Reduction of metal ions in dilute solutions using a GBC-reactor
Part I: Experimental study on the laboratory scale reduction of ferric ions

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To reduce metal ions in dilute solutions a new type of electrochemical reactor has been developed: the GBC-reactor. This reactor consists of a gas diffusion electrode coupled with a packed bed electrode. The working principle of the reactor is based upon two main reactions: the catalytic oxidation of hydrogen gas in the gas diffusion electrode and the simultaneous reduction of metal ions on the packed bed electrode. This process occurs spontaneously without the need for an external power supply when the Gibbs free energy of the total reaction is negative. To study the behaviour of the reactor the reduction of ferric ions was used as a model system. The experimental results, obtained from varying a number of key process parameters, could be described using a very simple macroscopic rate equation. It is concluded that the reduction of ferric ions in a GBC-reactor is controlled by both mass transfer and electrochemical kinetics. To carry out scale-up and optimization studies a reactor model incorporating the potential distribution in the packed bed electrode is, however, necessary.

Keywords: *GBC reactor, gas diffusion electrode, packed bed electrode, dilute solutions, metal ions, recycling*

List of symbols

a_e	specific surface area ($\mathrm{m^2_{cathode}\, m^{-3}_{reactor}}$)
c_i	concentration ferric ions in reservoir/reactor inlet ($\mathrm{mol\, m^{-3}}$)
c_o	concentration ferric ions in reactor ($\mathrm{mol\, m^{-3}}$)
c_{init}	initial concentration ferric ions in batch-recycle system ($\mathrm{mol\, m^{-3}}$)
G	$\ln((1/\tau_o)(c_i - c_o) - (\mathrm{d}c_o/\mathrm{d}t)/\mathrm{mol\, m^{-3}\, s^{-1}})$
$j_{GDE,lim}$	diffusion limited current density of hydrogen oxidation in gas diffusion electrode($\mathrm{A\, m^{-2}}$)
K	constant with value 1 ($\mathrm{mol^{1-\alpha_{ov}}\, m^{3\alpha_{ov}-3}}$)
k_{app}	apparent reaction rate constant ($\mathrm{m\, s^{-1}}$)

L_{bed}	bed thickness (mm)
Q	volumetric flow rate ($\mathrm{m^3\, s^{-1}}$)
r	reduction rate of ferric ions ($\mathrm{mol\, m^{-2}\, s^{-1}}$)
T	temperature (K)
U_s	superficial liquid velocity ($\mathrm{m\, s^{-1}}$)
V	volume ($\mathrm{m^3}$)

Greek characters

α_{app}	apparent reaction order ($-$)
ε_{bed}	bed porosity ($-$)
τ_i	residence time in reservoir ($V_{reservoir}/Q$) (s)
τ_o	true residence time in reactor ($\varepsilon_{bed} V_{reactor}/Q$) (s)

1. Introduction

There is a tendency in the metal finishing industries to (re-)design processes as closed systems. These systems make use of optimal recycling of raw materials within the process, thereby minimizing the amount of waste disposal. The reasons for incorporating such systems are due to economic factors, for example, the increasing costs of raw materials, and increasingly stringent legislation concerning the disposal of chemical waste.

In some cases the process liquids need to be regenerated before they can be recycled. The regeneration of process liquids may consist in the removal of metal ions as continuous recycling leads to the built up of these ions. The build up of metal ions in the system can lead to process disturbance or even to process failure (e.g., in the case of etching of metals or electrochemical machining [1]). There are several methods available to remove metal ions from process liquids such as ion exchange, electrodialysis or a combination of (electro-) chemical reduction and precipitation. The chosen method depends entirely upon the process conditions (e.g., type and concentrations of metal ions and pH of the liquid).

A new electrochemical reactor for the reduction of metal ions in dilute solutions has been proposed by Janssen [2, 3], called the Gas diffusion electrode

packed Bed electrode Cell (GBC-reactor). The reactor consists of a gas diffusion electrode coupled with a packed bed electrode. The working principle of the reactor is based upon two main reactions: the catalytic oxidation of hydrogen gas in the gas diffusion electrode (anodic reaction) and the simultaneous reduction of metal ions on the packed bed electrode (cathodic reaction). This process occurs spontaneously without the need for an external power supply when the Gibbs free energy of the total reaction is negative.

In previous work the reduction of chromate in dilute solutions using a GBC-reactor was described [3, 4]. It was concluded that during the experiments the overall reduction process of chromate consisted of a combination of two separate processes. Part of the chromate was reduced with the use of hydrogen gas according to the aforementioned principle. Another part of the chromate, however, was reduced by the oxidation of the carbon bed material.

The aim of this work is to investigate the behaviour of a laboratory scale GBC-reactor as a function of several key process parameters (e.g., fluid velocity, bed thickness) using the ferric\ferro couple as a model system. This couple cannot be reduced by the carbon bed material used and the experimental results therefore clearly establish the working principle of the reactor. The results presented here and those obtained with a pilot-scale GBC-reactor [5] will be used to validate a forthcoming concise GBC-reactor model. This model will be used for scale-up and optimization studies.

2. Theory

### 2.1. GBC-reactor working principle

The GBC-reactor consists of a combination of a gas diffusion electrode coupled, via direct or indirect contact, with a packed bed electrode, as schematically shown in Fig. 1. If the gas diffusion electrode is in direct contact with the packed bed then the reactor operates in an undivided mode. Conversely, when there is an electric insulator between the gas diffusion electrode and the packed bed electrode then the reactor operates in a divided mode. In the latter case the electrical contact is made through an external wire and a feeder plate behind the packed bed. Using the divided mode reactor operation makes it possible to measure the total current generated in the reactor.

Inside the reactor two main reactions occur. In the gas diffusion electrode the platinum catalysed oxidation of dissolved hydrogen gas takes place (Fig. 2):

$$H_2(aq) \xrightarrow{\text{Pt}} 2H^+(aq) + 2e^- \qquad (1)$$
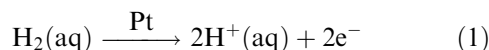
Simultaneously, the ferric ions, which are in solution, are being reduced on the carbon surface of the packed bed electrode:

$$2Fe^{3+}(aq) + 2e^- \xrightarrow{\text{C}} 2Fe^{2+}(aq) \qquad (2)$$
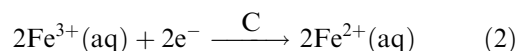
The resulting Gibbs free energy of these two reactions is negative and they therefore occur spontaneously in the reactor. The rate at which the reduction proceeds depends upon the rates of the reaction steps of the different species involved.

2.2. Analysis of the reaction steps

The overall process by which heterogeneous (electro-) catalytic reactions proceed can be broken down into a sequence of individual steps [6], as schematically for the GBC-process in Fig. 2. For the catalytic oxidation of hydrogen gas five steps can be identified:
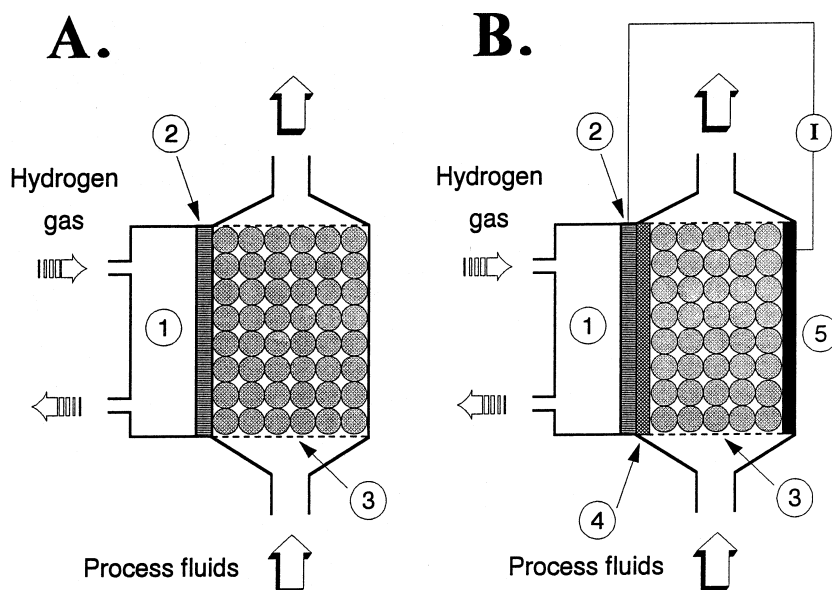

Fig. 1. Schematic presentation of the GBC-reactor: (a) undivided mode; (b) divided mode. Key: (1) gas chamber, (2) gas diffusion electrode, (3) packed bed electrode, (4) electrical insulator and (5) current feeder.
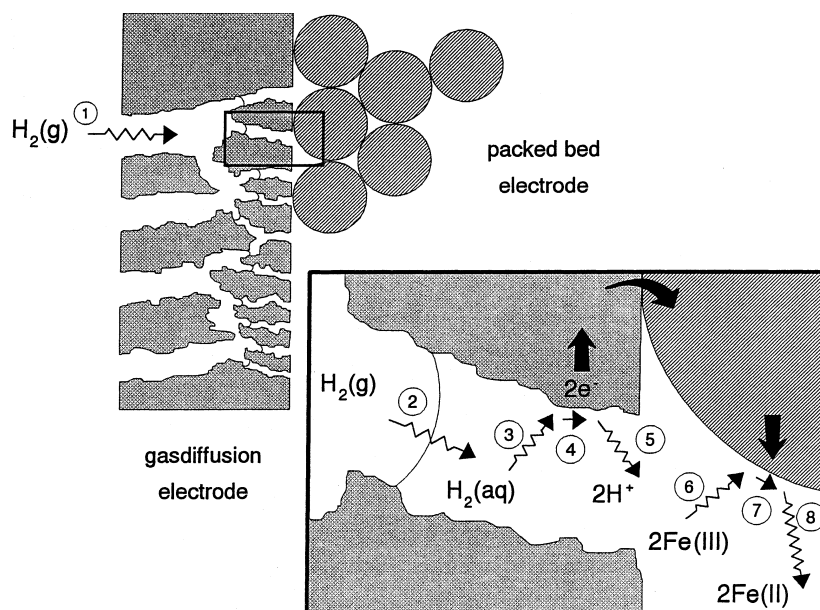
Fig. 2. Schematic presentation of the GBC-process with respect to the reduction of ferric ions.

(i) Mass transfer (diffusion) of hydrogen gas through the macropores of the gas diffusion electrode.

(ii) Absorption of hydrogen gas from the gas phase into the liquid phase in the micropores of the gas diffusion electrode.

(iii) Mass transfer (diffusion) of dissolved hydrogen in the micropores to the surface of the catalyst.

(iv) Adsorption and reaction of hydrogen on the surface of the catalyst.

(v) Mass transfer (diffusion) of hydrogen ions from the surface of the catalyst.

In the case that nonporous bed materials are used, three steps can be identified for the ferric ion reduction process:

(vi) Mass transfer (diffusion) of ferric ions from the bulk solution to the surface of the bed material.

(vii) Adsorption and reaction of ferric ions on the surface of the bed material.

(viii) Mass transfer (diffusion) of ferro ions from the surface of the bed material.

The rate of ferric ion reduction is determined by the rate of the slowest step of these eight reaction steps. The importance of these different steps can be estimated if some assumptions are made regarding the experimental conditions.

The behaviour of the hydrogen gas diffusion anode applied in the GBC-reactor during the experiments has been studied extensively by Vermeijlen and Janssen [7–10]. They estimated that the rate of oxidation of pure hydrogen gas becomes fully mass transfer limited at current densities of about $80 \, \text{kA m}^{-2}$. If we assume that the current density of the gas diffusion electrode in the GBC-reactor stays below $2.5 \, \text{kA m}^{-2}$ (less then 5% of $j_{\text{GDE,lim}}$) then the fourth step of the hydrogen oxidation mechanism can be considered rate determining. Thus the oxidation process is in that case (electro-) kinetically controlled.

With respect to the reduction process of ferric ions in the packed bed electrode the situation is more complex. This is due to the fact that electrochemical rate constants are a function of overpotential, which, in the case of porous electrodes, varies locally. The determination of the relative influences of mass transfer and electrochemical kinetics in the reduction reaction is, therefore, only possible by calculation of the potential distribution inside the packed bed electrode.

However, it seems reasonable to assume that the rate of the hydrogen oxidation reaction is faster then either the rates of mass transfer or the kinetics of the ferric reduction. Thus the reduction rate of ferric ions in the GBC-reactor is most likely determined by the processes taking place inside the packed bed electrode.

Instead of using a detailed description of the distribution of reduction activity within the packed bed electrode, which would necessitate the calculation of the potential distribution, a simpler approach has been adopted. The reduction rate in the packed bed electrode is described using a macroscopic equation with apparent reaction rate parameters:

$$-r = K \, k_{\text{app}} c^{\alpha_{\text{app}}} \qquad (3)$$

This equation combines the effects of mass transfer and electrochemical kinetics on the reduction reaction of ferric ions into two parameters: an apparent reaction rate constant, k_{app}, and an apparent reaction order, α_{app}. The parameter K is introduced as a constant which has a value of one and the dimensions of $\text{mol}^{1-\alpha_{\text{app}}} \, \text{m}^{3\alpha_{\text{app}}-3}$. By using this formulation k_{app} can have the standard dimensions of m s^{-1} while Equation 3 still preserves dimensional integrity.

2.3. *Batch-recycle operation*

The experiments have been performed with a batch-recycle system, in which the process liquids are continuously pumped from a reservoir through the laboratory scale GBC-reactor and back. In modelling the behaviour of this system several assumptions were made:

(i)   As the conversions per pass are low the GBC-reactor can be described as a CSTER (continuous stirred tank electrochemical reactor).
(ii) The porosity and specific surface areas are uniform and constant with time.
(iii) The process is isothermal.
(iv) The reservoir is well mixed.

It is then possible to define the system with two nonsteady mass balances; one with respect to the GBC-reactor:

$$\frac{dc_o}{dt} = \frac{1}{\tau_o}(c_i - c_o) - \frac{a_e K\, k_{app}}{\varepsilon_{bed}} c_o^{\alpha_{app}} \qquad (4)$$

with τ_o, the true residence time in the reactor, c_i, the ferric ion concentration in the reservoir/reactor inlet, c_o, the ferric ion concentration in the reactor, a_e, the specific surface area, and ε_{bed}, the packed bed porosity. The second mass balance describes the changes in the reservoir:

$$\frac{dc_i}{dt} = \frac{1}{\tau_i}(c_o - c_i) \qquad (5)$$

with τ_i, the residence time in the reservoir. If, during experiments, the change in the ferric ion concentration in the reservoir is monitored at discrete time intervals, then it is possible to extract the values for k_{app} and α_{app} from the concentration–time data. The procedure starts with the calculation of (dc_i/dt) at the discrete time intervals, using three-point differ-

entiation formulae [6]. Hence, both the concentration in the reservoir, c_i, and (dc_i/dt) are known at discrete time intervals, and the concentration in the reactor, c_o, can be calculated by use of Equation 5. Subsequently, (dc_o/dt) can be determined from the calculated reactor concentration–time data, again using three-point differentiation formulae.

Therefore, only k_{app} and α_{app} are left as unknown parameters. By rearranging Equation 4 and taking the natural logarithm of both sides:

$$\ln\left(\frac{1}{\tau_o}(c_i - c_o) - \frac{dc_o}{dt}\right) = \ln\left(\frac{a_e K\, k_{app}}{\varepsilon_{PBE}}\right) + \alpha_{app}\ln(c_o) \qquad (6)$$

The slope of a plot of the left-hand term of Equation 6 as a function of $\ln(c_o)$ is equal to the apparent reaction order. The apparent reaction rate constant can be calculated from the ordinate intercept of this plot.

The concentration–time behaviour of the system, for certain values of k_{app} and α_{app}, was calculated by solving the system of differential equations numerically using a Fortran computer program incorporating a generalized Bulirsch–Stoer method due to Bader and Deuflhard [11, 12].

3. Experimental details

3.1. *Experimental set-up*

The experimental setup consisted of a laboratory scale GBC-reactor, a pump, a reservoir and a three electrode automated measuring system (Fig. 3). The laboratory scale GBC-reactor was made from Perspex and is essentially similar to the cell described previously [3, 7]. The modular design of the cell made it possible to vary the thickness of the packed bed electrode. The gas diffusion electrode used was a fuel
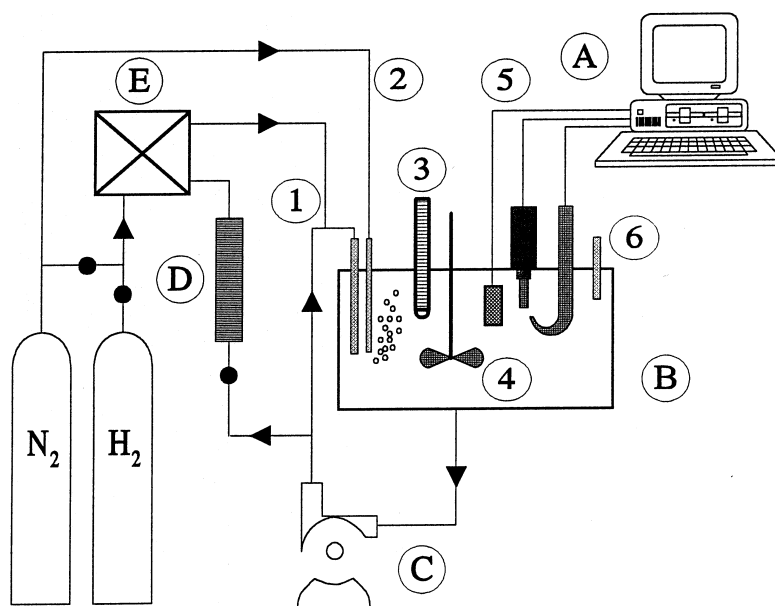

Fig. 3. Experimental setup: (A) computer controlled digital potentiostat, (B) reservoir, (C) pump, (D) flowmeter, (E) laboratory scale GBC-reactor. Key: (1) liquid inlet, (2) nitrogen sparger, (3) thermometer, (4) stirrer, (5) three–electrode measurement system and (6) water lock.

cell grade electrode on Toray paper, purchased from E-TEK (USA). The electrode had a geometric surface area of 20×20 mm. The active layer of the electrode was about 0.1 mm thick and consisted of platinum dispersed on Vulcan XC-72; the platinum loading was approximately 0.35 mg cm^{-2}. The total thickness of the electrode, incorporating the carbon backing, amounted to 0.55 mm. The gas diffusion electrode was supported by a perforated Perspex plate of about 3 mm thick, placed on the gas side of the electrode to enhance the mechanical stability.

The packed bed consisted of small carbon rods, 1 mm in diameter and a mean length of 3 mm (Norit RB1). In calculations a bed porosity of 0.4 was used, which, combined with the mean particle dimensions, gives a specific surface area of 2800 m^{-1}. The standard bed thickness was 18 mm, but it could be varied between 10 and 66 mm.

Due to the modular design of the cell, the number of flow entrance points in the reactor (i.e., number of liquid distributors) varied with the bed thickness. The flow rate through each liquid distributor was measured and controlled separately. The flow rate was measured using Fischer & Porter flow meters (type FP-3/8-25-G-5/36), all fitted with glass floats, and controlled by means of valves.

The reservoir was made of glass and had a volume of about four litres. The vessel was equipped with a mechanical stirrer, a thermometer, a liquid inlet and outlet tube, a gas inlet for nitrogen sparging, a three electrode system and a water lock device. All inlets and outlets to the vessel were made gas tight so that working under air free conditions was possible. Around the reservoir a heating/cooling jacket connected to a water bath was used to control the temperature of the electrolyte.

The three electrode system inserted into the reservoir consisted of a platinum rotating disc electrode, a spade shaped platinum counter electrode and a Luggin capillary filled with a salt bridge (Agar Agar/KCl) which was connected to a calomel reference electrode. This system was used to monitor the ferric ion concentration within the reservoir by measurement of the limiting current.

3.2. Procedures and solutions

The rotating disc system was calibrated with solutions of known ferric ion composition, under different experimental conditions (e.g., temperature, sulphuric acid concentration). By this method it was possible to accurately measure the ferric ion concentration in the range 40 to 1 mol m^{-3}. Furthermore, a minimum value for the rotation speed of the disc electrode was established, being 64 rps, for which no influence of the stirrer speed or liquid flow through the vessel on the limiting current was found. The limiting current was measured by means of cyclic voltammetry. The potentials were applied by using a computer controlled, digital potentiostat (Autolab PGSTAT20, EcoChemie).

The solutions were made with Millipore® water, sulphuric acid (Merck p.a.) and Fe$_2$SO$_4$.5H$_2$O (Fluka p.a.). Millipore® water was chosen as it was noticed that the use of demineralized water led to the slow spontaneous reduction of ferric ions, caused by certain impurities. With respect to the oxidation of ferro ions by dissolved oxygen the process liquid was very stable. This is because of the low pH of the solution which results in a very low oxidation rate of ferro ions [13].

Before an experiment, nitrogen was passed through the gas chamber of the GBC-reactor and also into the reservoir, to strip the system of oxygen. In the case of the gas diffusion electrode this is necessary to prevent damage caused by the reaction of hydrogen with oxygen inside the electrode. The process liquid was stripped of oxygen as it can be reduced easily in the GBC-reactor, especially when the metal ion concentration is lowered. After this procedure the first concentration measurement was made and the gas diffusion electrode was fed with pure hydrogen gas. During the whole experiment nitrogen gas was bubbled through the reservoir.

After an experiment the process liquid was regenerated by adding a stoichiometric amount (approximately 3–4 ml, but depending on ferric ion conversion) of hydrogen peroxide (Acros p.a.) to the solution. In this way the ferro ions were oxidized back to ferric ions and also the hydrogen ion balance was restored.

4. Results

During the experiments the influence of superficial liquid velocity, temperature, initial ferric ion concentration, sulphuric acid concentration and bed thickness on the ferric ion reduction rate was determined. These parameters were varied relative to a set of standard values, as shown in Table 1.

The results are given in terms of values of the apparent reaction rate parameters: k_{app} and α_{app}. These two parameters were determined using concentration–time curves. A typical experimental curve is given in Fig. 4. This curve shows that it took about 1200 s for the system to reach a pseudo-steady state. The parameters k_{app} and α_{app} were determined from this concentration-time data using a plot as shown in Fig. 5, where the left-hand side of Equation 6 (designated as G in the Figure) is plotted against $\ln(c_o)$. The pseudo-steady state concentration profiles were simulated numerically using the extracted values for

Table 1.   Set of standard values for experimental parameters

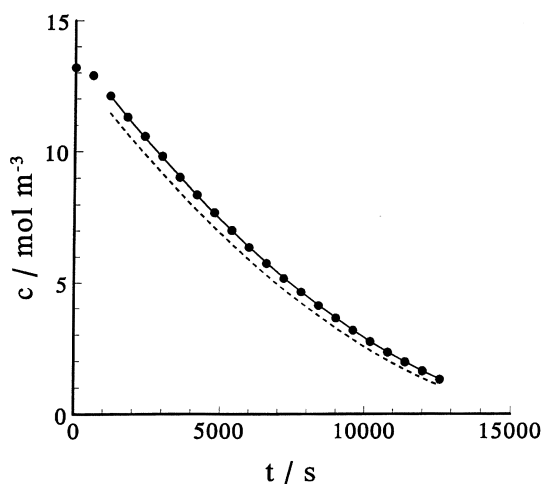| Parameter	Value
Superficial liquid velocity	0.02 m s^{-1}
Temperature	298 K
Initial concentration ferric ions	20 mol m^{-3}
Concentration sulphuric acid	1 M
Bed thickness	18 mm

Fig. 4. Typical concentration–time curve showing the measured ferric ion concentration in the reservoir (●). The drawn lines show the concentration profiles obtained by numerical simulation using the experimental determined values for k_{app} and α_{app} (—reservoir concentration, - - - - reactor concentration).

the reaction rate parameters (Fig. 4). The maximum difference between measured and calculated reservoir concentration profiles was for all experiments less than 2%.

4.1. Influence of superficial liquid velocity

If a process is partially or fully controlled by mass transfer then the reaction rate is dependent on the liquid velocity. To determine the influence of the superficial liquid velocity on the overall ferric ion reduction process, experiments were performed in the range 0.005 to 0.03 m s^{-1}. The results of these experiments are plotted in Fig. 6. From this it follows that the ferric ion reduction rate increases with increase in superficial liquid velocity. The increase in the apparent reaction rate constant in the range of variation is about 20%, while the apparent reaction order stays about constant. It is striking that the apparent reaction order has a value smaller than 1.
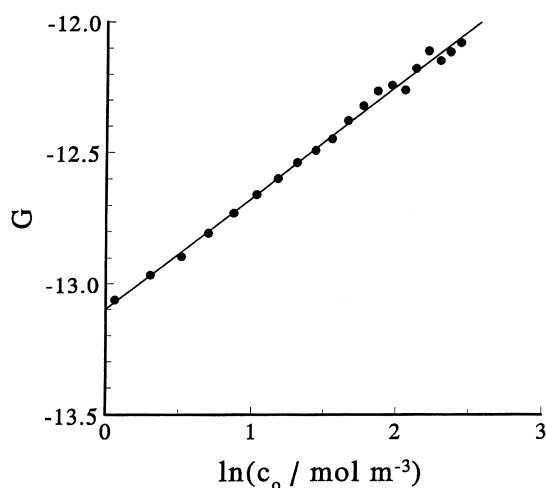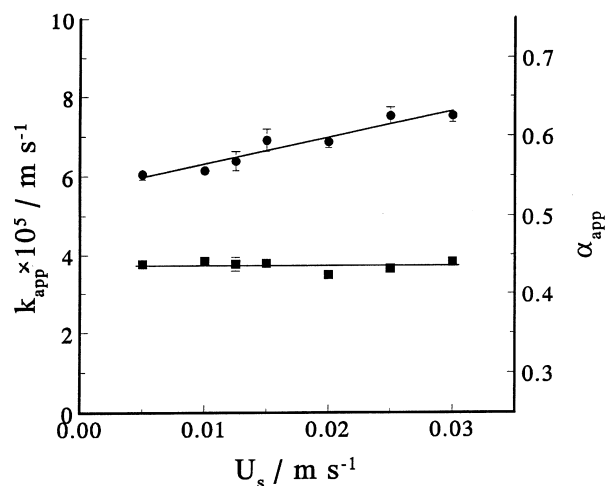

Fig. 6. Apparent reaction rate parameters k_{app} (●) and α_{app} (■) as a function of the superficial liquid velocity.

4.2. Influence of temperature

Most (electro-)chemical processes proceed at a higher rate when the temperature is increased, due to an increase in the reaction and/or the mass transfer rate.

During a set of experiments the temperature was varied between 298 and 343 K, results are shown in Fig. 7. It follows that the ferric ion reduction rate increases with increase in temperature. Within the experimental range the apparent reaction rate constant increased by 100% while at the same time there was a slight lowering of the apparent reaction order. Again the value of the apparent reaction order stayed below 1.

The results were plotted as the natural logarithm of k_{app} against $1/T$, which gives a straight line. Theoretically the slope of this line represents the value of the activation energy which, depending on the reaction conditions, can be assigned to mass transfer or kinetics. In this case it is only possible to determine a value for an apparent activation energy, which is about 12 kJ mol^{-1}.

Fig. 5. Plot of the left-hand term of Equation 6 as a function $\ln(c_o)$ for the concentration–time data shown in Fig. 4.
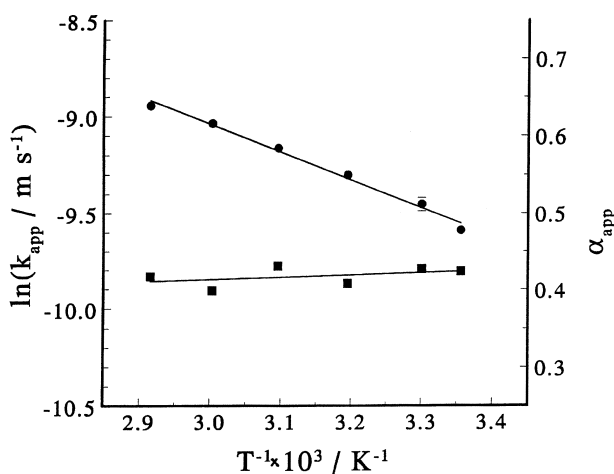

Fig. 7. Natural logarithm of k_{app} (●) and α_{app} (■) as a function of the reciprocal temperature.

4.3. *Influence of initial ferric ion concentration*

According to the Nernst equation, the equilibrium potential of a redox couple is determined by the concentrations of its oxidized and reduced species. The local overpotential in the spontaneous operating GBC-reactor is partly determined by the equilibrium potentials of the species involved. Accordingly, a change in the equilibrium potential would be expected to change the macroscopic reduction rate. To see this effect, the initial concentration of ferric ions in the batch-recycle system was varied, thereby changing the ratio ferric/ferro at a fixed ferric ion reactor concentration.

The initial concentration was varied between 40 and $5 \, mol \, m^{-3}$. The results in terms of k_{app} and α_{app} are shown in Fig. 8. It can be concluded that a decrease in the initial concentration causes the apparent reaction rate constant to increase, while the apparent reaction order decreases. Again the apparent reaction order stayed below 1.

The ultimate effect of varying the initial concentration from these results is not really clear as the reaction parameters change in opposite directions. Therefore another plot was constructed, Fig. 9, showing the reduction rates for ferric ion reactor concentrations in the range $1-5 \, mol \, m^{-3}$ as a function of the initial concentration. It becomes clear that lowering the initial ferric ion concentration leads to a higher reduction rate.

4.4. *Influence of sulphuric acid concentration*

To suppress the influence of migration and ohmic losses on the reduction of ferric ions in the GBC-reactor, sulphuric acid was used as a background electrolyte. However, the concentration of sulphuric acid also changes the density and the viscosity of the fluid and therefore the mass transfer coefficient.

During a set of experiments the sulphuric acid concentration was varied in the range 0.25 to $3 \, M$. The

Fig. 9. Macroscopic reduction rate with respect to the ferric ion reactor concentration plotted for different initial ferric ion concentrations.

results are presented in Fig. 10. The behaviour of the apparent reaction rate constant is, in this case, more complex. When the sulphuric acid concentration is increased from 0.25 to about $1.5 \, M$ then k_{app} also increases. A further increase in the sulphuric acid concentration leads first to a stabilization of k_{app} but after that it starts to decrease. The apparent reaction order increases steadily as the sulphuric acid concentration is increased, although the values stay smaller then 1.

It is clear that the trend of both reaction parameters is opposite. However, the decrease in k_{app} is small compared to the increase of α_{app}. Due to the power dependency of the reaction rate on α_{app}, it follows that increasing the sulphuric acid concentration has the effect of increasing the ferric ion reduction rate.

4.5. *Influence of bed thickness*

From electrochemical reactor theory it is known that three dimensional electrodes exhibit complex behaviour with respect to the potential distribution within
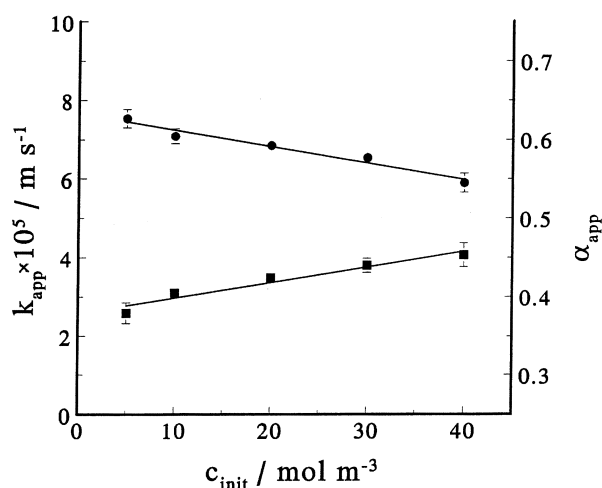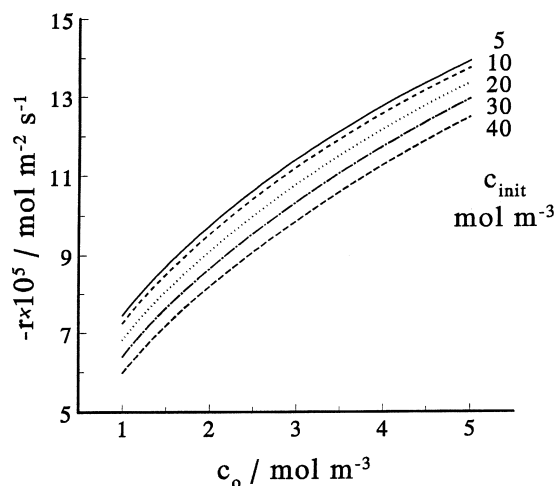
Fig. 8. Apparent reaction rate parameters k_{app} (●) and α_{app} (■) as a function of the initial ferric ion concentration in the batch-recycle system.
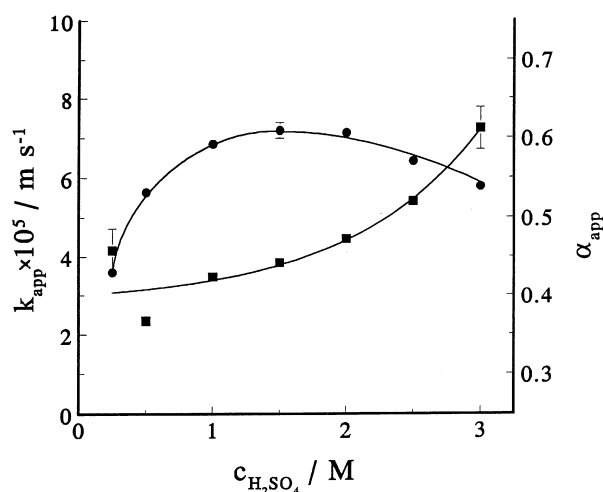
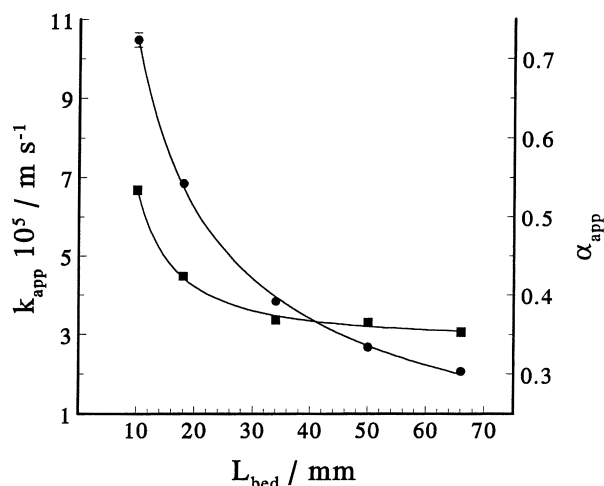Fig. 10. Apparent reaction rate parameters k_{app} (●) and α_{app} (■) as a function of the sulphuric acid concentration.

Fig. 11. Apparent reaction rate parameters k_{app} (●) and α_{app} (■) as a function of the bed thickness.

the electrode [14, 15]. An important parameter in this distribution is the thickness of the electrode. In general it can be said that for a specific process there exists a value for the bed thickness for which the efficiency of the electrode is optimal.

To examine the influence of the bed thickness on the ferric ion reduction process it was varied between 10 and 66 mm. The findings with respect to k_{app} and α_{app} are reported in Fig. 11. When the bed thickness is increased, then both the apparent reaction rate constant and the apparent reaction order decrease. This means that the smallest bed thickness of 10 mm gives the highest efficiency of the packed bed electrode. Again a value smaller then 1 is observed for α_{app}.

5. Discussion

5.1. Evaluation of the empirical model and the experimental results

With the use of an empirical macroscopic rate equation and the CSTER reactor model it has been possible to describe the behaviour of the spontaneous reduction of ferric ions with a laboratory scale GBC-reactor. In some cases the conversion per pass exceeded the limit of 5–10% in which case the assumption of a well mixed reactor becomes less appropriate [6].

During the measurements the current density of the gas diffusion electrode stayed well below $2.5\,kA\,m^{-2}$, so the assumption that the oxidation of hydrogen gas is kinetically controlled is valid in all cases.

The deviation from first order concentration behaviour can be assigned to several factors. One factor is the concentration dependency of the electrochemical reaction rate constant [14], which, in most cases, will lead to a concentration dependency of the electrochemical reaction rate smaller than one [14, 16]. Secondly, in the spontaneous GBC-process the existence of activity/overpotential in the packed bed electrode is strongly determined by the concentra-

tions of electroactive species inside the reactor. This latter influence on the concentration dependency of the process is not yet understood and needs further investigation.

With respect to changes in the apparent reaction order, as a function of varying process conditions, two limiting cases can be distinguished. If the reduction process starts to become fully mass transfer limited then α_{app} approaches the limiting value of 1. The second limiting value is approached when the reduction process becomes fully kinetically controlled. The absolute value of this kinetically limited apparent reaction order will be dependent on the process conditions.

The increase in the apparent reaction rate constant with superficial liquid velocity (Fig. 6) can only be caused by an increase in the mass transfer rate. The fact that α_{app} has a value less then 1, in the studied velocity range, indicates that there is also an influence of the electrochemical kinetics. This combined influence of mass transfer and kinetics is often referred to as a mixed controlled process.

The slight decrease of α_{app} with increasing temperature, indicates an increasing influence of the electrochemical kinetics on the reduction process. This is unusual, because the reduction process is at the lowest experimental temperature of 298 K, already influenced by mass transfer. Thus, a further increase in the temperature would show an increasing mass transfer influence [6] (i.e., increasing α_{app}). This indicates that the electrochemical reaction rate in the packed bed is highly dependent on another parameter, the solution conductivity, which has a weak temperature dependence. From literature data [17] an apparent activation energy of approximately $10\,kJ\,mol^{-1}$ for the conductivity of a 1 M sulphuric acid solution was calculated, which is of the same order as $12\,kJ\,mol^{-1}$, the value of the apparent activation energy of k_{app}.

The trends for the apparent reaction rate parameters as a function of the initial ferric concentration (Fig. 8), suggest that the reduction process becomes more kinetically controlled when the initial concentration is reduced, while the rate of reduction increases (Fig. 9). This can be explained by activation of part of the packed bed electrode which is less or not active (i.e., further away from the gas diffusion electrode). This activation is possible because of the shift to a higher equilibrium potential of the ferric/ferro couple, which leads to an increased polarization of the packed bed electrode (i.e., increased utilization).

The behaviour of the process as the sulphuric acid concentration is changed can be described as the result of two effects. First, an increase in the sulphuric acid concentration leads to an increasing solution conductivity, which causes an increase in the local electrochemical rate constants. Secondly, the increase in the sulphuric acid concentration causes a decrease of the mass transfer coefficient as a result of the increasing viscosity of the fluid. The first effect domi-

nates the behaviour of the process in the range from 0.25 to 1.5 M, a further increase in the sulphuric acid concentration causes the mass transfer effect to become dominant.

The fact that α_{app} increases as the bed thickness becomes less then approximately 30 mm, indicates that from that point the control of the process starts shifting. As L_b becomes smaller then 30 mm mass transfer starts to become a more important factor in the behaviour of the GBC-reactor. This is caused by two effects. First of all the potential distribution in the packed bed gets smoother at smaller bed thickness [15], thereby increasing the local electrochemical rate constants. Secondly, the part of the packed bed which has a stronger dependence on mass transfer (i.e., closer to the gas diffusion electrode) will be relatively increased as the bed thickness is decreased.

The behaviour of the reduction process of ferric ions in a GBC-reactor is strongly dependent on the studied key parameters. Although the effects of varying the different parameters independently were established it is still impossible to predict the behaviour of the system for an arbitrarily set of parameters. This acquires a more sophisticated model which takes the potential distribution in the packed bed into account. Such a model has been developed and is currently being tested, the results will be presented in a forthcoming publication [18].

5.2. The GBC-principle and its applications

The use of hydrogen gas to bring about spontaneous reduction reactions has been proposed and utilized before and several reactor configurations have been applied for this task [19–21]. To spontaneous reduce metal ions in dilute solutions the GBC-reactor principle should be superior to these other reactor configurations. This is inherent to the combination of a gas diffusion electrode, which is exceedingly suitable for hydrogen oxidation, with a three–dimensional porous electrode. The latter being the logical choice for electrode reactions with dilute reactants [1, 14, 15].

Cu^{2+}, Cr^{6+} and Ag^+ are examples of metal ions which can be reduced with a GBC-reactor working in the undivided mode. Although the reduction of ferric ions was chosen as an ideal model system it is of interest within the framework of the regeneration of Fenton's reagent [22, 23].

To reduce metal ions for which it is necessary to use an external power supply the use of the GBC-principle has the advantage of lowering the cell potential with respect to traditional electrochemical processes. In this respect it has been shown in metal winning electrolysis that the use of hydrogen gas anodes can achieve a significant decrease in the electric energy consumption [24–28].

An economic assessment of the advantage of using an undivided/divided GBC-reactor, compared to other electrochemical reactors, has still to be made.

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