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The oxidation of Fe(II) with Cu(II) in acidic sulfate solutions with air at elevated pressures

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ABSTRACT

The oxidation of ferrous ions in acidic sulfate solutions in the presence of cupric ions at elevated air pressures was investigated in a high-intensity gas–liquid contactor. The study was required for the design of the regeneration steps of the novel Vitrisol[®] desulphurization process. The effects of the Fe²⁺ concentration, Cu²⁺ concentration, Fe³⁺ concentration, initial H₂SO₄ concentration, and partial oxygen pressure on the reaction rate were determined at three different temperatures, i.e., *T* = 50 °C, 70 °C, and 90 °C. Most of the experiments were determined to be affected by the mass transfer of oxygen, and therefore true intrinsic kinetics could not be fully determined. An increase in Fe²⁺ and Cu²⁺ concentrations, as well as the partial pressure of oxygen and temperature, increased the Fe²⁺ oxidation rate. H₂SO₄ did not influence the Fe²⁺ oxidation rate. An increase in Fe³⁺ concentration decreased the Fe²⁺ oxidation rate. Although determined from experiments partially affected by mass transfer, a first order of reaction in Fe²⁺ was observed, fractional orders in both Cu²⁺ and O₂ were measured, a zero order in H₂SO₄ was determined, and a negative, fractional order in Fe³⁺ was obtained. The activation energy was estimated to be 31.3 kJ/mol.

KEYWORDS

Gas–liquid reaction; H₂S removal; Fe(II) oxidation; influence of Cu(II); mass transfer; reaction behavior

Introduction

Hydrogen sulfide (H₂S) is a highly toxic and corrosive gas. Removal of H₂S from acidic gas streams, such as natural gas, industrial gas, or biogas, is important for safety, health, environmental, and economic reasons. Apart from non-regenerative H₂S removal by the use of, e.g., adsorbents, all the regenerative desulphurization processes capture CO₂ for varying extents besides H₂S. Owing to the co-absorption of CO₂ capital costs, as well as operational costs, increase.

The novel Vitrisol[®] desulphurization process is based on the removal of H₂S by precipitation with copper sulfate (CuSO₄) in an aqueous, acidic solution (Versteeg and Ter Maat, 1997). Copper sulfide (CuS) and sulfuric acid are formed in the gas treating process (Ter Maat et al., 2005, 2007):

The Vitrisol[®] process is able to remove H₂S from acidic gas streams without the co-absorption of CO₂ (Ter Maat et al., 2005; Wermink and Versteeg, 2017a). The current status of the Vitrisol[®] process is scavenger-like. Cu²⁺, the active compound in the absorption liquid, becomes depleted during H₂S removal. It must be noted, however, that nowadays copper is an expensive commodity; increasing amounts of H₂S lead to increasing operational costs. To reduce the operational costs for large amounts of H₂S and/or large-scale applications, a regeneration step has to be developed to replenish Cu²⁺.

CuS can be leached with ferric sulfate (Fe₂(SO₄)₃), an operation encountered in copper ore processing (a/o CuS) (Peacey et al., 2004; Dutrizac and MacDonald, 1974). Copper sulfate, elemental sulfur (S⁰), and ferrous sulfate (FeSO₄) are produced in this process:

Ferrous sulfate can be re-oxidized to ferric sulfate with O_2 , according to:

Resulting in the overall net reaction for the removal of H_2S :

Wermink and Versteeg (2017a, 2017b) studied the oxidation of ferrous ions in acidic sulfate solutions (Reaction 3) and proposed kinetic equations derived by both fitting the initial reaction rates and the experimentally determined Fe^{2+} concentration profiles, respectively. As the dissolution of CuS and the oxidation of ferrous ions (Reactions 2 and 3 respectively) proceed parallel during leaching of CuS , cupric ions are released into the system. As reported previously, Cu^{2+} enhances the oxidation rate of Fe^{2+} (Lamb and Elder, 1931; Huffman and Davidson, 1956; McKay, 1957; McKay and Halpern, 1958; Mathews and Robins, 1972; Chmielewski and Charewics, 1984; Dreisinger and Peters, 1989). The study of the behavior of Fe^{2+} oxidation in the presence of Cu^{2+} in acidic sulfate solutions was required for the design of the regeneration section of the 100% selective Vitrisol[®] desulphurization process (Wermink et al., 2017).

Literature review

The oxidation reaction of pure ferrous sulfate with copper sulfate in aqueous sulfuric acid solutions has previously been investigated by several authors.

Lamb and Elder (1931) investigated the oxidation of ferrous ions in acidic sulfate solutions by means of electromotive force measurements. Experiments were performed in a glass reactor at a temperature of 30 °C. During the experiments, air was passed through the solution. For the experiments performed with $CuSO_4$, initial concentrations of H_2SO_4 , $FeSO_4$, and $CuSO_4$ were 0.008 M to 3.0 M, 0.146 M to 0.176 M, and 0.001 M to 0.1 M, respectively.

Lamb and Elder reported a pronounced increase in the oxidation rate of ferrous ions in acidic, aqueous solutions containing $CuSO_4$ compared to the oxidation rate of ferrous ions in solutions containing no $CuSO_4$. Contrary to solutions containing no $CuSO_4$, the oxidation

rate of ferrous ions increased with increasing H_2SO_4 concentrations in the presence of $CuSO_4$.

Huffman and Davidson (1956) studied the oxidation of ferrous ions in acidic sulfate solutions in Pyrex absorption cells. Ferrous sulfate oxidation experiments in the presence of Cu^{2+} were performed at a temperature of 30.5 °C and at partial oxygen pressures of either 0.0213 MPa, or 0.101 MPa oxygen. Ferrous ammonium sulfate was used as a source for ferrous ions; therefore, ammonium ions were present in the experimental solutions. Sodium sulfate was used to influence the sulfate concentration in some of the experiments. The initial concentrations of H_2SO_4 and Na_2SO_4 were 0.226 M and 0.354 M, respectively. The initial concentrations of Fe^{2+} and Cu^{2+} were not reported. However, it was mentioned that the reaction was first order in Cu^{2+} for reactions with an initial Fe^{2+} concentration of 0.001 M and a partial oxygen pressure of 0.0213 MPa. Furthermore, it was mentioned that for reactions with a Cu^{2+} concentration of 1.1×10^{-5} M the Fe^{2+} oxidation rate did not vary when the oxygen pressure was varied. Huffman and Davidson referred to Cher and Davidson (1955) for a possible explanation of the catalytic effect of Cu^{2+} on the oxidation of Fe^{2+} with oxygen. Cher and Davidson postulated the following reaction mechanism:

and

Huffman and Davidson assumed Reaction 5 to be the rate-determining step and Reaction 6 to proceed very rapidly. Huffman and Davidson reported a first order of reaction in Fe^{2+} , a first order in Cu^{2+} , and a zero order in oxygen for the Cu^{2+} -catalyzed oxidation of Fe^{2+} .

McKay (1957) and McKay and Halpern (1958) investigated the oxidation of ferrous ions in acidic sulfate solutions in a 316 stainless steel autoclave. Ferrous sulfate oxidation experiments in the presence of copper sulfate were performed at a temperature of 100 °C and at partial pressures of oxygen between 0.101 MPa and 0.405 MPa. Initial concentrations of H_2SO_4 , $FeSO_4$, and $CuSO_4$ were 0.08 M, around 0.04 M, and 0 M to 0.020 M, respectively.

McKay and McKay and Halpern observed that the order in FeSO_4 ceased to be second order for CuSO_4 concentrations above 0.0055 M. Therefore, they stated that the order of 0.5 in CuSO_4 is only valid for CuSO_4 concentrations below 0.0055 M. A first order of reaction in oxygen was reported. The influence of H_2SO_4 was not studied.

Mathews and Robins (1972) studied the oxidation of ferrous ions in acidic sulfate solutions in an airlift percolator. Ferrous sulfate oxidation experiments in the presence of copper sulfate were performed at a temperature of 50°C and at an oxygen partial pressure of 1.0 (it must be noted that the unit of pressure is not clearly mentioned in the paper). Studying the schematic scheme of the experimental setup suggests an open contact with the surroundings. Therefore, the unit of pressure is assumed to be atm. H_3O^+ concentrations were estimated from pH measurements at ambient temperature; H_2SO_4 concentrations were not reported. The initial pH, Fe^{2+} , and CuSO_4 concentration were 1.45, 0.2 M, and 0.001 M to 0.01 M, respectively. Mathews and Robins reported an order of 0.278 in Cu^{2+} . They did not derive orders in Fe^{2+} , oxygen, and H^+ for Fe^{2+} oxidation experiments in the presence of Cu^{2+} from first principles.

Chmielewski and Charewicz (1984) investigated the oxidation of ferrous ions in acidic sulfate solutions in an autoclave made of acid-resistant steel with a Teflon coated interior. Experiments were performed at temperatures between 313 K and 408 K and partial pressures of oxygen ranging from 0.132 MPa to 1 MPa. Initial concentrations of H_2SO_4 , Cu^{2+} , and Fe^{2+} were 0.41 M to 0.82 M, 0.16 M to 1.42 M and 0.54 M, respectively. The effect of impeller speed was studied. An increase in impeller speed above 11.7 rps did not result in a change in reaction rate, indicating that the reaction seemed not to be affected by mass transfer limitations, and pure kinetics was measured.

The dependency of the species was determined from Fe^{2+} oxidation experiments performed with 0.16 M Cu^{2+} . Chmielewski and Charewicz reported a second order of reaction in ferrous ions for concentrations exceeding 0.054 M to 0.14 M and a first order of reaction at lower concentrations. A first order of reaction in oxygen

was determined. An increase in Fe^{2+} oxidation rate was observed with increasing Cu^{2+} concentrations. A decrease in Fe^{2+} oxidation rate was observed with increasing sulfuric acid concentrations. However, this observation was based on experiments performed with an impeller speed of 2 rps, and it was mentioned that some experiments were affected by mass transfer limitations. The temperature dependence of the reaction was determined from Fe^{2+} oxidation experiments performed with 0.79 M Cu^{2+} . The activation energy was determined to be 56.9 kJ/mol. They reported a kinetic equation based on experiments performed with varying initial Cu^{2+} concentrations. However, the concentration of Cu^{2+} was not accounted for in their kinetic equation.

Dreisinger and Peters (1989) studied the oxidation of ferrous sulfate for zinc sulfide leaching conditions. Experiments were performed in a Parr titanium autoclave. Ferrous sulfate oxidation experiments in the presence of copper sulfate were performed at a temperature of 150°C and at an oxygen partial pressure of 0.138 MPa. The initial concentrations of H_2SO_4 , FeSO_4 , and CuSO_4 were 0.5 M, 0.2 M, and 0.001 M to 0.25 M, respectively. ZnSO_4 was added to obtain a constant sulfate concentration of 2.7 M. Experiments were conducted at an impeller speed of 10.8 rps. It was not examined whether the reaction was affected by mass transfer limitations at this impeller speed.

Dreisinger and Peters performed speciation calculation for Zn^{2+} – Fe^{2+} – H_3O^+ – SO_4^{2-} solutions and disregarded equilibria involving Cu^{2+} and Fe^{3+} . They assumed the FeSO_4 ion pair is formed in solution, which is more reactive than the unpaired Fe^{2+} -ion. They stated that varying the total sulfate content resulted in a variation in FeSO_4 ion pair concentration and consequently in the oxidation rate. One kinetic equation was derived from experiments performed in the presence of ZnSO_4 of which some experiments were performed in the presence of CuSO_4 .

Dreisinger and Peters reported half an order of reaction in CuSO_4 . They did not derive orders in Fe^{2+} , oxygen, and the FeSO_4 ion pair for Fe^{2+} oxidation experiments in the presence of CuSO_4 from first principles. However, they assumed

Table 1. Experimental conditions reported in previous studies.

Reference	T (K)	P _{O₂} (MPa)	Composition (M)		
			FeSO ₄	H ₂ SO ₄	CuSO ₄
Lamb and Elder	303.15	0.0213	0.146–0.176	0.008–3.0	0.001–0.1
Huffman and Davidson ^{a,b,c}	303.65	0.0213 and 0.101		0.226	
McKay and Halpern	373.15	0.101–0.405	0.04	0.08	0–0.02
Mathews and Robins	323.15	0.101	0.2		0.001–0.01
Chmielewski and Charewicz	313–408	0.132–1	0.54	0.41–0.82	0.16–1.42
Dreisinger and Peters ^d	423.15	0.138	0.2	0.5	0.001–0.25
Ruiz et al.	393–493	0.345–1.379	0.009	0.15–1.2	0.004–0.016

^aHuffman and Davidson (1956) used Fe(NH₄)₂(SO₄)₂ as a source for Fe²⁺, not FeSO₄.

^bHuffman and Davidson (1956) performed experiments in the presence of 0.354 M Na₂SO₄.

^cHuffman and Davidson (1956) did not clearly provide the initial concentrations of FeSO₄ and CuSO₄.

^dDreisinger and Peters (1989) performed experiments in the presence of ZnSO₄.

these orders to be equal with the orders determined for Fe²⁺ oxidation experiments without CuSO₄. Furthermore, the temperature dependence of the reaction was assumed to be equal to the temperature dependence of the Fe²⁺ oxidation reaction without CuSO₄. The activation energy of 80.3 kJ/mol was derived from experiments performed without CuSO₄.

Ruiz et al. (2016) investigated the oxidation of Fe²⁺ to Fe³⁺ by oxygen in sulfate solutions in a 2 L Parr titanium autoclave. Experiments were performed at temperatures between 393 K and 493 K and partial pressures of oxygen ranging from 0.345 MPa to 1.379 MPa. Initial concentrations of FeSO₄, CuSO₄, and H₂SO₄ were 0.009 M, 0.004 M to 0.016 M, and 0.15 M to 1.2 M, respectively. First, the effect of impeller speed was studied in the range of 3.33 rps to 13.3 rps at a temperature of 453 K and a partial oxygen pressure of 0.690 MPa. No increase in Fe²⁺ oxidation rate was observed above an impeller speed of 6.67 rps. All subsequent experiments were performed at an impeller speed of 13.3 rps. The authors mentioned that small amounts of precipitate were observed at sulfuric acid concentrations of 0.15 M but not at higher acid concentrations. They assumed the precipitate to be hematite.

Ruiz et al. reported a zero order of reaction in Cu²⁺, an order of reaction of 2.8 in Fe²⁺, a first order of reaction in oxygen, and a fractional order of reaction of 0.3 in H₂SO₄. The activation energy was determined to be 36.5 kJ/mol. Experimental conditions reported in previous studies are summarized in Table 1. Orders of reaction reported in previous studies are summarized in Table 2.

The presented rate laws on Fe²⁺ oxidation in the presence of Cu²⁺ are either valid for a specific

Table 2. Orders of reaction reported in previous studies.

Reference	Order of reaction					
	Fe ²⁺	FeSO ₄	O ₂	CuSO ₄	Cu ²⁺	H ₂ SO ₄
Huffman and Davidson ^a	1		0		1	
McKay and McKay and Halpern ^b		2	1	0.5		
Mathews and Robins					0.278	
Chmielewski and Charewicz	2		1			
Dreisinger and Peters				0.5		
Ruiz et al.	2.8		1		0	0.3

^aHuffman and Davidson (1956) reported that, for reactions with a Cu²⁺ concentration of 1.1×10^{-5} M, the Fe²⁺ oxidation rate did not vary when the oxygen pressure was varied.

^bMcKay (1957) and McKay and Halpern (1958) reported that above a concentration of 0.0055 M CuSO₄ the second order dependency in FeSO₄ ceases to be 2. They stated that the reported order in CuSO₄ of 0.5 is valid for CuSO₄ concentrations below 0.0055 M.

experimental setting at one temperature (Huffman and Davidson, 1956; McKay, 1957; McKay and Halpern, 1958; Mathews and Robins, 1972), or incorrectly derived (Chmielewski and Charewicz, 1984), or not derived from first principles (Dreisinger and Peters, 1989). Only Ruiz et al. (2016) reported temperature-dependent kinetics on the Fe²⁺ oxidation in the presence of Cu²⁺.

Materials and methods

Setup

The Fe²⁺ oxidation experiments in the presence of Cu²⁺ were performed in a 0.5 L glass Büchi autoclave. The reactor was operated batchwise with regard to the liquid phase and continuous with regard to the gas phase. Nitrogen was used to remove oxygen from the setup. During the experiment, air was supplied to the reactor via a mass flow controller. A water saturator was used to humidify the gas phase and maintain the water balance. The pressure in the reactor was controlled using a back-pressure controller. A pressure relief valve was attached to the reactor

Figure 1. Schematic diagram of the experimental setup.

as a safety precaution. The reactor temperature was regulated using a Julabo heater. A Büchi water bath heated the water saturator to the reactor temperature. A four-blade Teflon gas entrainment impeller was used to obtain a high level of gas dispersion in the liquid phase. The impeller was operated using a magnetic drive. Glass baffles were introduced in the reactor to promote mixing. The steel interior of the reactor was protected using Teflon. Sampling was performed through Teflon tubing and Teflon valves. 3.5 mL UV cuvettes were used to collect samples. A Varian Cary 50 UV-Vis spectrophotometer (EL98123254) was used to analyze sample compositions. Samples were stored in a refrigerator. Temperature in the reactor was monitored using a Teflon-protected PT100 thermometer, temperature in the water saturator was registered using a regular PT100 thermometer. The pressure inside the experimental setup was measured using a pressure transducer connected to a data acquisition computer. A schematic

diagram of the experimental setup is shown in Figure 1.

Materials

ACS reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ [7782-63-0], 97% and puriss p.a. grade $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ [15244-10-7], ACS reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [7758-99-8], and ACS reagent grade H_2SO_4 [7664-93-9] were used as supplied from Sigma-Aldrich. Demineralized water was used.

Procedures

An amount of 400 mL of solution was prepared and added to the reactor. The reactor was flushed three times with N_2 in order to remove oxygen from the setup. When the setup reached the required temperature, the reactor was flushed two times with air. At the required air pressure the first sample was taken. The reaction was initiated by starting the impeller. Sampling was performed

periodically; the samples were directly stored in a refrigerator after sampling and analyzed at the end of each experiment at a temperature of 25 °C. From each experiment, the overall mass balance was determined.

Analytical techniques

Pure ferrous sulfate and ferric sulfate solutions, in the presence of sulfuric acid and copper sulfate, absorb light at different wavelengths. A wavelength scan from 200 nm to 1100 nm was performed using the UV Vis spectrophotometer on a pure acidic ferrous sulfate solution and a pure acidic ferric sulfate solution. The scan indicated that at a wavelength of 410 nm to 430 nm, $\text{Fe}_2(\text{SO}_4)_3$ had a significant absorbance, whereas FeSO_4 and CuSO_4 had almost no absorbance. A wavelength of 420 nm was chosen to analyze the sample compositions. At this wavelength, the absorbance of $\text{Fe}_2(\text{SO}_4)_3$ was 140 times higher compared to the absorbance of FeSO_4 and 475 times higher compared to the absorbance of CuSO_4 . As $\text{Fe}_2(\text{SO}_4)_3$ is present in low amounts at the start of an experiment, this is an accurate method of determining compositions.

Calibration curves were made for each experiment, depending on the starting composition and resulting time dependent Fe^{2+} concentration profile of the experiment. Therefore, the effect of compounds present in solution on the absorbance of light, like FeSO_4 , CuSO_4 , H_2SO_4 , and $\text{Fe}_2(\text{SO}_4)_3$, is accounted for.

Considerations

To ensure a sufficiently large contact area between gas and liquid phase and high mass transfer coefficients, a gas entrainment impeller was used. Experiments at several impellers speed up to 38.3 rps were performed to determine if the reaction was affected by mass transfer limitations. From these experiments could be concluded that some experiments were not affected by mass transfer limitations for oxygen, but some experiments could be hindered by mass transfer limitations. The oxygen supply was at least five times higher than stoichiometrically required according to Reaction 3.

Experiments were performed at temperatures of 50 °C, 70 °C, and 90 °C and at air pressures ranging from 0.1 MPa to 0.5 MPa. Some experiments were performed using enriched air with the composition of 60 vol.% N_2 and 40 vol.% O_2 in order to be able to increase the oxygen partial pressure. Oxygen partial pressures varied between 0.0225 MPa and 0.180 MPa. Initial concentrations of H_2SO_4 , FeSO_4 , and CuSO_4 , were 0.25 M to 2.0 M, 0.125 M to 0.5 M, and 0.0156 M to 0.5 M, respectively.

The accuracy of the PT100 thermometers is temperature dependent. At temperatures of 50 °C, 70 °C, and 90 °C the accuracies are ± 0.25 °C, ± 0.29 °C, and ± 0.33 °C, respectively. The accuracy of the pressure transducer is ± 0.005 MPa. The photometric and wavelength accuracies of the UV-Vis spectrophotometer are ± 0.01 Abs and ± 0.5 nm, respectively. The reproducibility of the experiments in this study is estimated to be within 5%.

Mass transfer model

A high-intensity gas–liquid contactor was used to study the behavior of the oxidation of Fe^{2+} in the presence of Cu^{2+} . Compared to previous Fe^{2+} oxidation experiments, not in the presence of Cu^{2+} and not hindered by mass transfer limitations (Wermink and Versteeg, 2017a, 2017b), the Fe^{2+} oxidation rate increased significantly when Cu^{2+} was present. Some experiments in this study were suspected to be limited by mass transfer of O_2 .

Gas–liquid reactions occur when the gas reactant(s) diffuse(s) into the liquid phase and react with component(s) present in the liquid phase.

In case of no reaction, the gas component(s) diffuse(s) into the liquid phase according to concentration gradients in either the gas and/or liquid phase (Fick's law of diffusion). The mass transfer rate can be described, e.g., according to the film theory for gas–liquid reactions with liquid bulk. In the film theory, it is assumed that stagnant layers exist at the G/L interface in which the resistance to mass transfer is located (Westerterp et al., 1988).

If there is a reaction, the reaction takes place parallel with mass transfer. The two processes

(mass transfer and chemical reaction) cannot be regarded as an independent (Danckwerts, 1970). Therefore, the reaction could affect the concentration gradient in either the gas and/or liquid phase and enhance the transfer of the gas component into the liquid phase according to:

$$E_A = \frac{\text{Actual flux}}{\text{Physical flux with same driving force}} \quad (7)$$

$$= \frac{J_A}{J_{A,\text{physical}}} = \frac{J_A}{k_L(c_{A,i,L} - c_{A,L})}.$$

For example, if the reaction occurs at a relative low rate compared to mass transfer of the gas component(s) in absence of reaction, the reaction does not enhance the rate of mass transfer.

To determine the kinetics of a homogeneous G/L reaction, it is preferred that the reaction proceeds slowly relative to the mass transfer of the gas component(s). Furthermore, the liquid bulk should be fully saturated with the gas component(s) at any given moment during an experiment.

Kinetics could be obtained if the following (set of) conditions were satisfied:

$$Ha < 0.3 \quad (8)$$

and

$$(Al - 1)Ha^2 \ll 1, \quad (9)$$

where Ha is the Hatta number; a dimensionless number defined as the ratio of the maximum attainable rate of reaction in the liquid film to the maximal rate of transport through the film. For a first order irreversible reaction, Ha equals:

$$Ha = \sqrt{\frac{k_1 D_A}{k_L^2}}. \quad (10)$$

A Hatta number below 0.3 indicates that the rate of the chemical reaction in the film is relatively low compared to the mass transfer rate. According to Westerterp et al. (1988), for Ha numbers below 0.3, it can be derived that:

$$\frac{c_{A,L}}{c_{A,i,L}} = \frac{1}{1 + (Al - 1)Ha^2}. \quad (11)$$

This implies that, e.g., for values of $(Al - 1)Ha^2$ of 0.01, 0.05, 0.15, and 0.30 the values of $c_{A,L}/c_{A,i,L}$ were 0.99, 0.95, 0.87, and 0.77, respectively.

Al is the Hinterland ratio, a ratio which compares the total liquid volume of the reactor with the film volume in the reactor:

$$Al = \frac{V_{L,\text{total}}}{V_{L,\text{film}}} = \frac{(1 - \varepsilon)k_L}{aD_A}. \quad (12)$$

The $(Al - 1)Ha^2$ ratio describes whether the liquid bulk is fully saturated with the gas component, i.e., the interfacial concentration equals the bulk concentration ($(Al - 1)Ha^2 \ll 1$), or the concentration of the gas component in the liquid bulk equals zero ($(Al - 1)Ha^2 \gg 1$).

For kinetic measurements, the $(Al - 1)Ha^2$ ratio has to preferably be 0.05 or lower (liquid bulk concentration of the gas component is 95% or higher of the interfacial liquid concentration).

If the (set of) Conditions 8 and 9 were satisfied, the equation for the flux of component A into the liquid phase becomes:

$$J_A = k_L(c_{A,i,L} - c_{A,L}) = \frac{k_1 V_L c_{A,i,L}}{aV_R}. \quad (13)$$

For the instance that the reaction volume equals the liquid volume:

$$R = \frac{dc_A}{dt} = aJ_A = k_L a(c_{A,i,L} - c_{A,L}) = \frac{k_1 a V_L c_{A,i,L}}{aV_R} = k_1 c_{A,i,L}. \quad (14)$$

For more details, the interested reader is referred to Westerterp et al. (1988).

Mass transfer parameters

In this study, the Hatta number is defined as:

$$Ha = \sqrt{\frac{k_{ps} D_{O_2}}{k_L^2}}. \quad (15)$$

And the Hinterland ratio is defined as:

$$Al = \frac{(1 - \varepsilon)k_L}{aD_{O_2}}. \quad (16)$$

The diffusion coefficient of O_2 in aqueous systems can be predicted from the empirically modified Stokes–Einstein equation developed by Wilke and Chang (1955):

$$D_{L,O_2} = \frac{7.4 \times 10^{-11} (\phi M)^{0.5} T}{\mu V_{m,O_2}^{0.6}}. \quad (17)$$

In which M is the molecular mass of water, V_{m,O_2} is the molecular volume of oxygen

(25.6 cm³/g for O₂) and ϕ is an association parameter for the solvent. Reid et al. (1977) reported a value of 2.26 for the association parameter of water. In this study, it is assumed that the diffusion coefficient of O₂ in the liquid equals the diffusion coefficient of O₂ in water.

As explained by Koetsier et al. (1973), Van't Riet (1979), and Zuidervaart et al. (2000), the mass transfer parameter $k_L a$ for aqueous, ionic solutions is higher than water. Koetsier et al. and Van't Riet stated that the coalescence rate of gas bubbles in an aqueous, ionic solution is very low compared to water, resulting in an increase in $k_L a$. Moreover, Van't Riet reported that the gas holdup increases for aqueous, ionic solutions. No distinction was made concerning type of ion in solution. Zuidervaart et al. showed in their figure 3 that the increase in $k_L a$ is independent on the type of metal sulfate used. Moreover, above a concentration of metal sulfate ions of approximately 0.18 M the $k_L a$ is increased with a factor of 2 to 2.5 compared to water.

The mass transfer parameter $k_L a$ for aqueous, ionic solutions can be determined using relationships reported by Koetsier et al. (1973) and Van't Riet (1979):

$$\text{Koetsier et al.: } k_L a = 0.11 \left(\frac{P \times 10^{-3}}{V_L} \right)^{0.7} \left(\frac{d_i}{d_R} \right)^{0.7} d_R^{-0.35} \quad (18)$$

and

$$\text{Van't Riet: } k_L a = 2 \times 10^{-3} \left(\frac{P}{V_L} \right)^{0.7} v_s^{0.2}. \quad (19)$$

According to Van't Riet (1979), it is unimportant what type of impeller is used for the correlation of $k_L a$ with the power input of the impeller.

Koetsier and Thoenes (1973) reported a relationship to calculate the mass transfer parameter k_L for aqueous, ionic solutions:

$$k_L = 3.25 \times 10^{-4} \left(\frac{P \times 10^{-3}}{V_L} \right)^{0.3} \left(\frac{d_i}{d_R} \right)^{0.7} d_R^{-0.35}. \quad (20)$$

They derived experimentally that the liquid phase mass transfer coefficient was hardly influenced by the gas holdup.

From Equations (18) to (20), it can be concluded that the power input of the impeller P and the superficial gas velocity v_s are the only

unknown parameters. According to Van't Riet (1979), the superficial gas velocity is of minor importance and only incorporated to obtain a slightly improved fit.

Lemoine and Morsi (2005) performed an extensive literature review and obtained a large number of experimental data points, to develop a/o empirical correlations for the prediction of hydrodynamic and mass transfer parameters for surface aeration reactors (SARs), gas-inducing reactors (GIRs), and gas-sparging reactors (GSRs). They used the empirical correlation reported by Heim et al. (1995) to determine the power input of gas-inducing impellers:

$$P_{GIR} = P_{SAR} \left(1 - \exp \left\{ A + \frac{a_1}{\sqrt{Fr^*}} + a_2 Re \right\} \right). \quad (21)$$

The constants A , a_1 , and a_2 are dependent on the type of impeller used. Heim et al. reported for A , a_1 , and a_2 values of 0.166, -0.934 , and -7.00×10^{-7} , respectively for a four-pipe impeller. In this study, an impeller with four hollow blades was used; therefore, these values were applied in this study.

The power input P_{SAR} can be described by:

$$P_{SAR} = N_P d_i^5 \rho_L N^3. \quad (22)$$

The power number N_P is dependent on the Reynolds number and the impeller geometry. N_P becomes constant above a specific Reynolds number. According to Ramachandran and Chaudhari (1983), four-blade impellers have a value of N_P is 4 for Reynolds numbers above approximately 10^4 . The modified Froude number Fr^* is given by:

$$Fr^* = \frac{N^2 d_i}{gH}. \quad (23)$$

And the impeller Reynolds number:

$$Re = \frac{N d_i^2 \rho_L}{\mu_L}. \quad (24)$$

Pseudo-first order reaction rate constant

As described by Wermink and Versteeg (2017a, 2017b), the rate of oxidation of Fe²⁺ is affected by the concentrations of Fe²⁺, Fe³⁺, H₂SO₄, and O₂. As described in the literature review in this study, Cu²⁺ enhances the oxidation rate of Fe²⁺.

Therefore, the oxidation of Fe^{2+} is not first order, and the pseudo-first order reactant rate constant k_{ps} is required to determine the Hatta number. The rate constant k_{ps} can be calculated from the experimentally derived Fe^{2+} reaction rate and the oxygen bulk concentration if Conditions 8 and 9 are satisfied.

$$-\frac{1}{4}R_{\text{Fe}^{2+}} = -R_{\text{O}_2} = k_{ps}[\text{O}_2]_L \quad (25)$$

When Conditions 8 and 9 are satisfied, the liquid bulk is fully saturated with oxygen, and therefore the oxygen bulk concentration equals the oxygen concentration at the G/L interface. From the literature review, it can be concluded that the oxidation of Fe^{2+} in the presence of Cu^{2+} is dependent on a/o the Fe^{2+} , Cu^{2+} , O_2 , and H_2SO_4 concentrations. If Reaction 5 is plausible, the Fe^{2+} oxidation reaction in the presence of Cu^{2+} could be dependent on Fe^{3+} . Therefore, k_{ps} can be described by

$$k_{ps} = k_1[\text{Fe}^{2+}]^a[\text{Cu}^{2+}]^b[\text{H}_2\text{SO}_4]^c[\text{Fe}^{3+}]^d \quad (26)$$

Oxygen concentration

Gas solubilities in electrolyte solutions are often lower compared to the solubility in pure water. The model by Weisenberger and Schumpe (1996) can be used to estimate the solubility of a gas, like oxygen, in an electrolyte. It must be noted that the model by Weisenberger and Schumpe does not account for the bisulfate ion (HSO_4^-).

In this study, the model by Weisenberger and Schumpe (1996) was extended with the bisulfate ion. Experimental data from previous studies on oxygen solubilities in aqueous solutions, containing $\text{Fe}_2(\text{SO}_4)_3$, CuSO_4 , and/or H_2SO_4 , was evaluated (Bruhn et al., 1965; Narita et al., 1983; Lang and Zander, 1986; Manku, 1994). The speciation of the aqueous solutions presented by Wermink and Versteeg (2017a) was determined with the relation derived by Knopf et al. (2003) for the second dissociation constant of H_2SO_4 . The first dissociation step of aqueous H_2SO_4 was regarded to be complete, as explained by Wermink and Versteeg. The value of the model parameter for the bisulfate ion was derived using fitting oxygen solubilities according to the Newton-Raphson

method (see value in Table 3). The experimental data points were obtained at temperatures ranging from 298 K to 333 K, at an oxygen partial pressure of 0.101 MPa, with H_2SO_4 concentrations ranging from 0.77 M to 2.5 M, and CuSO_4 concentrations of either 0.47 M or 0.94 M. The other model parameters, as published by Weisenberger and Schumpe (1996), were kept constant.

The actual oxygen partial pressure was determined via correction of the total pressure for water vapor pressure. The saturated water vapor pressure was calculated according to the Antoine equation:

$$P_{\text{H}_2\text{O}} = \frac{101325}{760} 10^{\left(A - \frac{B}{(C+T-273.15)}\right)}, \quad (27)$$

where $A = 8.07131$, $B = 1730.63$, and $C = 233.426$ in the range of $274.15 \text{ K} < T < 372.15 \text{ K}$.

The oxygen concentration in pure water was determined from the actual oxygen partial pressure via Henry's law for oxygen solubility in pure water using the Procede Process Simulator (Hamborg et al., 2011).

$$P_{\text{O}_2} = K_{\text{H},\text{O}_2} x_{\text{O}_2} \quad (28)$$

$$K_{\text{H},\text{O}_2} = \exp \left\{ A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T \right\} \quad (29)$$

Where $A = 155.92$, $B = -7775$, $C = -18.397$, and $D = -0.0094435$ in the range of $273 \text{ K} < T < 600 \text{ K}$.

Results

The oxidation of Fe^{2+} in the presence of Cu^{2+} was studied at temperatures ranging from 50°C to 90°C . Experimental conditions are presented in Table 4.

Mass transfer calculations

The effect of mass transfer limitations is more pronounced at the start of a Fe^{2+} oxidation experiment because the rate of oxidation of Fe^{2+} is initially highest. As the reaction continues, the reaction rate decreases and limitations by mass transfer become less pronounced. Therefore, the initial reaction rate is used to determine the effect of mass transfer.

The pseudo-first order reaction rate constant k_{ps} can be determined from the initial O_2

Table 3. Model parameter of the bisulfate ion.

Model parameter
HSO_4^-
0.0808

reaction rate and the oxygen bulk concentration if Conditions 8 and 9 are fulfilled and $(Al-1)Ha^2 < 0.05$; i.e., kinetics were measured and the liquid bulk is at equilibrium with the gas phase concentration. The oxygen interface concentration can be determined from the oxygen partial pressure, the Henry coefficient of oxygen in water, the speciation of the solution, and the model by

Weisenberger and Schumpe extended with the bisulfate ion. Values are reported in Table 5.

Table 6 gives the values of the parameters used to determine the power consumption of the impeller according to Lemoine and Morsi (2005). The density and the viscosity of the solution were assumed to be equal to water. Table 7 gives the values of measured and estimated parameters, required to determine mass transfer parameters. During the experiments, the gas holdup was equal to approximately $\varepsilon_G = 0.3$. The power number of the impeller was estimated to be $N_P = 4$ based on impeller geometry.

Table 4. Fe^{2+} oxidation experiments in the presence of Cu^{2+} .

Exp	T (°C)	P_{O_2} (MPa)	$[\text{Fe}^{2+}]$ (kmol · m ⁻³)	$[\text{H}_2\text{SO}_4]$ (kmol · m ⁻³)	$[\text{Cu}^{2+}]$ (kmol · m ⁻³)	$[\text{Fe}^{3+}]$ (kmol · m ⁻³)	N (rps)
61	90	0.0901	0.250	0.269	0.125	0	28
62	90	0.0901	0.250	0.272	0.250	0	28
71	90	0.0901	0.250	2.021	0.125	0	28
72	90	0.0901	0.247	0.499	0.125	0	28
76	90	0.0901	0.244	1.018	0.125	0	28
77	90	0.0901	0.059	0.268	0.500	0	29
78b	90	0.0901	0.244	0.516	0.250	0.0683	29
78c	90	0.0901	0.246	0.517	0.250	0.0663	29
79	90	0.0901	0.244	0.519	0.250	0.131	29
79b	90	0.0901	0.245	0.519	0.250	0.130	29
79c	90	0.0901	0.246	0.520	0.250	0.129	29
80	90	0.0901	0.242	0.516	0.250	0.258	29
80b	90	0.0901	0.236	0.513	0.250	0.265	29
80c	90	0.0901	0.237	0.513	0.250	0.263	29
80d	90	0.0901	0.240	0.515	0.250	0.261	29
81	90	0.0901	0.247	0.518	0.250	0.503	29
81d	90	0.0901	0.243	0.516	0.250	0.507	29
82	90	0.0901	0.246	0.269	0.500	0	29
82b	90	0.0901	0.244	0.269	0.500	0	29
82c	90	0.0901	0.246	0.269	0.500	0	33
82d	90	0.0901	0.246	0.269	0.500	0	39
83	90	0.0901	0.248	0.271	0.250	0	29
83b	90	0.0901	0.249	0.271	0.250	0	33
84	90	0.0901	0.248	0.269	0.125	0	29
85	90	0.0901	0.251	0.270	0.0628	0	29
86	90	0.0901	0.248	0.270	0.0312	0	29
87	90	0.0901	0.249	0.270	0.0156	0	29
88	90	0.0901	0.123	0.270	0.500	0	29
89	90	0.0225	0.250	0.272	0.250	0	29
90	90	0.0450	0.249	0.271	0.250	0	29
91	90	0.180	0.245	0.270	0.250	0	29
91b	90	0.180	0.246	0.270	0.250	0	29
91c	90	0.180	0.248	0.271	0.250	0	33
91d	90	0.180	0.247	0.270	0.250	0	39
92	90	0.0901	0.500	0.272	0.500	0	33
93	70	0.0901	0.499	0.521	0.0625	0	33
94	70	0.0901	0.501	0.519	0.125	0	33
95	70	0.0901	0.500	0.518	0.250	0	33
96	70	0.0901	0.503	0.527	0.500	0	33
97	50	0.0901	0.501	0.518	0.125	0	33
98	50	0.0451	0.502	0.519	0.125	0	33
99	50	0.0226	0.503	0.519	0.125	0	33
100	50	0.180	0.501	0.519	0.125	0	39
101	50	0.102	0.124	0.270	0.500	0	36
102	70	0.0451	0.126	2.003	0.125	0	36
103	70	0.0901	0.246	0.516	0.250	0.504	36
104	70	0.0901	0.252	0.518	0.250	0.0601	36
105	50	0.0901	1.009	0.522	0.246	0	36
107	50	0.0901	1.011	0.276	0.246	0	36
108	50	0.0901	1.009	1.001	0.246	0	36

Table 5. Speciation, O₂ solubilities, pseudo-first order reaction rate constant.

Exp	Speciation			Solubilities		R _{O2} (mol · m ⁻³ · s ⁻¹)	k _{ps} (s ⁻¹)
	[H ⁺] (kmol · m ⁻³)	[HSO ₄ ⁻] (kmol · m ⁻³)	[SO ₄ ²⁻] (kmol · m ⁻³)	[O ₂] _{i,H2O} (kmol · m ⁻³)	[O ₂] _{i,electrolyte} (kmol · m ⁻³)		
61	0.00782	0.531	0.113	0.715 × 10 ⁻³	0.578 × 10 ⁻³	-0.0602	0.104
62	0.00389	0.541	0.231	0.715 × 10 ⁻³	0.540 × 10 ⁻³	-0.0870	0.161
71	1.65	2.39	0.00221	0.715 × 10 ⁻³	0.498 × 10 ⁻³	-0.0614	0.123
72	0.136	0.865	0.0105	0.715 × 10 ⁻³	0.568 × 10 ⁻³	-0.0630	0.111
76	0.649	1.39	0.00343	0.715 × 10 ⁻³	0.543 × 10 ⁻³	-0.0566	0.104
77	0.003028	0.538	0.295	0.715 × 10 ⁻³	0.519 × 10 ⁻³	-0.0150	0.0290
78b	0.018056	1.02	0.0925	0.715 × 10 ⁻³	0.514 × 10 ⁻³	-0.0213	0.0415
78c	0.018073	1.02	0.0925	0.715 × 10 ⁻³	0.514 × 10 ⁻³	-0.0222	0.0433
79	0.009697	1.03	0.175	0.715 × 10 ⁻³	0.497 × 10 ⁻³	-0.0193	0.0389
79b	0.009702	1.03	0.175	0.715 × 10 ⁻³	0.497 × 10 ⁻³	-0.0135	0.0271
79c	0.009688	1.03	0.175	0.715 × 10 ⁻³	0.497 × 10 ⁻³	-0.0163	0.0327
80	0.004686	1.04	0.360	0.715 × 10 ⁻³	0.466 × 10 ⁻³	-0.0117	0.0251
80b	0.004684	1.04	0.360	0.715 × 10 ⁻³	0.466 × 10 ⁻³	-0.00915	0.0196
80c	0.004683	1.04	0.360	0.715 × 10 ⁻³	0.466 × 10 ⁻³	-0.0139	0.0299
80d	0.004682	1.04	0.360	0.715 × 10 ⁻³	0.466 × 10 ⁻³	-0.0143	0.0306
81	0.002297	1.04	0.733	0.715 × 10 ⁻³	0.408 × 10 ⁻³	-0.0126	0.0309
81d	0.002297	1.04	0.732	0.715 × 10 ⁻³	0.408 × 10 ⁻³	-0.0167	0.0409
82	0.001871	0.541	0.480	0.715 × 10 ⁻³	0.471 × 10 ⁻³	-0.0586	0.124
82b	0.001872	0.541	0.480	0.715 × 10 ⁻³	0.472 × 10 ⁻³	-0.0594	0.126
82c	0.001872	0.541	0.480	0.715 × 10 ⁻³	0.471 × 10 ⁻³	-0.0712	0.151
82d	0.001872	0.541	0.480	0.715 × 10 ⁻³	0.471 × 10 ⁻³	-0.0689	0.146
83	0.003863	0.540	0.232	0.715 × 10 ⁻³	0.540 × 10 ⁻³	-0.0560	0.104
83b	0.003851	0.539	0.232	0.715 × 10 ⁻³	0.540 × 10 ⁻³	-0.0658	0.122
84	0.007847	0.533	0.113	0.715 × 10 ⁻³	0.578 × 10 ⁻³	-0.0578	0.0999
85	0.014997	0.525	0.0580	0.715 × 10 ⁻³	0.598 × 10 ⁻³	-0.0485	0.0811
86	0.024661	0.517	0.0349	0.715 × 10 ⁻³	0.608 × 10 ⁻³	-0.0396	0.0652
87	0.031419	0.509	0.0269	0.715 × 10 ⁻³	0.613 × 10 ⁻³	-0.0351	0.0573
88	0.002515	0.539	0.357	0.715 × 10 ⁻³	0.502 × 10 ⁻³	-0.0309	0.0614
89	0.00386	0.540	0.232	0.179 × 10 ⁻³	0.135 × 10 ⁻³	-0.0210	0.155
90	0.003868	0.540	0.232	0.357 × 10 ⁻³	0.270 × 10 ⁻³	-0.0357	0.132
91	0.003862	0.540	0.232	1.43 × 10 ⁻³	1.08 × 10 ⁻³	-0.0836	0.0775
91b	0.003859	0.540	0.232	1.43 × 10 ⁻³	1.08 × 10 ⁻³	-0.0827	0.07662
91c	0.00386	0.540	0.232	1.43 × 10 ⁻³	1.08 × 10 ⁻³	-0.0958	0.0888
91d	0.00387	0.541	0.232	1.43 × 10 ⁻³	1.08 × 10 ⁻³	-0.0965	0.0894
92	0.001224	0.542	0.730	0.715 × 10 ⁻³	0.415 × 10 ⁻³	-0.124	0.298
93	0.037898	1.00	0.0793	0.737 × 10 ⁻³	0.520 × 10 ⁻³	-0.0565	0.109
94	0.023419	1.01	0.130	0.737 × 10 ⁻³	0.502 × 10 ⁻³	-0.0621	0.124
95	0.012498	1.02	0.245	0.737 × 10 ⁻³	0.468 × 10 ⁻³	-0.0688	0.147
96	0.006494	1.05	0.480	0.737 × 10 ⁻³	0.405 × 10 ⁻³	-0.0773	0.191
97	0.036978	1.000	0.143	0.830 × 10 ⁻³	0.550 × 10 ⁻³	-0.0340	0.0618
98	0.037094	1.00	0.143	0.415 × 10 ⁻³	0.275 × 10 ⁻³	-0.0232	0.0843
99	0.037062	1.00	0.143	0.208 × 10 ⁻³	0.138 × 10 ⁻³	-0.0148	0.108
100	0.037099	1.00	0.143	1.66 × 10 ⁻³	1.10 × 10 ⁻³	-0.0431	0.0392
101	0.007939	0.534	0.362	0.941 × 10 ⁻³	0.631 × 10 ⁻³	-0.00650	0.0103
102	1.756353	2.25	0.00361	0.368 × 10 ⁻³	0.256 × 10 ⁻³	-0.0171	0.0667
103	0.004151	1.03	0.736	0.737 × 10 ⁻³	0.403 × 10 ⁻³	-0.00415	0.0103
104	0.029676	1.01	0.102	0.737 × 10 ⁻³	0.517 × 10 ⁻³	-0.00781	0.0151
105	0.007427	1.04	0.731	0.830 × 10 ⁻³	0.385 × 10 ⁻³	-0.0691	0.180
107	0.002993	0.549	0.973	0.830 × 10 ⁻³	0.394 × 10 ⁻³	-0.0736	0.187
108	0.035672	1.97	0.282	0.830 × 10 ⁻³	0.367 × 10 ⁻³	-0.0784	0.214

Table 8 reports the values of the mass transfer parameters according to Koetsier et al. (1973), the diffusion coefficient of O₂ in water and the dimensionless numbers *Ha*, *Al*, and $(Al-1)Ha^2$. It is assumed that the diffusion coefficient of O₂ in the solution is equal to O₂ in water.

The equation by Van't Riet (1979) to determine k_La cannot be used because the superficial gas velocity through the liquid cannot be measured. However, based on the k_La determined by the relation by Koetsier et al. the superficial gas

velocity was estimated to be v_s , $G=0.0588$ m/s according to Equation (19).

As it can be concluded from Table 8, for all experiments *Ha* was below 0.3. However, $(Al-1)Ha^2$ ranged from 0.00897 to 0.290; in most experiments $(Al-1)Ha^2$ was above 0.05. Therefore, most experiments were affected by mass transfer of O₂.

Order of reaction

Orders of reaction have been determined through the so-called pseudo-first order approach

Table 6. Impeller power consumption.

Exp	<i>N</i> (rps)	$\rho_{\text{H}_2\text{O}}$ (kg/m ³)	P_{SAR} (W)	$\mu_{\text{H}_2\text{O}}$ (mPa.s)	Fr*	Re	P_{GIR} (W)
61	28	955	5.20	0.316	1.32	1.11×10^5	2.68
62	28	955	5.20	0.316	1.32	1.11×10^5	2.68
71	28	955	5.12	0.316	1.30	1.10×10^5	2.65
72	28	955	5.12	0.316	1.30	1.10×10^5	2.65
76	28	955	5.12	0.316	1.30	1.10×10^5	2.65
77	29	955	5.64	0.316	1.39	1.14×10^5	2.86
78b	29	955	5.64	0.316	1.39	1.14×10^5	2.86
78c	29	955	5.64	0.316	1.39	1.14×10^5	2.86
79	29	955	5.64	0.316	1.39	1.14×10^5	2.86
79b	29	955	5.64	0.316	1.39	1.14×10^5	2.86
79c	29	955	5.64	0.316	1.39	1.14×10^5	2.86
80	29	955	5.64	0.316	1.39	1.14×10^5	2.86
80b	29	955	5.64	0.316	1.39	1.14×10^5	2.86
80c	29	955	5.64	0.316	1.39	1.14×10^5	2.86
80d	29	955	5.64	0.316	1.39	1.14×10^5	2.86
81	29	955	5.64	0.316	1.39	1.14×10^5	2.86
81d	29	955	5.64	0.316	1.39	1.14×10^5	2.86
82	29	955	5.64	0.316	1.39	1.14×10^5	2.86
82b	29	955	5.64	0.316	1.39	1.14×10^5	2.86
82c	33	955	8.62	0.316	1.84	1.31×10^5	3.95
82d	39	955	13.3	0.316	2.46	1.51×10^5	5.51
83	29	955	5.64	0.316	1.39	1.14×10^5	2.86
83b	33	955	8.62	0.316	1.84	1.31×10^5	3.95
84	29	955	5.64	0.316	1.39	1.14×10^5	2.86
85	29	955	5.64	0.316	1.39	1.14×10^5	2.86
86	29	955	5.64	0.316	1.39	1.14×10^5	2.86
87	29	955	5.64	0.316	1.39	1.14×10^5	2.86
88	29	955	5.64	0.316	1.39	1.14×10^5	2.86
89	29	955	5.64	0.316	1.39	1.14×10^5	2.86
90	29	955	5.64	0.316	1.39	1.14×10^5	2.86
91	29	955	5.64	0.316	1.39	1.14×10^5	2.86
91b	29	955	5.64	0.316	1.39	1.14×10^5	2.86
91c	33	955	8.62	0.316	1.84	1.31×10^5	3.95
91d	39	955	13.3	0.316	2.46	1.51×10^5	5.51
92	33	955	8.62	0.316	1.84	1.31×10^5	3.95
93	33	969	8.75	0.405	1.84	1.04×10^5	3.92
94	33	969	8.75	0.405	1.84	1.04×10^5	3.92
95	33	969	8.75	0.405	1.84	1.04×10^5	3.92
96	33	969	8.75	0.405	1.84	1.04×10^5	3.92
97	33	983	8.87	0.549	1.84	7.75×10^4	3.88
98	33	983	8.87	0.549	1.84	7.75×10^4	3.88
99	33	983	8.87	0.549	1.84	7.75×10^4	3.88
100	39	983	13.7	0.549	2.46	8.96×10^4	5.32
101	36	983	11.2	0.549	2.15	8.38×10^4	4.60
102	36	969	11.0	0.405	2.15	1.12×10^5	4.66
103	36	969	11.0	0.405	2.15	1.12×10^5	4.66
104	36	969	11.0	0.405	2.15	1.12×10^5	4.66
105	36	983	11.2	0.549	2.15	8.38×10^4	4.60
107	36	983	11.2	0.549	2.15	8.38×10^4	4.60
108	36	983	11.2	0.549	2.15	8.38×10^4	4.60

(Wermink and Versteeg, 2017a). By varying the initial concentration of one of the reactants in several experiments, the order in this reactant can be determined from the initial reaction rates of the experiments. The reactants with equal initial concentrations are lumped together with the reaction rate constant. Therefore, it is not necessary to have reactants present in excess.

The initial reaction rates of experiments are determined by fitting the data points via a polynomial equation. From the slope, at $t=0$ (calculated from the derivative of the polynomial fit) the initial reaction rate is derived.

Table 7. Measured and estimated parameters.

N_p	4
d_i (m)	0.036
z_G	0.3
H (m)	0.08
d_R (m)	0.085

Table 8. Calculated mass transfer parameters.

Exp	$k_L a$ (s ⁻¹)	k_L (m/s)	a (m ² /m ³)	D_{L,O_2} (m ² /s)	Ha	Al	(Al - 1)Ha ²
61	0.541	7.47×10^{-4}	725	7.76×10^{-9}	0.0381	93.0	0.133
62	0.541	7.47×10^{-4}	725	7.76×10^{-9}	0.0473	93.0	0.206
71	0.537	7.44×10^{-4}	721	7.76×10^{-9}	0.0416	93.1	0.159
72	0.537	7.44×10^{-4}	721	7.76×10^{-9}	0.0394	93.1	0.143
76	0.537	7.44×10^{-4}	721	7.76×10^{-9}	0.0382	93.1	0.135
77	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0197	92.4	0.0355
78b	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0236	92.4	0.0508
78c	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0241	92.4	0.0530
79	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0228	92.4	0.0476
79b	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0190	92.4	0.0332
79c	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0209	92.4	0.0400
80	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0183	92.4	0.0307
80b	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0162	92.4	0.0240
80c	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0200	92.4	0.0366
80d	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0203	92.4	0.0375
81	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0203	92.4	0.0378
81d	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0234	92.4	0.0501
82	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0408	92.4	0.152
82b	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0411	92.4	0.154
82c	0.710	8.39×10^{-4}	846	7.76×10^{-9}	0.0408	89.5	0.147
82d	0.896	9.27×10^{-4}	966	7.76×10^{-9}	0.0363	86.5	0.113
83	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0372	92.4	0.127
83b	0.710	8.39×10^{-4}	846	7.76×10^{-9}	0.0366	89.5	0.119
84	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0366	92.4	0.122
85	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0330	92.4	0.0993
86	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0295	92.4	0.0798
87	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0277	92.4	0.0701
88	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0287	92.4	0.0752
89	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0456	92.4	0.190
90	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0421	92.4	0.162
91	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0322	92.4	0.0948
91b	0.566	7.61×10^{-4}	743	7.76×10^{-9}	0.0320	92.4	0.0938
91c	0.710	8.39×10^{-4}	846	7.76×10^{-9}	0.0313	89.5	0.0866
91d	0.896	9.27×10^{-4}	966	7.76×10^{-9}	0.0284	86.5	0.0691
92	0.710	8.39×10^{-4}	846	7.76×10^{-9}	0.0573	89.5	0.290
93	0.706	8.37×10^{-4}	843	5.71×10^{-9}	0.0298	122	0.107
94	0.706	8.37×10^{-4}	843	5.71×10^{-9}	0.0318	122	0.122
95	0.706	8.37×10^{-4}	843	5.71×10^{-9}	0.0346	122	0.145
96	0.706	8.37×10^{-4}	843	5.71×10^{-9}	0.0395	122	0.188
97	0.701	8.35×10^{-4}	840	3.97×10^{-9}	0.0188	175	0.0613
98	0.701	8.35×10^{-4}	840	3.97×10^{-9}	0.0219	175	0.0836
99	0.701	8.35×10^{-4}	840	3.97×10^{-9}	0.0248	175	0.107
100	0.874	9.17×10^{-4}	953	3.97×10^{-9}	0.0136	170	0.0312
101	0.789	8.78×10^{-4}	899	3.97×10^{-9}	0.00729	172	0.00909
102	0.797	8.82×10^{-4}	904	5.71×10^{-9}	0.0221	120	0.0581
103	0.797	8.82×10^{-4}	904	5.71×10^{-9}	0.00870	120	0.00897
104	0.797	8.82×10^{-4}	904	5.71×10^{-9}	0.0105	120	0.0132
105	0.789	8.78×10^{-4}	899	3.97×10^{-9}	0.0304	172	0.158
107	0.789	8.78×10^{-4}	899	3.97×10^{-9}	0.0310	172	0.164
108	0.789	8.78×10^{-4}	899	3.97×10^{-9}	0.0332	172	0.188

Order of reaction in Cu^{2+}

The order of reaction in Cu^{2+} was determined at two different temperatures, i.e., $T=90^\circ\text{C}$ and 70°C , from experiments 82c, 83b, 84, 85, 86, 87 and 93, 94, 95, 96, respectively. The experimental

Figure 2. $\ln R_{\text{Fe}^{2+}, t=0}$ versus $\ln[\text{Cu}^{2+}]$. Initial conditions for $T = 90^\circ\text{C}$: $P_{\text{air}} = 0.50$ MPa, $[\text{Fe}^{2+}] = 0.25$ M, $[\text{H}_2\text{SO}_4] = 0.27$ M, $[\text{Cu}^{2+}] = 0.0156, 0.0312, 0.0628, 0.125, 0.25$, and 0.5 M. Initial conditions for $T = 70^\circ\text{C}$: $P_{\text{air}} = 0.46$ MPa, $[\text{Fe}^{2+}] = 0.5$ M, $[\text{H}_2\text{SO}_4] = 0.5$ M, $[\text{Cu}^{2+}] = 0.0625, 0.125, 0.25$, and 0.5 M.

Figure 3. $\ln R_{\text{Fe}^{2+}, t=0}$ versus $\ln[\text{Fe}^{2+}]$. Initial conditions: $T = 90^\circ\text{C}$, $P_{\text{air}} = 0.50$ MPa, $[\text{Cu}^{2+}] = 0.5$ M, $[\text{H}_2\text{SO}_4] = 0.27$ M, $[\text{Fe}^{2+}] = 0.0588, 0.123, 0.25$, and 0.5 M.

data for the initial reaction rates are given in Figure 2.

From the results in Figure 2 it can be concluded that the slope is either 0.15 or 0.24. These values indicate that a fractional order in Cu^{2+} is observed, moreover, the order in Cu^{2+} seems to be concentration dependent.

Order of reaction in Fe^{2+}

The order of reaction in Fe^{2+} was determined at one temperature, i.e., $T = 90^\circ\text{C}$, from experiments 77, 82c, 82d, 88, and 92. The experimental data for the initial reaction rates are given in Figure 3.

From the results in Figure 3, it can be concluded that the slope is 1, so this indicates that for conditions studied a first order dependency in Fe^{2+} is observed.

Order of reaction in H_2SO_4

The order of reaction in H_2SO_4 was determined at two temperatures, i.e., $T = 90^\circ\text{C}$ and 50°C , from experiments 61, 72, 76, 71 and 105, 107, 108, respectively. The experimental data for the initial reaction rates are given in Figure 4.

From the results in Figure 4, it can be concluded that slopes were near zero, so this indicates that for conditions studied and within the experimental accuracies a zero order dependency in H_2SO_4 is observed.

Order of reaction in Fe^{3+}

An extensive set of experiments was performed at a temperature of $T = 90^\circ\text{C}$, i.e., experiments 78b, 78c, 79, 79b, 79c, 80, 80b, 80c, 80d, 81, and 81d. Two indicative experiments were performed at

Figure 4. $\ln R_{\text{Fe}^{2+}, t=0}$ versus $\ln[\text{H}_2\text{SO}_4]$. Initial conditions for $T = 90^\circ\text{C}$: $P_{\text{air}} = 0.50$ MPa, $[\text{Fe}^{2+}] = 0.25$ M, $[\text{Cu}^{2+}] = 0.125$ M, $[\text{H}_2\text{SO}_4] = 0.27, 0.5, 1$, and 2 M. Initial conditions for $T = 50^\circ\text{C}$: $P_{\text{air}} = 0.44$ MPa, $[\text{Fe}^{2+}] = 1$ M, $[\text{Cu}^{2+}] = 0.25$ M, $[\text{H}_2\text{SO}_4] = 0.27, 0.52$, and 1 M.

Figure 5. $\ln R_{\text{Fe}^{2+}, t=0}$ versus $\ln[\text{Fe}^{3+}]$. Initial conditions for $T = 90^\circ\text{C}$: $P_{\text{air}} = 0.50$ MPa, $[\text{Fe}^{2+}] = 0.25$ M, $[\text{Cu}^{2+}] = 0.25$ M, $[\text{H}_2\text{SO}_4] = 0.5$ M, $[\text{Fe}^{3+}] = 0.067, 0.13, 0.26$, and 0.50 M. Initial conditions for $T = 70^\circ\text{C}$: $P_{\text{air}} = 0.46$ MPa, $[\text{Fe}^{2+}] = 0.25$ M, $[\text{Cu}^{2+}] = 0.25$ M, $[\text{H}_2\text{SO}_4] = 0.5$ M, $[\text{Fe}^{3+}] = 0.060$ and 0.50 M.

Figure 6. $\ln R_{\text{Fe}^{2+}, t=0}$ versus $\ln P_{\text{O}_2}$. Initial conditions for $T = 90^\circ\text{C}$: $[\text{Fe}^{2+}] = 0.25$ M, $[\text{Cu}^{2+}] = 0.25$ M, $[\text{H}_2\text{SO}_4] = 0.27$ M, $P_{\text{air}} = 0.18, 0.29, 0.50$, and 0.52 (40 vol.% O_2) MPa. Initial conditions for $T = 50^\circ\text{C}$: $[\text{Fe}^{2+}] = 0.5$ M, $[\text{Cu}^{2+}] = 0.125$ M, $[\text{H}_2\text{SO}_4] = 0.5$ M, $P_{\text{air}} = 0.12, 0.23, 0.44$, and 0.46 (40 vol.% O_2) MPa.

Figure 7. Fe^{2+} concentration profiles for varying oxygen partial pressures and temperatures. For experimental conditions see Table 9.

Figure 8. Fe^{2+} concentration profiles for varying Cu^{2+} concentrations. For experimental conditions see Table 10.

Figure 9. Fe^{2+} concentration profiles for varying Fe^{2+} concentrations. For experimental conditions see Table 11.

$T = 70^\circ\text{C}$, i.e., experiments 103 and 104, to determine an order of reaction in Fe^{3+} . The experimental data for the initial reaction rates are given in Figure 5.

From the results in Figure 5, it can be concluded that the slope is either -0.24 or -0.30 . However, a highly inaccurate curve fit for the experimental data at $T = 90^\circ\text{C}$ was obtained, and

Figure 10. Fe^{2+} concentration profiles for varying H_2SO_4 concentrations. For experimental conditions see Table 12.

Figure 11. Fe^{2+} concentration profiles for varying Fe^{3+} concentrations. For experimental conditions see Table 13.

only two experiments were performed at $T=70^\circ\text{C}$. It can be stated that Fe^{3+} seems to have a negative influence on the Fe^{2+} oxidation in the presence of Cu^{2+} . However, the order of reaction in Fe^{3+} is not well defined but is about -0.25 .

Order of reaction in O_2

The order of reaction in O_2 was determined at two temperatures, i.e., $T=90^\circ\text{C}$ and 50°C , from experiments 83b, 89, 90, 91c, 91d and 97, 98, 99, 100, respectively. The experimental data for the initial reaction rates are given in Figure 6.

From the results in Figure 6, it can be concluded that slopes of 0.73 and 0.52 were obtained. Based on these results it cannot be concluded that the reaction is first order in O_2 . It seems more in between 0.50 and 0.75.

Table 9. Experimental settings of experiments in Figure 7.

Exp	T ($^\circ\text{C}$)	P_{O_2} (MPa)	$[\text{Cu}^{2+}]$ ($\text{kmol} \cdot \text{m}^{-3}$)	$[\text{Fe}^{2+}]$ ($\text{kmol} \cdot \text{m}^{-3}$)	$[\text{H}_2\text{SO}_4]$ ($\text{kmol} \cdot \text{m}^{-3}$)
99	50	0.0226	0.125	0.500	0.519
98	50	0.0451	0.125	0.500	0.519
97	50	0.0901	0.125	0.500	0.518
100	50	0.180	0.125	0.500	0.519
94	70	0.0901	0.125	0.500	0.519

Concentration profiles

Because most of the experiments were affected by the mass transfer of oxygen to varying extents, no true intrinsic kinetics could be obtained for the oxidation of Fe^{2+} in the presence of Cu^{2+} . Therefore, the effect of a change in experimental condition on the Fe^{2+} oxidation profile is clarified in Figures 7 to 11. The experimental settings are provided in Tables 9 to 13.

Figure 7 shows the effect of a change in partial pressure of O_2 and temperature on the oxidation

Table 10. Experimental settings of experiments in Figure 8.

Exp	T (°C)	P_{O_2} (MPa)	$[Cu^{2+}]$ (kmol · m ⁻³)	$[Fe^{2+}]$ (kmol · m ⁻³)	$[H_2SO_4]$ (kmol · m ⁻³)
87	90	0.0901	0.0156	0.250	0.270
84	90	0.0901	0.125	0.250	0.270
82c	90	0.0901	0.500	0.250	0.271

Table 11. Experimental settings of experiments in Figure 9.

Exp	T (°C)	P_{O_2} (MPa)	$[Cu^{2+}]$ (kmol · m ⁻³)	$[Fe^{2+}]$ (kmol · m ⁻³)	$[H_2SO_4]$ (kmol · m ⁻³)
77	90	0.0901	0.500	0.0624	0.270
88	90	0.0901	0.500	0.125	0.271
82c	90	0.0901	0.500	0.250	0.271
92	90	0.0901	0.500	0.500	0.272

Table 12. Experimental settings of experiments in Figure 10.

Exp	T (°C)	P_{O_2} (MPa)	$[Cu^{2+}]$ (kmol · m ⁻³)	$[Fe^{2+}]$ (kmol · m ⁻³)	$[H_2SO_4]$ (kmol · m ⁻³)
107	50	0.0901	0.246	1.00	0.276
105	50	0.0901	0.246	1.00	0.522
108	50	0.0901	0.246	1.00	1.00

rate of Fe^{2+} . The experimental settings are described in Table 9. From Figure 7, it can be concluded that an increase in both the partial pressure of O_2 and temperature, increases the rate of oxidation of Fe^{2+} .

Figure 8 shows the effect of a change in the concentration of Cu^{2+} on the oxidation rate of Fe^{2+} . The experimental settings are described in Table 10. From Figure 8, it can be concluded that increasing the Cu^{2+} concentration increases the rate of oxidation of Fe^{2+} .

Figure 9 shows the effect of a change in the concentration of Fe^{2+} on the oxidation rate of Fe^{2+} . The experimental settings are described in Table 11. From Figure 9, it can be concluded that increasing the Fe^{2+} concentration increases the rate of oxidation of Fe^{2+} .

Figure 10 shows the effect of a change in the concentration of H_2SO_4 on the oxidation rate of Fe^{2+} . The experimental settings are described in Table 12. From Figure 10, it can be concluded that increasing the H_2SO_4 concentration hardly influences the rate of oxidation of Fe^{2+} .

Figure 11 shows the effect of a change in the concentration of Fe^{3+} on the oxidation rate of Fe^{2+} . The experimental settings are described in Table 13. From Figure 11, it can be concluded that increasing the Fe^{3+} concentration decreases the rate of oxidation of Fe^{2+} .

Activation energy

The temperature dependence of a reaction can be determined from the Arrhenius equation:

$$k = A \exp \left\{ -\frac{E_A}{RT} \right\}. \quad (30)$$

In this study, a kinetic equation for the oxidation of Fe^{2+} in the presence of Cu^{2+} , describing the Fe^{2+} oxidation rates of all experiments, could not be established. However, the activation energy of the oxidation reaction can be estimated from reaction rates according to Equations (25), (26), and (30): if the speciation of the solutions are equal, the concentrations can be lumped with the pre-exponential factor.

The activation energy was estimated from initial Fe^{2+} conversion rates from experiments performed at 50 °C (experiments 105, 107, 108), 70 °C (experiments 93, 94, 95, 96), and 90 °C (experiment 82c, 82d, 83b). The oxygen partial pressure was constant, Fe^{3+} was not present initially, the stirrer speed was at least 33 rps, and the $(Al-1)Ha^2$ number was in between 0.107 and 0.188. Fe^{2+} oxidation rates were corrected for concentration differences with the experimentally derived orders of reaction in Fe^{2+} , Cu^{2+} , and H_2SO_4 of 1.0, 0.15, and 0, respectively. Experiment 95 was used as a base case. The activation energy was estimated to be 31.3 kJ/mol (see Figure 12).

Discussion

Previous studies

As explained in the previous paper by Wermink and Versteeg (2017a), Chmielewski and Charewicz (1984) determined a kinetic equation for the oxidation of Fe^{2+} based on experiments performed with initial Cu^{2+} concentrations of either 0.16 M or 0.79 M, respectively. As Chmielewski and Charewicz explained, the rate of oxidation is affected by the concentration of Cu^{2+} . In this study, it is demonstrated that Cu^{2+} has an enhancing effect on the oxidation rate (see Figures 2 and 8). From their Figure 4, it can be concluded that an increase in Cu^{2+} concentration increased the Fe^{2+} oxidation rate. Therefore, it was incorrect of them to report a kinetic

equation that did not account for the concentration of Cu^{2+} .

Dreisinger and Peters (1989) studied the oxidation of Fe^{2+} in the presence of ZnSO_4 and CuSO_4 . They reported one kinetic equation based on ferrous sulfate oxidation with and without CuSO_4 . The reported activation energy of the respective rate equation was based on experiments performed without CuSO_4 .

Cupric ions act as a catalyst in the oxidation of Fe^{2+} , and therefore either lowers the activation energy, increases the pre-exponential, or affects both. If a first order dependency in the catalyst is obtained, it is highly likely that only the pre-exponential factor is affected. However, Dreisinger and Peters stated that an order of 0.5 was obtained in CuSO_4 . Therefore, it is highly likely that Cu^{2+} is affecting the activation energy, and consequently, the activation energy should be determined from experiments with Cu^{2+} at varying temperatures.

Bruhn et al. (1965) reported oxygen solubilities in the form of Bunsen coefficients for several salts. A comparison of their oxygen solubility data in cupric sulfate solutions with oxygen solubilities predicted using the model by Weisenberger and Schumpe (1996) resulted in a high average difference of 39% (9 experimental data points).

A comparison of the oxygen solubilities in zinc sulfate solutions by Narita et al. (1983) and Lang and Zander (1986), and in cupric sulfate solutions by Manku (1994) and Lang and Zander (1986) with oxygen solubilities predicted using the model by Weisenberger and Schumpe (1996) resulted in an average difference of only 3.8% (18 experimental data points).

Lang and Zander (1986) compared the salting-out parameter for oxygen, according to Setchenov's concept, with a/o Bruhn et al. (1965) for cupric sulfate solutions. Their salting-out parameter was a factor 2.3 higher compared to Bruhn et al.

Based on these considerations it was decided to disregard the oxygen solubility data of Bruhn et al. (1965) in establishing the model parameter for the bisulfate ion in the extended model by Weisenberger and Schumpe (1996).

Ruiz et al. (2016) performed Fe^{2+} oxidation experiments in the presence of Cu^{2+} at a temperature of 453 K and a partial pressure of oxygen of 0.69 MPa to study the effect of impeller speed in the range of 3.33 rps to 13.3 rps. It was concluded that impeller speeds above 6.67 rps did not affect the Fe^{2+} oxidation rate. They carried out experiments at 13.3 rps.

However, experiments were performed up to a temperature of 493 K and up to an oxygen partial pressure of 1.379 MPa. The effect of impeller speed should have been verified at these experimental settings to rule out mass transfer limitations.

This study

The bisulfate ion parameter in the extended model of Weisenberger and Schumpe (1996) was fitted on experimental data points at temperatures ranging from 298 K to 333 K. In this study, the oxidation of Fe^{2+} in the presence of Cu^{2+} was investigated at temperatures ranging from 323 K to 363 K. Moreover, the experimental data used to evaluate the model parameter for oxygen in the original model by Weisenberger and Schumpe (1996) was obtained in the temperature range of 273 K to 353 K. Therefore, in this study, oxygen solubilities of experiments performed at either 343 K or 363 K were extrapolated.

The power consumption of gas-inducing impellers as proposed by Lemoine and Morsi (2005) was determined from the equation by Van Heim et al. (1995). Their equation was derived from experiments performed with rotational speeds varying between 10.7 rps and 25.7 rps. Rotational speeds varied between 26.7 rps and 38.7 rps in this study. Moreover, their equation is dependent on the geometry and type of impeller. The blades of the impeller in this study were rectangular and not cylindrical as in the study by Van Heim et al. Therefore, the impeller power consumptions determined in this study according to the relationship by Van Heim et al., as well as the mass transfer parameters, are approximations.

The values of $(Al - 1)Ha^2$ were determined to be always lower than 0.30. Therefore, it can be concluded that the concentration of oxygen in the liquid is overestimated by a maximum of

Table 13. Experimental settings of experiments in Figure 11.

Exp	T (°C)	P_{O_2} (MPa)	$[Cu^{2+}]$ (kmol · m ⁻³)	$[Fe^{2+}]$ (kmol · m ⁻³)	$[H_2SO_4]$ (kmol · m ⁻³)	$[Fe^{3+}]$ (kmol · m ⁻³)
78c	90	0.0901	0.250	0.250	0.519	0.0625
79	90	0.0901	0.250	0.250	0.522	0.125
80c	90	0.0901	0.250	0.250	0.520	0.250
81d	90	0.0901	0.250	0.250	0.520	0.500

Figure 12. $\ln R_{Fe^{2+}}$ versus T^{-1} .

30% under the assumption of a fully saturated liquid bulk (see Equation (11)). The derived pseudo-first order kinetic constants of the experiments are therefore underestimated (up to 30%).

The orders of reaction were determined from initial reaction rates. However, some of the experiments were affected by mass transfer of oxygen. For example, it was determined that experiment 92 was controlled by mass transfer, and that kinetics were measured in experiment 77. However, the two corresponding experiments were used in determining the order of reaction in Fe^{2+} (Figure 3). Therefore, the comparison of the various orders of reaction published in previous studies to the orders determined in this study is an indication.

A stepwise behavior in the order of Cu^{2+} was observed in this study, i.e., a fractional order of either 0.15 or 0.24 is obtained which seems to be concentration dependent. The order of 0.24 agrees well with the order reported by Mathews and Robins (1972), i.e., an order of 0.278. McKay (1957) and McKay and Halpern (1958) reported a fractional order of 0.5 which is only valid for $CuSO_4$ concentrations below 0.0055 M. Dreisinger and Peters (1989) reported a fractional order of 0.5 in $CuSO_4$. Huffman and Davidson (1956) reported a first order in Cu^{2+} . Ruiz et al. (2016) reported a zero order of reaction in Cu^{2+} .

The first order dependency in Fe^{2+} determined in this work agrees well with the first order in Fe^{2+} reported by Huffman and Davidson (1956). McKay (1957) and McKay and Halpern (1958) observed that the order in $FeSO_4$ ceased to be second order for $CuSO_4$ concentrations above 0.0055 M. It is not mentioned what the dependency in $FeSO_4$ becomes at higher $CuSO_4$ concentrations. Ruiz et al. (2016) reported an order of reaction of 2.8 in Fe^{2+} .

A zero order dependency in H_2SO_4 was derived from initial reaction rates in this study. Contrary to our findings, Lamb and Elder (1931) reported an increase in Fe^{2+} oxidation rate with increasing H_2SO_4 concentrations in the presence of $CuSO_4$. Ruiz et al. reported a fractional order of 0.3 in H_2SO_4 . Although a zero order dependency was derived from initial reaction rates, it can be observed from the concentration profiles in Figure 10 that an increase in H_2SO_4 concentration resulted in a slight increase in Fe^{2+} oxidation rate.

A fractional, negative order in Fe^{3+} was determined in this study. It proved to be difficult to obtain reproducible initial reaction rates. Based on Fe^{2+} concentration profiles, it could be clearly concluded that Fe^{3+} has a negative influence on the Fe^{2+} oxidation rate. In previous studies, the dependency in Fe^{3+} was not investigated.

Fractional orders in O_2 were observed in this study, i.e., 0.73 and 0.52, respectively. McKay (1957), McKay and Halpern (1958), and Ruiz et al. (2016) reported a first order dependency in O_2 . Huffman and Davidson (1956) observed a zero order dependency in O_2 . This dependency was determined for Fe^{2+} and Cu^{2+} concentrations significantly lower compared to the concentrations investigated in the present study (0.001 M and 1.1×10^{-5} M, respectively).

An activation energy of 31.3 kJ/mol was reported in this study, which agrees reasonably with the activation energy of 36.5 kJ/mol reported by Ruiz et al. (2016).

Conclusion

The oxidation of ferrous ions in acidic sulfate solutions in the presence of cupric ions at elevated air pressures was investigated in a high-intensity gas-liquid contactor. The study was required for the design of the regeneration steps of the novel Vitrisol[®] desulphurization process.

The effect of the Fe^{2+} concentration, Cu^{2+} concentration, Fe^{3+} concentration, initial H_2SO_4 concentration, and partial oxygen pressure on the reaction rate were determined at three different temperatures, i.e., $T = 50^\circ C$, $70^\circ C$, and $90^\circ C$. Most of the experiments were determined to be affected by the mass transfer of oxygen, and therefore true intrinsic kinetics could not be fully determined.

An increase in Fe^{2+} and Cu^{2+} concentrations, as well as the partial pressure of oxygen and temperature, increased the Fe^{2+} oxidation rate. H_2SO_4 did not influence the Fe^{2+} oxidation rate. An increase in Fe^{3+} concentration decreased the Fe^{2+} oxidation rate.

Although determined from experiments partially affected by mass transfer, a first order of reaction in Fe^{2+} was observed, fractional orders in both Cu^{2+} and O_2 were measured, a zero order in H_2SO_4 was determined, and a negative, fractional order in Fe^{3+} was obtained. The activation energy was determined to be 31.3 kJ/mol.

Notation

a	interfacial area [m^2/m^3]
A	pre-exponential factor

A, B, C, D, a_1, a_2	constants
Al	Hinterland number [-]
c	concentration [$kmol.m^{-3}$]
d	diameter [m]
D	diffusion coefficient [$m^2.s^{-1}$]
ε_G	gas holdup [-]
E_A	enhancement factor [-]
Fr^*	modified Froude number [-]
G	gravitational acceleration [m/s^2]
H	liquid level above the impeller [m]
Ha	Hatta number [-]
J	molar flux [$mol.m^{-2}.s^{-1}$]
K_H	Henry's law [Pa]
k_L	mass transfer coefficient [$m.s^{-1}$]
k_{ps}	pseudo-first order reactant rate constant [s^{-1}]
k_1	reaction rate constant
M	molecular mass [kg/mol]
N	impeller rotational speed [rps]
N_P	power number [-]
μ	viscosity [Pa.s]
P	pressure [Pa]
P	power input impeller [W]
ρ	density [kg/m^3]
R	reaction rate [$kmol.m^{-3}.s^{-1}$]
Re	Reynolds number [-]
t	time [s]
T	temperature [$^\circ C$, K]
ϕ	association parameter [g/mol]
V	volume [m^3]
V_m	molar volume [cm^3/g]
x	mole fraction [-]

Subscripts and superscripts

A	component A
a, b, c, d	orders of reaction
$film$	stagnant layer near G/L interface
Fe^{2+}	ferrous ion
GIR	gas-induced reactor
H_2O	water
O_2	oxygen
i	interface
i	impeller
L	liquid
R	reaction phase
SAR	surface aerated reactor

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References

- Bruhn, G., Gerlach, J., and Pawlek, F. (1965). Untersuchungen über die löslichkeiten von salzen und gasen in wasser und wässrigen lösungen bei temperaturen oberhalb 100°C, *Z Anorg. Allg. Chem.*, **337**, 68–79.
- Cher, M., and Davidson, N. (1955). The kinetics of the oxygenation of ferrous iron in phosphoric acid solution, *J. Am. Chem. Soc. Soc.*, **77**, 793–798.
- Chmielewski, T., and Charewicz, W. A. (1984). The oxidation of Fe(II) in aqueous sulphuric acid under oxygen pressure, *Hydrometallurgy*, **12**, 21–30.
- Danckwerts, P. V. (1970). *Gas-Liquid Reactions*, McGraw-Hill, New York, USA.
- Dreisinger, D. B., and Peters, E. (1989). The oxidation of ferrous sulphate by molecular oxygen under zinc pressure-leach conditions, *Hydrometallurgy*, **22**, 101–119.
- Dutrizac, J. E., and MacDonald, R. J. C. (1974). The kinetics of dissolution of covellite in acidified ferric sulphate solutions, *Can. Metall. Q.*, **13**, 423–433.
- Hamborg, E. S., Derks, P. W. J., Elk, E. P. V., and Versteeg, G. F. (2011). Carbon dioxide removal by alkanolamines in aqueous organic solvents. A method for enhancing the desorption process, *Energy Procedia*, **4**, 187–194.
- Heim, A., Kraslawski, A., Rzycki, E., and Stelmach, J. (1995). Aeration of bioreactors by self-aspirating impellers, *Chem. Eng. J.*, **58**, 59–63.
- Huffman, R. E., and Davidson, N. (1956). Kinetics of the ferrous iron-oxygen reaction in sulfuric acid solution, *J. Am. Chem. Soc. Soc.*, **78**, 4836–4842.
- Knopf, D. A., Luo, B. P., Krieger, U. K., and Koop, T. (2003). Thermodynamic dissociation constant of the bisulfate ion from raman and ion interaction modeling studies of aqueous sulfuric acid at low temperatures, *J. Phys. Chem. A*, **107**, 4322–4332.
- Koetsier, W. T., Thoenes, D., and Frankena, J. F. (1973). Mass transfer in a closed stirred gas/liquid contactor. Part 1: The mass transfer rate $k_L S$, *Chem. Eng. J.*, **5**, 61–69.
- Koetsier, W. T., and Thoenes, D. (1973). Mass transfer in a closed stirred gas/liquid contactor. Part 2: The liquid phase mass transfer coefficient k_L , *Chem. Eng. J.*, **5**, 71–75.
- Lamb, A. B., and Elder, L. W. (1931). The electromotive activation of oxygen, *J. Am. Chem. Soc. Soc.*, **53**, 137–166.
- Lang, W., and Zander, R. (1986). Salting-out of oxygen from aqueous electrolyte solutions: prediction and measurement, *Ind. Eng. Chem. Fund. Fundam.*, **25**, 775–782.
- Lemoine, R., and Morsi, B. I. (2005). An algorithm for predicting the hydrodynamic and mass transfer parameters in agitated reactors, *Chem. Eng. J.*, **114**, 9–31.
- Manku, G. (1994). Solubilities of oxygen in selected alkane solvents and in aqueous copper electrorefining solutions (thesis, University of Ottawa, Ottawa).
- Mathews, C. T., and Robins, R. G. (1972). The oxidation of aqueous ferrous sulphate solutions by molecular oxygen, *Proc. Aust. Inst. Min. Met.*, **242**, 47–57.
- McKay, D. R. (1957). A kinetic study of the oxidation of pyrite in aqueous suspension (thesis, University of British Columbia, Vancouver).
- McKay, D. R., and Halpern, J. (1958). A kinetic study of the oxidation of pyrite in aqueous suspension, *Trans. Metall. Soc. AIME*, **212**, 301–309.
- Narita, E., Lawson, F., and Han, K. N. (1983). Solubility of oxygen in aqueous electrolyte solutions, *Hydrometallurgy*, **10**, 21–37.
- Peacey, J., Guo, X.-J., and Robles, E. (2004). Copper hydrometallurgy – current status, preliminary economics, future direction and positioning versus smelting, *Trans. Nonferrous Met. Soc. China*, **14**, 560–568.
- Ramachandran, P. A., and Chaudhari, R. V. (1983). *Three-Phase Catalytic Reactors*, 2nd vol., Gordon and Breach Science Publishers, London, United Kingdom.
- Reid, R. C., Prausnitz, J. M., and Sherwood, T. K. (1977). *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York.
- Ruiz, M. C., Jerez, O., and Padilla, R. (2016). Kinetics of the cupric catalyzed oxidation of Fe^{II} by oxygen at high temperature and high pressure, *Min. Proc. Ext. Met. Rev.*, **37**, 160–167.
- Ter Maat, H., Hogendoorn, J. A., and Versteeg, G. F. (2005). The removal of hydrogen sulfide from gas streams using an aqueous metal sulfate absorbent. Part I. The absorption of hydrogen sulfide in metal sulfate solutions, *Sep. Purif. Technol.*, **43**, 183–197.
- Ter Maat, H., Al-Tarazi, M., Hogendoorn, J. A., Niederer, J. P. M., and Versteeg, G. F. (2007). Theoretical and experimental study of the absorption rate of H₂S in CuSO₄ solutions. The effect of enhancement of mass transfer by a precipitation reaction, *Chem. Eng. Res. Des.*, **85**, 100–108.
- Van't Riet, K. (1979). Review of measuring methods and results in nonviscous gas-liquid mass transfer in stirred vessels, *Ind. Eng. Chem. Proc. Des.*, **18**, 357–364.
- Versteeg, G. F., and ter Maat, H. (1997). Method and system for selective removal of contamination from gas flows. WO patent 1998055209.
- Weisenberger, S., and Schumpe, A. (1996). Estimation of gas solubilities in salt solutions at temperatures from 273 K to 363 K, *AIChE J.*, **42**, 298–300.
- Wermink, W. N., and Versteeg, G. F. (2017a). The oxidation of Fe(II) in acidic sulphate solutions with air at elevated pressures. Part 1. Kinetics above 1 M H₂SO₄, *Ind. Eng. Chem. Res. Res.*, **56**, 3775–3788.
- Wermink, W. N., and Versteeg, G. F. (2017b). The oxidation of Fe(II) in acidic sulphate solutions with air at elevated pressures. Part 2. Influence of H₂SO₄ and Fe(III), *Ind. Eng. Chem. Res. Res.*, **56**, 3789–3796.

- Wermink, W. N., Ramachandran, N., and Versteeg, G. F. (2017). Vitrisol[®] a 100% selective process for H₂S removal in the presence of CO₂, *J. Natural Gas Eng.*, **2**, 50–83.
- Westerterp, K. R., Van Swaaij, W. P. M., and Beenackers, A. A. C. M. (1988). *Chemical Reactor Design and Operation. Chapter VII, Multiphase Reactors, Single Reactions*, 2nd ed., John Wiley & Sons Ltd., Chichester, United Kingdom.
- Wilke, C. R., and Chang, P. (1955). Correlation of diffusion coefficients in dilute solutions, *AIChE J.*, **1**, 264–270.
- Zuidervaat, E., Reuter, M. A., Heerema, R. H., Van der Lans, R. G. J. M., and Derksen, J. J. (2000). Effect of dissolved metal sulphates on gas-liquid oxygen transfer in agitated quartz and pyrite slurries, *Miner. Eng.*, **13**, 1555–1564.