

Electrogenerative oxidation of ferrous ions with graphite electrodes

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Electrogenerative oxidation of ferrous ions in $\text{Fe}^{2+}/\text{O}_2$ cells to regenerate ferric ions for further use is demonstrated and some results for a hybrid type laboratory-scale reactor are presented. The use of graphite particle, packed-bed anodes for ferrous oxidation with gas diffusion type cathodes for oxygen reduction enables these cells to produce ferric ions at moderate current densities and low cell voltages in sulphuric acid solutions. These cells which utilize the rapid electrochemical, ferrous oxidation rate on graphite catalytic electrodes without any need for an external power source have potential application in hydrometallurgical leaching systems as well as in sulphur dioxide cleanup processes which incorporate the use of ferric ions. Continuous feed stream operation under mild conditions is a special advantage.

1. Introduction

Ferric ions are potential oxidizing agents for a number of industrially important chemical processes. These include the leaching of copper and iron from metal ores and scrap [1, 2], and sulphur dioxide (SO_2) removal from flue gases in aqueous sulphuric acid solution [3, 4]. Whereas regeneration is a feature of some processes, this is frequently slow and energy demanding. However, both modern environmental regulations and process economics mandate that spent ferric ions should be regenerated for further use where ferric based procedures are to be incorporated into processing schemes.

Hydrometallurgical leaching processes with ferric sulphate in aqueous sulphuric acid have been investigated for leaching copper, iron and silver from ores [1, 2, 5–8]. These processes were selected in preference to ferric chloride in hydrochloric acid solution for a variety of reasons including the extremely corrosive nature of ferric chloride and the powdery copper deposits which sometimes are obtained from chloride solutions [1, 2, 6–11]. In order to regenerate and maximize the utilization of ferric ions, both chemical and electrolytic methods have been suggested for oxidizing relatively stable ferrous ions in aqueous sulphuric acid. Both reaction kinetics and mechanisms for ferrous oxidation with oxygen in aqueous sulphuric acid have been extensively investigated at various temperatures and pressures [12, 13]. However, the oxidation rate under ambient conditions is generally not fast enough for practical application with leaching processes. Furthermore, the oxidation rate is reported to be depressed with increasing sulphuric

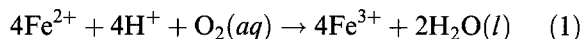
acid concentrations [1, 5, 13]. To overcome these problems, a pressure oxidation process with oxygen has been proposed [5, 7]. Oxygen pressures as high as 1000 kPa were investigated to increase oxygen concentrations in solutions and mass transfer rates of oxygen gas to the sulphuric acid solution; temperatures as high as 125 °C to promote the ferrous oxidation rate were also investigated. Such conditions were chosen because under ambient conditions alone, a large absorption device would be required for complete oxidation. Electrolytic oxidation has also been investigated for rapid ferrous ion conversion to ferric ions [1, 7, 9]. However, additional costs for electrical power as well as relatively expensive power equipment would be required.

For SO_2 cleanup processes, ferric ions and sulphuric acid solutions have been proposed for increasing scrubbing capacity. They are claimed to be effective agents for SO_2 oxidation [3, 4]. After SO_2 is scrubbed with the aqueous ferric containing sulphuric acid solution, dissolved SO_2 is oxidized to sulphate with ferric ions reduced to ferrous. For regeneration of the ferric ions, oxygen and other chemical oxidizing agents have been considered. For economic reasons, air is preferred over pure oxygen. However, the ferrous oxidation rate with oxygen is too slow for practical application under ambient conditions. Chemical oxidation is generally limited by the expense of chemical oxidants and gas scrubbing process complications. Furthermore, residues can remain in solution and limit the subsequent use of the sulphuric acid generated from these processes. Electrolytic ferrous oxidation also has been suggested for this application implying again additional costs for power as well as power generating equipment [4].

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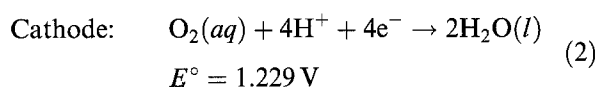
2. Electrogenative ferrous oxidation in Fe²⁺/O₂ cells

On the basis of thermodynamics, ferrous ion oxidation to ferric ion is a very favourable, spontaneous exothermic process. For the reaction in aqueous solutions,

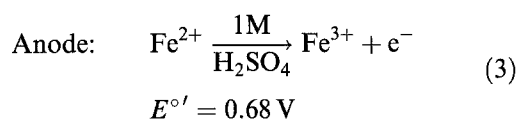


the reaction enthalpy is $-3.88 \times 10^5 \text{ J mol}^{-1}$ and the Gibbs free energy change is $-7.88 \times 10^5 \text{ J mol}^{-1}$ [14]. Since electrochemical ferrous oxidation rates on catalytic graphite surfaces are fast, there was the possibility of retrieving some of the favourable thermodynamic energy of the reaction as electrical energy, while producing ferric ions more efficiently [15, 16]. The concept of electrogenerative ferrous oxidation with an oxygen cathode as an ancillary operation in a copper leaching process with ferric chloride was suggested earlier by Langer and Sakellariopoulos [15]. The cells for this process, then, were difficult to operate since platinum cathodes for oxygen reduction are susceptible to chloride ion poisoning. In sulphuric acid solutions which are considered in this study, platinum cathodes can perform satisfactorily while maintaining their activity, so that Fe²⁺/O₂ cell operations now seem viable for ferric ion regeneration.

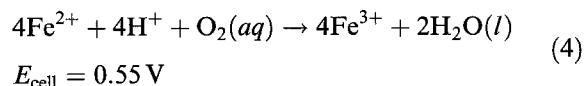
In this electrogenerative system, ferrous ions in sulphuric acid would be electrochemically oxidized in a graphite particle packed-bed anode while oxygen is reduced at a counter gas diffusion-type cathode in aqueous sulphuric acid. With a positive potential being generated between the anode and the cathode, the need for an external power source to drive the ferrous oxidation could be eliminated. The overall anodic and cathodic reactions can be represented as



The potential for Equation 2 is the standard one for the oxygen electrode. However in the sulphuric acid anolyte with ferric/ferrous ions present, at the anode the formal potential is more convenient and relevant [17, 18]. Thus,



The formal potential, $E^{\circ'}$, differs from the standard potential and applies specifically to the 1 M sulphuric acid solutions of this study. It is an experimental value which takes into account many solution effects from the presence of iron ions including complexation. The net overall cell reaction becomes



with acid and oxygen being consumed in the course of ferrous oxidation. The calculated potential for this

electrogenative cell using half cell values, then would be 0.55 V. The oxygen electrode, however, very seldom operates reversibly so that from experience we can anticipate open circuit cell potentials 0.15 to 0.2 V below this value. The cell exploits the favourable thermodynamics for ferrous oxidation with oxygen by coupling two effective electrode reactions. Thus, desired ferric ions are produced efficiently by electrochemical means while the reaction free energy is converted into d.c. electrical currents eliminating the need for an external power source. Given the large quantity of ferric ions of potential use to industry, this type of cell is attractive and of special interest for application in regeneration. Here, some promising results from a laboratory scale cell are presented. The effectiveness of the graphite particle packed-bed anode for ferrous oxidation and the availability of high performance oxygen cathodes enables these cells to produce ferric ions at relatively high current densities (high ferrous oxidation rate), albeit at low cell voltages. With steady advances in electrochemical cell design, it would appear that scale-up and advantageous modification of this type of cell would be quite feasible.

3. Experimental details

3.1. Electrogenative cells and equipment

The electrogenerative cell was a hybrid sandwich type with a rectangular shaped packed-bed anode and a gas diffusion type LAA-2 cathode separated by both an electrolyte and a membrane. It resembles several developed earlier in our laboratories [19, 21]. The cell body is constructed from stress-relieved polypropylene while gaskets are Teflon or Viton. Schematic representations of the electrogenerative cell components and an experimental array are shown in Figs 1 and 2, respectively.

A graphite particle bed (Superior Graphite Company, 9012 Desulco, US Mesh 16 ~ 18) was used for ferrous oxidation. To remove impurities from the graphite particles, they were treated in concentrated sulphuric acid for 1 h and then rinsed thoroughly in deionized water. The particles then were placed in the packed-bed chamber where a platinum current collector (Engelhard Corp., 45 mesh) in front of the bed produced slight compression. A gas diffusion type LAA-2 electrode (American Cyanamid, Pt-black) [22] with a platinum current collector in front of the electrode was used for oxygen reduction. An anion exchange membrane (RAI Research Corp., R4030) separator was placed between the anode compartment and the cathode compartment to hinder oxygen cathode deactivation by any ferrous/ferric ion transfer from the anode compartment.

The potential differences between the anode and the cathode and between the anode and a NaCl-saturated calomel reference electrode (SSCE) (Fisher Scientific, model 13-620-57) were measured with high impedance digital multimeters. For current measurement, either

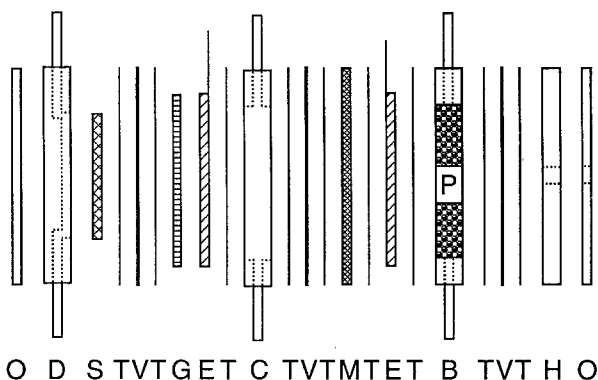


Fig. 1. Components of electrogenerative cells. (O) aluminium support, (D) cathode gas chamber, 63.5 mm \times 88.9 mm \times 6.4 mm, (S) spacer, (T) Teflon gasket, (V) Viton gasket, (G) gas diffusion electrode, 19.1 mm \times 57.2 mm, (E) Pt current collector, 19.1 mm \times 57.2 mm, (C) catholyte chamber, 63.5 mm \times 88.9 mm \times 6.4 mm, 12.7 mm \times 50.8 mm hole at the centre, (M) R4030 membrane, (B) packed bed chamber, 63.5 mm \times 88.9 mm \times 3.2 mm, 12.7 mm \times 50.8 mm hole at the centre, (P) graphite particle packed-bed electrode, 12.7 mm \times 50.8 mm \times 3.2 mm. (H) aluminium support.

a digital multimeter or an analogue ammeter was used. The low resistance analogue ammeter permitted higher current generation in the external circuit at low cell potentials. A variable resistor was used for the external load. To supply external currents in the packed-bed anode pretreatment, the resistor was replaced with a constant current supply with a digital coulometer (Electrosynthesis Company, Inc., model 600).

3.2. Electrogenerative cell polarization experiments

Appropriate sulphuric acid concentrations were prepared through dilution of reagent-grade sulphuric acid with deionized water. The resulting sulphuric acid solution was then purged with argon for at least an hour to remove dissolved oxygen, before dissolution of proper amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Since the fast electrochemical ferrous oxidation rate would tend to dominate any effects from impurity reactions and the large electrode surface area (1 m^2 for the 2 cm^3 packed-bed) was high enough to keep the ratio of the active surface area to any impurity large, no attempt was made to maintain ultra-high purity conditions.

The graphite particle packed-bed anode and the LAA-2 cathode were pretreated before cell polarization experiments to obtain desired initial catalytic states and reproducible results. To catalytically reduce platinum oxides on the LAA-2 electrode, hydrogen was fed to the cathode gas compartment. After 10 min of cathode hydrogen treatment, the anode and the cathode were connected through a variable resistor and a current of 5 mA was drawn from the cell with the LAA-2 electrode at reversible hydrogen electrode potential. When the short circuit current fell below 5 mA, the resistor was replaced with the constant current supply. Reducing currents of 5 mA or less were then applied to the

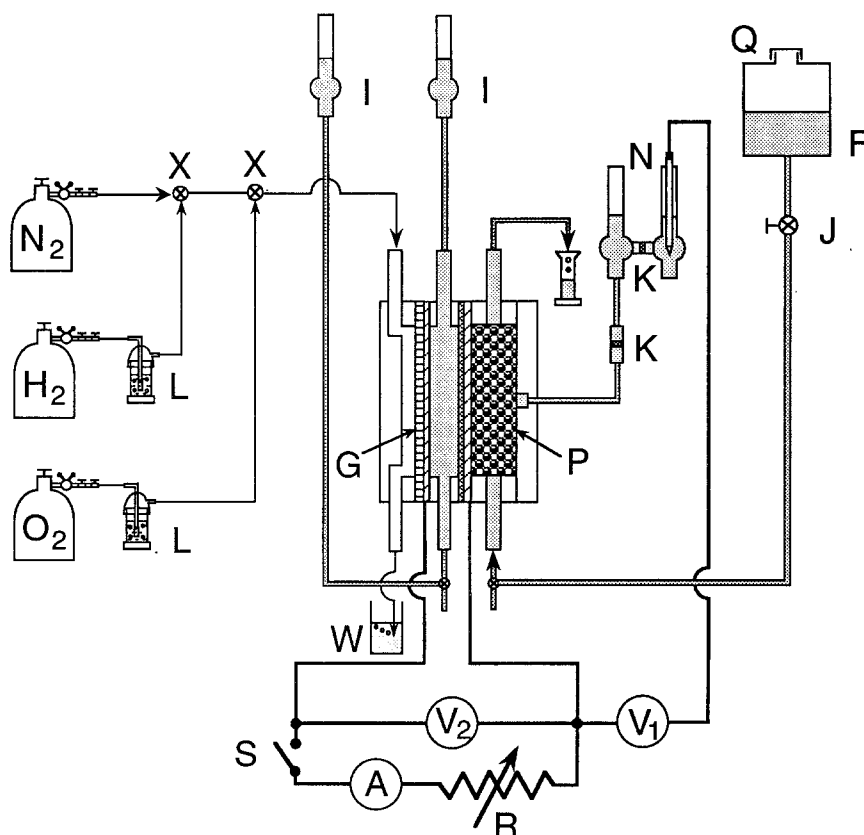


Fig. 2. Schematic representation of an experimental setup. (A) ammeter, (F) feed, (G) gas diffusion electrode, (I) catholyte reservoir, (J) valve with PTFE plug, (K) fine glass frit, (L) gas sparger with water, (P) packed-bed electrode, (N) NaCl-saturated calomel electrode, (V_1 , V_2) high impedance voltmeter, (Q) glass cap, (R) variable resistor, (S) switch, (W) water seal.

packed-bed anode to keep the cell potential at 0.0–0.5 mV. Because slight hydrogen gas evolution occurred at the packed-bed anode during the pretreatment, bubbles were removed periodically from the chamber with rubber bulb suction at the anode outlet. The reduction was carried out for 30 min since the voltaic efficiency for ferrous oxidation has been reported to be the greatest on fresh graphite surfaces [23]. The constant current supply was then disconnected, and the SSCE potential against the LAA-2 cathode with excess adsorbed hydrogen was recorded. Thus, the SSCE potential was referenced to a reversible hydrogen electrode (RHE). The cathode compartment then was purged with nitrogen, before feeding excess oxygen to the cathode gas chamber. Currents of 5 mA were then drawn from the cell through adjustment of the external variable resistor until the anode potential rose above 250 mV/RHE to remove residual hydrogen in the packed-bed anode pores. Sulphuric acid solutions of iron ions were then introduced to the packed-bed anode to replace the 3 M H₂SO₄ solution.

Polarization curves were obtained through external resistor load decrease from open circuit. Each potential in a polarization experiment was determined after three minute equilibration at the given current density to obtain a steady state value. As a precaution, the anode potential was never allowed to exceed 800 mV/RHE to limit any irreversible oxide formation which might be detrimental to the electrocatalytic activity for ferrous oxidation.

4. Results

Electrogenerative Fe²⁺/O₂ cell performance under typical experimental conditions with 0.47 M FeSO₄ in 3 M H₂SO₄ is shown in Fig. 3. Thus, ferrous ions were oxidized to ferric ions within the graphite particle packed-bed electrode while oxygen was reduced to water at the gas diffusion type LAA-2 electrode with d.c. production under conditions indicated

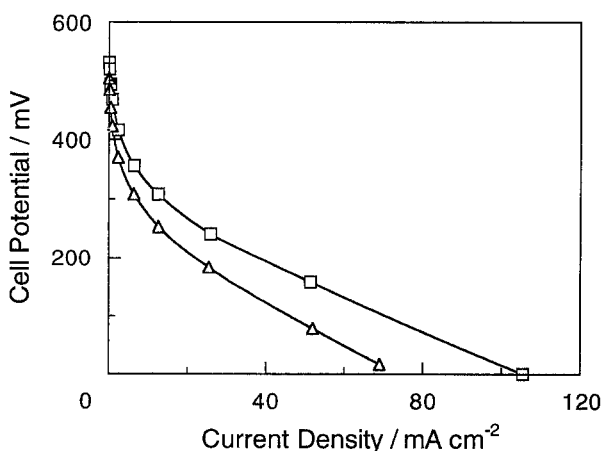


Fig. 3. Performance curves for electrogenerative Fe²⁺/O₂ cells. Anode: graphite particle packed-bed electrode. Cathode: LAA-2. Anolyte: 0.47 M FeSO₄ in 3 M H₂SO₄, 3.0 cm³ min⁻¹. Catholyte: 3 M H₂SO₄, static. Cathode gas: (□) O₂, (△) air. Membrane: R4030; 24.6 °C.

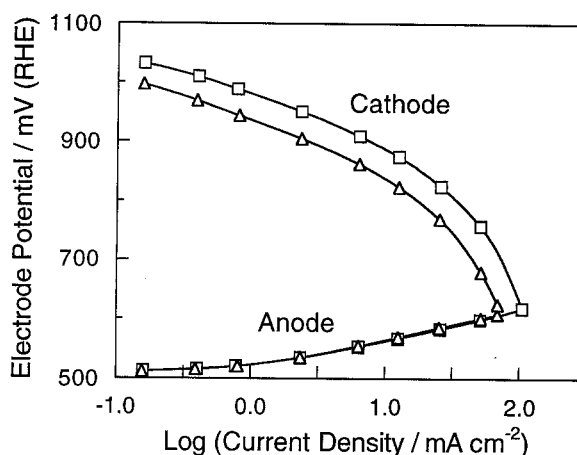


Fig. 4. Anode and cathode polarization curves. A: anode polarization curves; C: cathode polarization curves. (Same conditions as for Fig. 3.)

in the caption. After testing with sulphuric acid concentrations of 2 to 4 M H₂SO₄, 3 M H₂SO₄ was identified as being in the range of the optimum overall sulphuric acid concentration and was employed in many other experiments. This was consistent with past experience with similar types of electrogenerative cells [19–21]. Feed rates and temperatures were selected with consideration of experimental convenience and reasonable conditions for the laboratory scale cell.

With graphite particle electrodes, current densities up to 105 mA cm⁻² could be achieved at a 3.0 cm³ min⁻¹ flowrate. This is equivalent to a calculated ferrous oxidation rate of 7.0 × 10⁻⁶ mol s⁻¹, in the 2 cm³ graphite particle packed-bed and a ferrous ion conversion of 30% for a single pass. The cell was also operated with air to investigate the possibility of using it directly at the cathode. Even with the lower oxygen concentration (~20%) of the air, the maximum current from the cell was still 69 mA cm⁻². The respective anode and cathode performances are shown in Fig. 4. As expected with the air feed, the cathode potential fell more rapidly at higher currents because of concentration polariz-

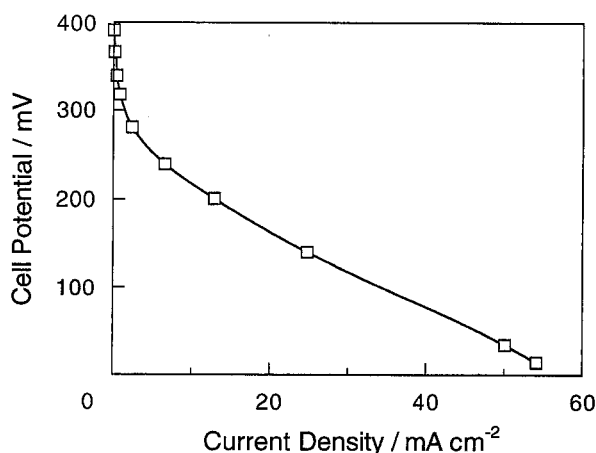


Fig. 5. Performance curve with 0.5 M FeSO₄ and 0.25 M Fe₂(SO₄)₃ in 1 M H₂SO₄. Anode: graphite particle packed-bed electrode. Cathode: LAA-2. Anolyte: 0.5 M FeSO₄ and 0.25 M Fe₂(SO₄)₃ in 1 M H₂SO₄, 3.0 cm³ min⁻¹. Catholyte: 1 M H₂SO₄, static. Cathode gas: O₂. Membrane: R4030. Temperature: 23.7 °C.

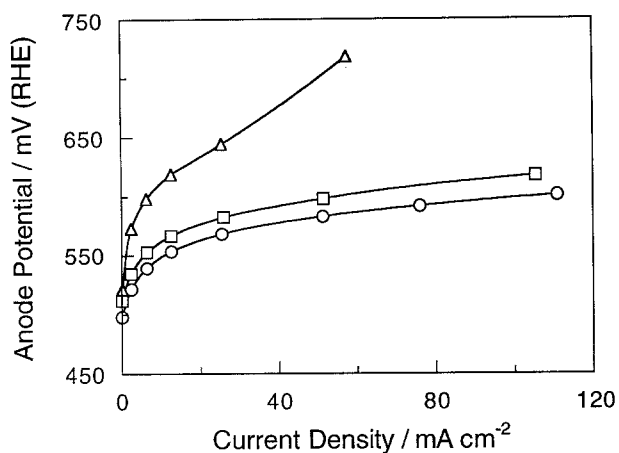


Fig. 6. Effect of FeSO_4 concentration on anode performance. Anolyte: (Δ) 0.10 M, (\square) 0.47 M, (\circ) 0.87 M FeSO_4 in 3 M H_2SO_4 . (Same condition as for Fig. 3.)

ation. However, there appears to be a good possibility that this inexpensive oxidant could be substituted for pure oxygen in these cells.

To further characterize the cell, additional experiments were performed under conditions close to those used for obtaining the formal potential. The polarization curve for a 1 M H_2SO_4 solution containing 0.5 M FeSO_4 and 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ solution using an oxygen cathode is shown in Fig. 5. The open circuit potential of 0.391 V is within 0.16 V of that which would have been expected on the basis of calculations for Reaction 4 and expectations for the oxygen electrode performance because of irreversibility as indicated earlier. Under the operating conditions, it can be seen that currents as large as 50 mA cm^{-2} can still be attained.

The effects of ferrous concentrations to 0.87 M FeSO_4 in 3 M H_2SO_4 and higher anolyte flowrates for the anolyte composition of Fig. 3 (up to $6 \text{ cm}^3 \text{ min}^{-1}$) are shown in Figs 6 and 7, respectively. The packed-bed anode polarized significantly less at higher ferrous ion concentrations and flowrates, consistent with the anticipated mass transfer process effects at the graphite particle surfaces under these conditions. With reduced concentration polarization

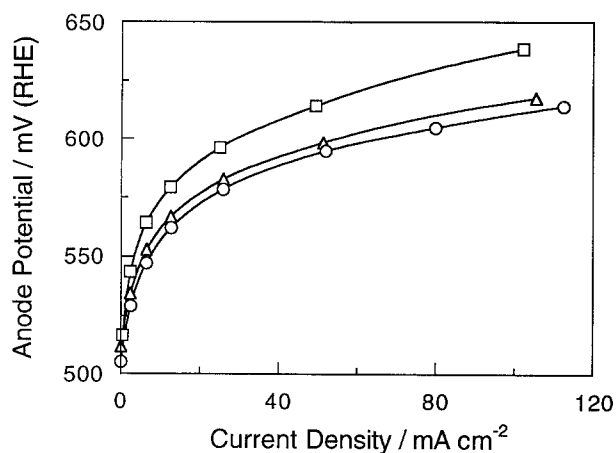


Fig. 7. Effect of anolyte flowrate on anode performance. Anolyte: 0.47 M FeSO_4 in 3 M H_2SO_4 : (\square) 1.5, (Δ) 3.0 and (\circ) $6.0 \text{ cm}^3 \text{ min}^{-1}$. (Same condition as for Fig. 3.)

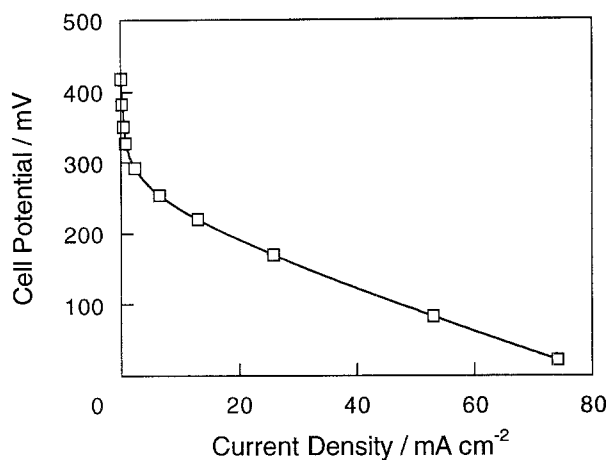


Fig. 8. Performance curve with 0.5 M FeSO_4 and 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ in 3 M H_2SO_4 . Anode: graphite particle packed-bed electrode. Cathode: LAA-2. Anolyte: 0.5 M FeSO_4 and 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ in 3 M H_2SO_4 , $3.0 \text{ cm}^3 \text{ min}^{-1}$. Catholyte: 3 M H_2SO_4 , static. Cathode gas: O_2 . Membrane: R4030. Temperature: 23.7°C .

at the anode, the cell provided somewhat higher cell potentials for selected current densities. Higher ferrous ion concentrations and flowrates beyond the investigated range might be expected to improve cell performance slightly for this type of cell arrangement.

A ferric ion leaching process is not always driven to completion and considerable amounts of unreacted ferric ions may remain in the leaching solutions. For comparison purposes, results for a 3 M H_2SO_4 solution which is 0.5 M in FeSO_4 and 0.25 M in $\text{Fe}_2(\text{SO}_4)_3$ are shown in Fig. 8. It can be seen that an open circuit potential of 0.418 V and currents as large as 74 mA cm^{-2} are achieved.

Since the anode and cathode are separated by an ion exchange membrane and the cathode compartment can be flushed, the effects of ferric/ferrous ion concentration variations mainly occur at the anode. Their effect was investigated further using 0 to 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ with 0.5 M FeSO_4 . The results are illustrated in Fig. 9. As expected on the basis of Nernst type calculations, $+ (RT/nF) \ln [\text{Ox}]/[\text{Red}]$, the anode potential at equilibrium was higher in the presence of ferric ions (for example, 647 mV/RHE

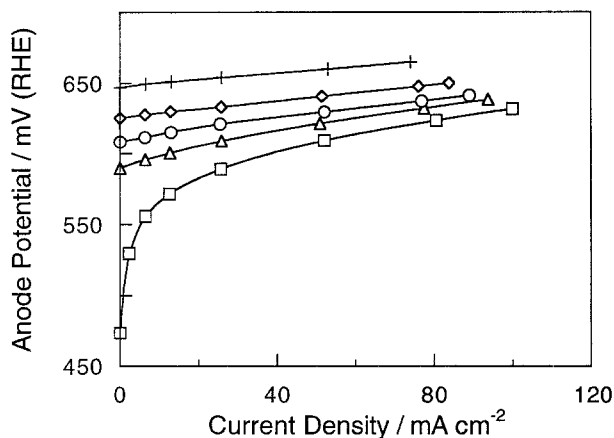


Fig. 9. Effect of $\text{Fe}_2(\text{SO}_4)_3$ concentration on anode performance. Anolyte: 0.5 M FeSO_4 : (\square) 0 M, (Δ) 0.025 M, (\circ) 0.05 M; (\diamond) 0.10 M, (+) 0.25 M $\text{Fe}_2(\text{SO}_4)_3$ in 3 M H_2SO_4 . (Same condition as for Fig. 3.)

Table 1. Open circuit potentials with 0.5 M FeSO₄ and various concentrations of Fe₂(SO₄)₃ in 3 M H₂SO₄.

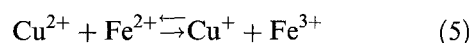
| Fe ₂ (SO ₄) ₃ concentration/M | E _{anode} /V(RHE) | Predicted E _{anode} /V(RHE) |
|---|----------------------------|--------------------------------------|
| 0.00 | 0.470 | — |
| 0.025 | 0.590 | 0.588 |
| 0.05 | 0.608 | 0.606 |
| 0.10 | 0.625 | 0.623 |
| 0.25 | 0.647 | — |

(measured) in 0.5 M FeSO₄ and 0.25 M Fe₂(SO₄)₃; 590 mV/RHE (measured) in 0.5 M FeSO₄ and 0.0025 M Fe₂(SO₄)₃. Significant amounts of ferrous ions can still be oxidized in the cell in the presence of ferric ions (20% conversion for a single pass at a 3 cm³ min⁻¹ flowrate). Although there is a large effect of ferric ions in the low current density region, the effect in the high current density region is diminished since the significant amounts of ferric ions generated at the anode during cell polarization cause the initial bulk ferric concentration to be relatively less important.

It is of interest to note that open circuit potentials measured at the anode relative to the reversible hydrogen electrode through use of a reference electrode can still reflect thermodynamic reversibility and properties at the anode. The open circuit values for various ratios of bulk concentrations of ferric and ferrous sulphate can apparently be predicted. In Table 1, the open circuit potential for the anode referenced to the reversible hydrogen electrode is given for a 3 M H₂SO₄ solution which is 0.5 M in FeSO₄ and 0.25 M in Fe₂(SO₄)₃. With some corrections it could be related to a formal potential value for 3 M H₂SO₄. However, if we apply the Nernst correction for various concentration ratios of Fe²⁺ and Fe³⁺ from FeSO₄ and Fe₂(SO₄)₃ to the experimental open circuit potential from 0.5 M FeSO₄ and 0.25 M Fe₂(SO₄)₃ in 3 M H₂SO₄, open circuit potentials can be predicted fairly well as shown in Table 1. This is a consequence of the high exchange current and thermodynamic reversibil-

ity of the Fe²⁺/Fe³⁺ couple on catalytic graphite electrodes. The measured open circuit potential of 0.47 V with ferrous sulphate alone reflects the absence of ferric ion except for equilibrium concentrations which might be generated through the exchange reaction at open circuit.

Because applications to copper leaching processes were envisioned, some cupric ion effects at the anode also were investigated. Results from these experiments are shown in Fig. 10. Because the cupric ions were added in the completely oxidized form, these ions might not at first glance be expected to affect the graphite anode performance. The cupric-ferrous equilibrium, which is rapid although unfavourable,



can result in the formation of some cuprous ions with ferric ions [24]. The anode potential, if there is an effect, would be lowered by the small fraction of cuprous ions produced from this equilibrium. Since such cuprous ions can also be oxidized at the anode and the cupric/cuprous potential ($E^{\circ} = 0.153$ V) is lower than the ferric/ferrous potential ($E^{\circ'} = 0.68$ V), there is the possibility that the mixed potential at the anode will be lowered. As can be seen in Fig. 10, there was a slight decrease of the anode potential by about 3 mV at 50 mA cm⁻². This anode potential decrease did not vary much with the copper concentrations investigated.

5. Suggested applications of electrogenerative Fe²⁺/O₂ cells

A modified copper leaching process based on the work of Letowski *et al.* [1] incorporating an electrogenerative stage of the type described here is represented in Fig. 11. However, a ferrous sulphate crystallization step is eliminated. Instead, after ferric ion depletion from copper concentrate leaching (for example, chalcocite, Cu₂S, or chalcopyrite, CuFeS₂), most cupric ion is removed from the pregnant product stream by solvent extraction to be delivered to an electrowinning stage. (See, for example [25].) With bypassing of the electrolytic copper recovery stage the aqueous raffinate now containing predominantly ferrous ions can then be recycled through the electrogenerative Fe²⁺/O₂ cell to reoxidize ferrous ions to ferric ions under relatively mild conditions. Provision is made for some make-up acid addition if needed at the electrogenerative stage because of acid consumption in oxygen reduction (see Equation 2). Some low voltage electrical energy might even be recovered as a byproduct during the ferric ion regeneration. Higher sulphuric acid concentrations can be employed relative to the pressurized oxidation process because the deleterious effects of higher sulphuric acid concentrations on homogeneous ferrous oxidation kinetics are no longer a concern [5, 13]. Higher sulphuric acid concentrations also

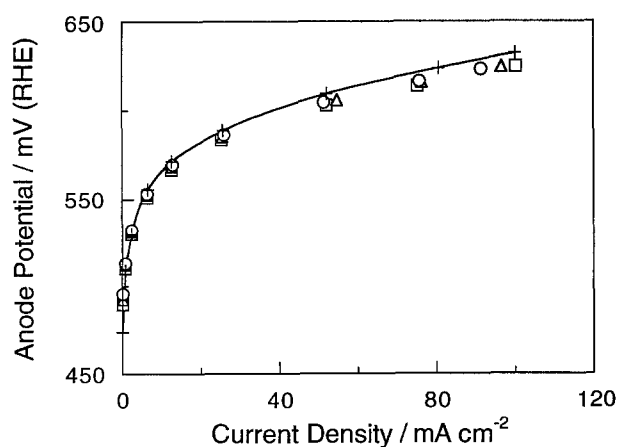


Fig. 10. Effect of CuSO₄ on anode performance. Anolyte: 0.5 M FeSO₄: (+) 0M, (□) 0.1M, (△) 0.2M, (○) 0.4M CuSO₄ in 3 M H₂SO₄. (Same condition as for Fig. 3.)

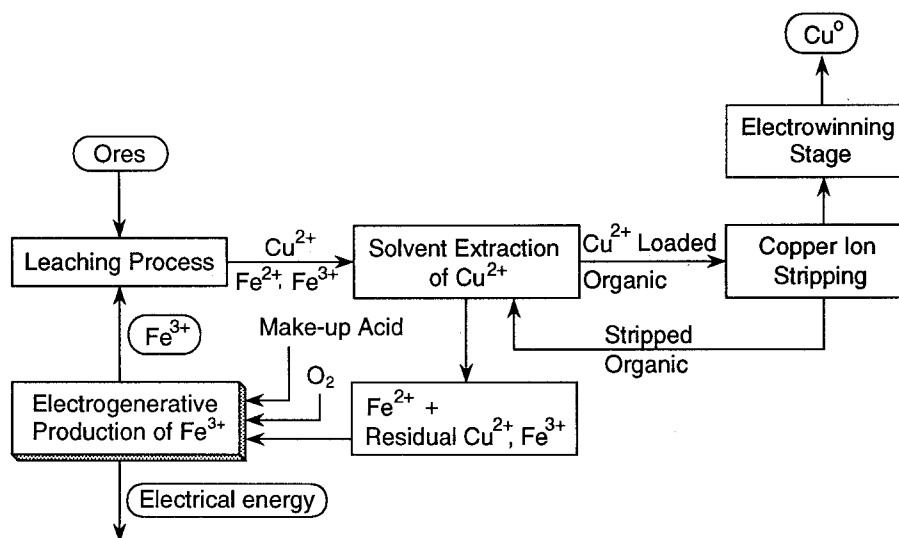
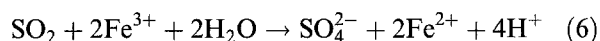


Fig. 11. A proposed hydrometallurgical flowsheet for copper recovery from copper concentrates incorporating an electrogenerative stage for ferric ion regeneration.

might help to minimize the tendency for copper sulphate coprecipitation during ferrous sulphate crystallization [1, 5]. Continuous feed stream treatment under relatively mild conditions is a further advantage of electrogenerative cell use for oxidation, since pressurized oxidation processes at high temperature are operated in the batch mode.

These electrogenerative $\text{Fe}^{2+}/\text{O}_2$ cells also have possibilities for incorporation into SO_2 scrubbing processes [3, 4]. After SO_2 is removed through scrubbing with ferric ion-containing sulphuric acid solution, dissolved SO_2 can be oxidized to sulphate by ferric ions



to produce sulphuric acid. The resulting ferrous ion, sulphuric acid solutions then can be returned to the ferric state in the electrogenerative $\text{Fe}^{2+}/\text{O}_2$ cells with some useful electrical energy production.

Another possibility for utilizing this concept is the oxidation of ferrous ions from acid mine water solutions as suggested by Newman and Tiedemann [26]. However, this might well require cell modifications. These cells might also be incorporated into the production of partially oxidized carbonaceous materials (e.g. humic acids) from chars, tars and hydrocarbon residues as suggested by Vaughan in several patents [27–29]. After oxidation by ferric ions in sulphuric acid solutions, the spent iron ions can be reoxidized to the ferric state in $\text{Fe}^{2+}/\text{O}_2$ cells.

6. Conclusion

It appears that electrogenerative $\text{Fe}^{2+}/\text{O}_2$ cells can be employed to advantage to regenerate process ferric ions in solution with relatively inexpensive graphite particle packed-bed anodes and gas diffusion type cathodes. Current densities as high as 100 mA cm^{-2} were obtained in $3 \text{ M H}_2\text{SO}_4$ solutions which were 0.5 M in FeSO_4 . These cells also bring about the electrochemical oxidation with low voltage d.c. electrical energy production. It is clear that further refinement of

cell design and operation with favourable ferrous ion concentrations and flowrates would make these kinds of cells more attractive for practical applications, particularly because of their capacity for continuous feed stream operation under such mild conditions.

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References

- [1] F. Letowski, B. Kolodziej, M. Czernecki, A. Jedrczak and Z. Adamski, *Hydrometallurgy* **4** (1979) 169.
- [2] R. M. Morrison, *ibid.* **21** (1989) 67.
- [3] M. Noguchi and H. Yanagioka, *US Patent 3 836 630* (1974).
- [4] L. Pessel, *US Patent 4 284 608* (1981).
- [5] T. Chmielewski and W. A. Charewicz, *Hydrometallurgy* **12** (1984) 21.
- [6] J. E. Dutrizac and R. J. C. MacDonald, *Can. Metall. Q.* **11** (1972) 469.
- [7] *Idem*, *Minerals Sci. Engng* **6** (1974) 59.
- [8] J. E. Dutrizac, *Metall. Trans. B* **12** (1981) 371.
- [9] Z. Yongfeng, L. Hongjie, C. Haiyong, Y. Ying and Z. Yajie, *Adv. Hydrogen Energy* **8** (Hydrogen Energy Prog. 8, Vol. 2) (1990) 523.
- [10] D. L. Jones and E. Peters, 'The Leaching of Chalcopyrite with Ferric Sulfate and Ferric Chloride,' in *Extr. Metall. Copper, Int. Symp., Vol. 2* (edited by J. C. Yannopoulos and J. C. Agarwal), AIME, New York (1976) pp. 633–653.
- [11] L. W. Beckstead, P. B. Munoz, J. L. Sepulveda, J. A. Herbst, J. D. Miller, F. A. Olson and M. E. Wadsworth, 'Acid Ferric Sulfate Leaching of Attritor-Ground Chalcopyrite Concentrates,' in *Extr. Metall. Copper, Int. Symp., Vol. 2* (edited by J. C. Yannopoulos and J. C. Agarwal), AIME, New York (1976) pp. 611–632.
- [12] D. R. McKay and J. Halpern, *AIME J. Trans. Metall. Soc.* **212** (1958) 301.
- [13] C. T. Mathews and R. G. Robins, *Proc. Aust. Inst. Min. Met.* **242** (1972) 47.
- [14] 'Handbook of Chemistry and Physics', 68th edn; CRC Press, Boca Raton, FL (1987).

- [15] S. H. Langer and G. P. Sakellaropoulos, *Ind. Eng. Chem. Process Des. Dev.* **18** (1979) 567.
- [16] S. H. Langer, J. C. Card and M. J. Foral, *Pure & Appl. Chem.* **58** (1986) 895.
- [17] J. J. Lingane, 'Electroanalytical Chemistry,' 2nd edn; Interscience Publishers, New York (1958) pp. 58–59.
- [18] E. H. Swift and E. A. Butler, 'Quantitative Measurements and Chemical Equilibria,' W. H. Freeman & Co., San Francisco (1972) p. 79 and p. 694.
- [19] J. C. Card, S. E. Lyke and S. H. Langer, *J. Appl. Electrochem.* **20** (1990) 269.
- [20] S. E. Lyke and S. H. Langer, *J. Electrochem. Soc.* **138** (1991) 1682.
- [21] *Idem, ibid.* **138** (1991) 2327.
- [22] R. G. Haldeman, W. P. Colman, S. H. Langer and W. A. Barber, in 'Adv. Chem. Ser.', Vol. **47** (American Chemical Society, Washington D.C., 1965) p. 116.
- [23] L. W. Hruska and R. F. Savinell, *J. Electrochem. Soc.* **128** (1981) 18.
- [24] M. Cher and N. Davidson, *J. Amer. Chem. Soc.* **77** (1955) 793.
- [25] A. R. Lillo-Ramirez, 'SX/EW for the Copper Industry' in 'Hydrometallurgy and Electrometallurgy of Copper', *Copper 87*, Vol. **3** (edited by W. C. Cooper, G. E. Lagos and G. Ugarte), University of Chile (1988) pp. 287–97.
- [26] J. Newman and W. Tiedemann, *AIChE J.* **21** (1975) 25.
- [27] R. J. Vaughan, *US Patent 4 592 814* (1986).
- [28] R. J. Vaughan, *US Patent 4 608 138* (1986).
- [29] R. J. Vaughan, *US Patent 4 608 137* (1986).