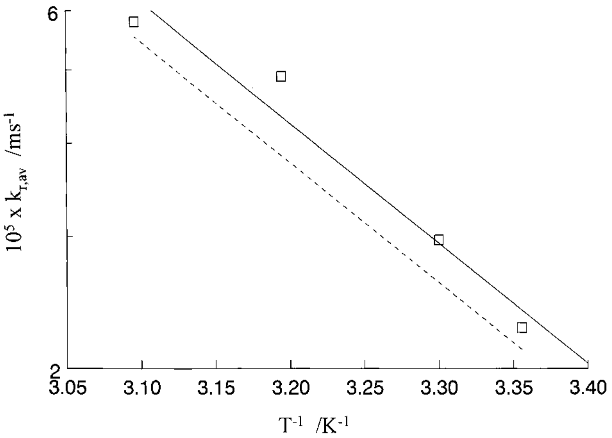

Fig. 12. Correlation of $k_{r,av}$ on temperature: supporting electrolyte: 0.2 M H_2SO_4, $C_{in} = 20$ mM and residence time $\tau = 10$ s. [----]: calculated with Equation 12, [□]: calculated from $k_{m,av}$ and $k_{o,av}$ with Equation 3.

and an inlet Fe^{3+} concentration of 20 mM. The mass transport coefficient was evaluated by Equation 7. The variation of diffusion coefficient, D, with temperature was calculated from

$$D = D_{298} \exp\left[-\frac{E_D}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad (10)$$

where E_D for $Fe^{3+} = 20\,\text{kJ mol}^{-1}$ [15].

The contribution of conductivity to the temperature dependence was cancelled out by plotting $k_{r,av} \exp(-0.31\,\kappa_{eff})$ against T^{-1}. The results are shown in Fig. 11. It follows that

$$k_{r,av} \exp(-0.31\,\kappa_{eff}) \propto \exp(-3100/T) \quad (11)$$

The results of Equations 4, 8 and 12 were used to describe $k_{r,av}$ by an empirical relationship involving C_{in}, κ_{eff} and T as follows:

$$k_{r,av} = 1.21 \times 10^{-3}\, C_{in}^{-1.59} \times \exp\left[0.31\,\kappa_{eff} - 3100\left(\frac{1}{T} - \frac{1}{298}\right)\right] \quad (12)$$

Equation 12 was used to recalculate $k_{r,av}$ at different temperatures. The effect of conductivity was obtained from the measurements at various sulphuric acid concentrations. Results were compared with the experimental values. Figure 12 shows the temperature dependence of $k_{r,av}$ for $C_{SE} = 0.2$ M, $C_{in} = 20$ mM and $\tau = 10$ s. It can be seen that $k_{r,av}$ from Equation 12 agrees well with $k_{r,av}$ calculated from $k_{o,av}$ and $k_{m,av}$ using Equation 3. The discrepancy between the two is 13%, and may be attributed to experimental error.

5. Conclusion

The GBC is a promising tool for the removal of heavy metals in dilute solution. For ferric reduction high conversions are achievable at relatively low residence times in a single pass mode. The conversion depends on the rate parameters of the reactions, the concentration levels of reacting species and the concentration and composition of the treated solution.

A cathode ensuring good contact with the GDE is necessary for the optimal operation of the GBC reactor.

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