Hydrometallurgy 166 (2016) 123–129

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Kinetics of the oxidation of iron(II) by oxygen and hydrogen peroxide in concentrated chloride solutions – A re-evaluation and comparison with the oxidation of copper(I)

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ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form 7 October 2016
Accepted 9 October 2016
Available online 11 October 2016

Keywords:
Iron(II)
Copper(I)
Oxygen
Kinetics
Chloride
Mechanisms

ABSTRACT

The kinetics of the oxidation of iron(II) in 4 M sodium chloride solutions has been studied in order to resolve differences in the rates and rate equations from previously published studies. It has been confirmed that the rate is second order in iron(II) and first order in dissolved oxygen. The presence of trace concentrations of copper in the iron(II) solutions and catalysis by platinum metal used to monitor the solution potentials in previous studies have been experimentally identified as points of difference. The rates of oxidation of iron(II) and copper(I) by peroxide under similar conditions have been studied and the rate equations shown to be first order in both metal ion and peroxide. It is shown that peroxide is not a detectable intermediate in the reduction of oxygen by iron(II). Comparison with published data for the oxidation of copper(I) and that of iron(II) by oxygen in the presence of strongly complexing anions for iron(III) suggests that both outer-sphere and inner-sphere mechanisms are involved in the oxidation of iron(II) depending on the equilibrium for the transfer of the first electron to oxygen. This interpretation is supported by thermodynamic calculations and published kinetic data for the oxidation of iron(II) and copper(I) by the perhydroxyl radical.

1. Introduction

The kinetics of the reaction between iron(II) and dissolved oxygen in acidic chloride solutions have previously been studied by several authors (Posner, 1953a, b; Macejevskis et al., 1965; Colborn and Nicol, 1973; Yano et al., 1974; Awakura et al., 1986; Bouboukas et al., 1987). Despite relatively similar conditions, there is little agreement on the reaction order with respect to iron(II) with some studies suggesting 1st-order and some 2nd-order while one study noted that the reaction can vary from 1st to 2nd depending on the concentration of iron(II). It should also be noted that the reaction is indisputably 2nd order in iron(II) when conducted in acidic sulphate or perchlorate solutions (George, 1954; Mathews and Robins, 1972).

There are also significant differences in the observed rates of the reaction

$$4Fe(II) + O_2 + 4H^+ = 4Fe(III) + 2H_2O \quad (1)$$

as obtained in the various studies in chloride solutions. In order to attempt to resolve these differences a study of the kinetics of this reaction has been undertaken as part of a larger investigation of the kinetics of the reactions involved in the heap leaching of copper sulphide minerals in concentrated chloride solutions. Because of the similarity of the oxidation of iron(II) and copper(I) in chloride solutions, reference will be made to published data on the latter reaction where appropriate. As peroxide is likely to be an intermediate in the reduction of oxygen, a limited series of tests were also conducted on the rate of oxidation of iron(II) (and copper(I)) by peroxide

$$2Fe(II) + H_2O_2 + 2H^+ = 2Fe(III) + 2H_2O \quad (2)$$

under similar conditions.

2. Experimental

2.1. Measurement of the consumption of dissolved oxygen

The rate of the oxidation of iron(II) by dissolved oxygen (DO) was measured using a YSI model 5301 biological oxygen probe to measure the dissolved oxygen concentration. 5 mL of solution with known concentrations of NaCl and HCl was placed into the cell which was stirred by a small magnetic bar. The dissolved oxygen probe holder was designed to act like a plunger that fitted the cylindrical glass cell. A small groove machined along the length of the probe allowed air to be expelled as the probe was lowered into the cell. The cell was immersed in a temperature controlled water bath maintained at 35 °C. After temperature equilibration a weighed amount of solid $FeCl_2$ was added to the

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http://dx.doi.org/10.1016/j.hydromet.2016.10.014

solution and the probe re-immersed. The solid visibly dissolved after about 10 min. The relative dissolved oxygen concentration (as measured by the probe current) was recorded as a function of time using a National Instruments data acquisition system controlled with Labview software. Two cells were run in parallel under the same conditions to give duplicate results. Experiments were conducted at either 35 °C or 27 °C.

2.2. Electrochemical measurements

Electrochemical measurements were used to monitor the rate of oxidation of iron(II) by peroxide and also to investigate catalysis by platinum of the oxidation of iron(II) by oxygen. The experiments were carried out using a thermostatted standard three-electrode system with rotating working platinum electrodes. Potentials and currents were measured and controlled by a Solartron potentiostat operated with corrosion measurement software. The silver/silver chloride (3 mol/L potassium chloride) reference electrode (0.207 V versus SHE) was separated by a Luggin capillary from the solution in the cell and the potentials were measured and controlled relative to this electrode at room temperature.

The rate of oxidation of iron(II) and copper(I) by peroxide was studied by monitoring the limiting current due to oxidation of iron(II) or copper(I) at a rotating (1500 rpm) platinum disk electrode as a function of time. The potential of the electrode was potentiostatted at 0.9 V at which value peroxide is electrochemically inactive. The reactions were initiated by injecting a small volume (generally 0.2 mL) of iron(II) or copper(I) solution into the cell which contained the other solution components including a large excess of peroxide and was also stirred magnetically to ensure rapid mixing. The initial metal ion concentrations after injection was generally <0.2 mM.

Electrochemical measurements on the oxidation of iron(II) by oxygen were carried out using the following procedure. 50 cm^3 of electrolyte of the required composition was added to the cell and, depending on requirements, nitrogen or oxygen bubbled through the solution for 15 min and the temperature allowed to stabilize. The platinum disk electrode was polished with 3000 grit water paper before each experiment. The appropriate electrode was immersed into the electrolyte and, depending on the experiment the open-circuit potential of the rotating electrode recorded for a period of up to 60 min. In some cases, cyclic voltammetry was carried out at 1 mV/s from the open-circuit potential initially in a negative direction. Potentiostatic experiments were conducted by immersing a freshly polished electrode in the solution, the potential set to the desired value and the resulting current recorded for 5 min. Unless otherwise stated, the electrodes were rotated at 500 rpm during the electrochemical measurements. All potentials are shown relative to the standard hydrogen electrode (SHE). All solutions were made up with high purity water from a Millipore system and all runs were carried out at 25 °C.

3. Results and discussion

3.1. Oxidation of iron(II) by dissolved oxygen

Fig. 1 shows typical oxygen probe current-time transients for three experiments with varying initial iron(II) concentrations. In all experiments, the initial concentration of iron(II) was at least 100-fold greater than that of dissolved oxygen. Plots of ln[probe current] versus time were linear in all experiments confirming that the rate of reduction of oxygen is first-order in the concentration of dissolved oxygen.

The pseudo-first-order rate constants (k_{obs}) obtained from the slopes of the 1st-order plots are shown as a function of the initial iron(II) concentration for a number of experiments conducted with varying initial iron(II) concentrations under otherwise identical conditions in Fig. 2.

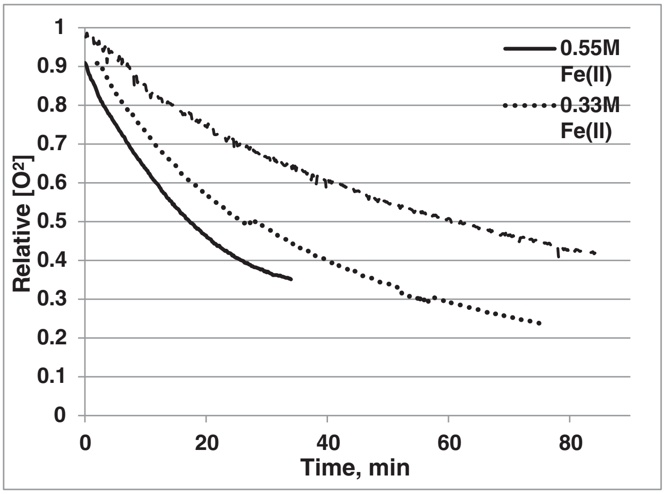

Fig. 1. Typical oxygen probe current-time transients showing the effect of the initial concentration of iron(II) on the reduction of oxygen in 4 M NaCl + 0.17 M HCl at 35 °C.

It is obvious that the rate is not 1st-order in iron(II) and a plot of k_{obs} versus $[Fe(II)]^2$ is linear with zero intercept confirming the 2nd order dependence under these conditions.

Two experiments were conducted with an initial iron(II) concentration of 0.05 M with the addition of 0.25 M iron(III) as the chloride and the value of k_{obs} was unchanged from the values obtained in the absence of excess iron(III). This observation contrasts with decreased rates of oxidation of copper(I) in the presence of added copper(II) ions (Nicol, 1983).

Thus, one can write for the oxidation of iron(II) under these conditions

$$-d[O_2]/dt = -0.25d[Fe(II)]/dt = k_1[Fe(II)]^2[O_2] \tag{3}$$

with a mean value for k_1 over all experiments of 0.193 ± 0.031 M^{-2} min^{-1} in 4 M NaCl + 0.17 M HCl at 35 °C. Note that the above assumes that peroxide is not a kinetically important intermediate i.e. the ratio of oxygen consumed to iron(II) oxidised is 4.0 as will be demonstrated in a subsequent section. The rate constant k_1 increases strongly with increasing chloride concentration (Colborn and Nicol, 1973) but this is not the focus of this study.

Several additional experiments were conducted in which small amounts of copper(II) ions were initially added. The rate was found to increase even at low concentrations as shown in Fig. 3.

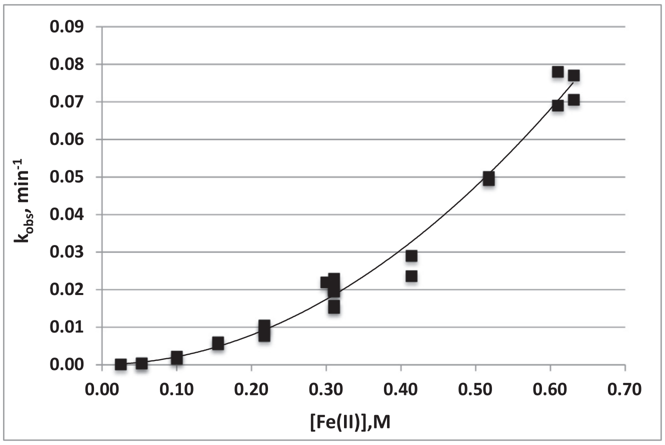

Fig. 2. Effect of the initial iron(II) concentration on the rate of reduction of oxygen in 4 M NaCl + 0.17 M HCl at 35 °C.