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**DERIVING A RATE EQUATION FOR THE REMOVAL OF MANGANESE FROM
SOLUTION USING A GAS MIXTURE OF SULFUR DIOXIDE AND OXYGEN**

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SYNOPSIS

The use of a sulfur dioxide – oxygen gas mixture to selectively remove manganese from other metals, such as cobalt and nickel, from leach solutions is kinetically favourable and inexpensive. However, this technology for precipitating manganese has not been used commercially, mainly due to a lack of understanding of the reaction mechanism by which the sulfur dioxide - oxygen gas mixture oxidises the manganese and the need to control the concentration of aqueous sulfur dioxide in the solution to ensure oxidising conditions. From the literature, the gas mixture is postulated to form a free radical in solution which in turn oxidises the manganese(II) into the manganese(III) species, which can precipitate as manganese oxides (MnO_2 , Mn_2O_3 , etc.).

Due to the complicated and unknown reaction pathways for the oxidation of the manganese by the sulfur dioxide – oxygen gas mixture, a need arose to describe the rate at which the manganese is precipitated from solution, not in terms of the exact species responsible for the oxidation, but rather as a function of the easily measurable operating parameters.

From the literature, the operating parameters identified as playing a role in the rate of manganese precipitation are: the gas composition; the dissolved sulfur dioxide concentration; the dissolved oxygen concentration; the solution temperature, and the solution pH.

To derive the relationship between the rate of manganese precipitation and each of the operating parameters, batch tests were conducted where one of the operating parameters was varied at a time. The dissolved sulfur species arising from the dissolution of the sulfur dioxide gas were not kept constant during the batch tests due to the high solubility of sulfur dioxide in water (the concentration of the dissolved sulfur species increased throughout all of the batch experiments). However, each of the operating parameters could be assessed as long as the concentration of the sulfur species in solution increased at the same rate for every test.

From the batch data the following relationships between the rate of manganese removal and the operating parameters were obtained:

$$d[\text{Mn}]/dt = \text{Constant}_1 \times (P_{\text{SO}_2}/P_{\text{Total}}) \times e^{(-18[S \text{ from gas}])}$$

$$d[\text{Mn}]/dt = \text{Constant}_2 \times [\text{O}_2]$$

$$d[\text{Mn}]/dt = \text{Constant}_3 \times e^{(-E_a/RT)}$$

$$d[\text{Mn}]/dt = \text{Constant}_4 \times (1/\text{pH} - \text{Constant}_5)$$

The relationship between the sulfur dioxide and the rate of manganese precipitation was described by both the sulfur dioxide content of the gas mixture, as well as the concentration of the dissolved sulfur

species arising from the dissolution of the sulfur dioxide gas. The term “[S from gas]” refers to the total sulfur concentration in solution attributed to the dissolution of the sulfur dioxide gas (i.e. it excludes only the sulfur species present in solution before the gas sparging commenced).

The rate of manganese precipitation was found to be first order with respect to the dissolved oxygen concentration and an Arrhenius relationship was used to relate the solution temperature to the rate of manganese precipitation. An activation energy of 23.5 kJ/mol was calculated for the precipitation of the manganese from the batch tests in the temperature range investigated. The rate of manganese precipitation was found to be inversely proportional to the pH of the solution. The manganese concentration was seen to have little influence on the rate of manganese precipitation, except at low concentrations (less than 50 mg/l manganese).

The rate equations stated for each of the operating parameters were combined into one rate equation for the precipitation of manganese:

$$d[\text{Mn}]/dt = A \cdot [\text{O}_2] \cdot (P_{\text{SO}_2}/P_{\text{tot}}) \cdot e^{(B \cdot [\text{S from gas}])} \cdot (1/\text{pH} + C) \cdot e^{(-E_a/RT)}$$

with $d[\text{Mn}]/dt$ in mol/litre/min
 $[\text{O}_2]$ in mol/litre
 P_{SO_2} in atmospheres
 P_{tot} in atmospheres
 $[\text{S from gas}]$ in mol/litre
 T in Kelvin

with $A = -6.8 \times 10^5$
 $B = -18$
 $C = -0.3$
 $E_a = 23.5 \text{ kJ/mol}$

Ignoring the induction period noticed at the start of some of the batch tests, the combined rate equation was found to accurately describe all of the batch data.

For the rate equation to be of value for circuit design, the rate equation also had to be tested on a continuous basis. Continuous tests were performed in the same reactor in which the rate equation was derived, to compare the actual steady-state concentration of the manganese with that calculated by the rate equation. The rate equation was used in the mass balance over a one-stage continuous reactor and a steady-state manganese concentration was calculated by inserting the steady state values of the dissolved sulfur concentration attributed to the dissolution of the gas; the dissolved oxygen concentration; the gas composition; the solution temperature and the pH into the rate equation. The rate equation was found to still apply in a continuous environment, the accuracy of the calculated steady-state manganese

removal in most cases being close to 100 % (the least accurate calculated manganese removal was 123 % of the actual measured manganese removal).

An empirical rate equation was thus produced in this work that is useful in describing the rate at which manganese precipitates from solution by using a gas mixture of sulfur dioxide and oxygen, both under batch and continuous operation.

On its own, the rate equation cannot be used as a predictive tool since the dissolved oxygen concentration and the dissolved sulfur concentration need to be measured with time to calculate a manganese removal rate. To convert the rate equation into a predictive tool, the rate of oxygen mass transfer and the rate of sulfur dioxide mass transfer into the solution need to be combined with the above mentioned rate equation. Thus, there will be three differential equations that must be solved simultaneously using a numerical method. The three equations needed to predict the rate of manganese precipitation are:

$$d[\text{Mn}]/dt = A \cdot [\text{O}_2]_{\text{bulk}} \cdot (P_{\text{SO}_2}/P_{\text{tot}}) \cdot e^{(B \cdot [\text{S from gas}])} \cdot (1/\text{pH} + C) \cdot e^{(-Ea/RT)}$$

$$d[\text{O}_2]/dt = K_L a_1 ([\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{bulk}})$$

$$d[\text{S from gas}]/dt = K_L a_2 ([\text{S}_{\text{total}}]_{\text{sat}} - [\text{S from gas}])$$

In this work it was found that the rate of oxygen transfer as well as the rate of sulfur dioxide transfer from the gas phase into solution were not influenced by the rate of the manganese precipitation reaction. Therefore, the rate of oxygen transfer and the rate of sulfur dioxide transfer could be described by assuming that no reaction was taking place in solution and that physical dissolution alone described the rate at which oxygen and sulfur dioxide were absorbed by the solution.

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1. INTRODUCTION

Manganese is often an unwanted constituent of leach solutions in hydrometallurgical circuits. The manganese is leached along with the metals of interest, for example cobalt and nickel, and has to be rejected from the circuit before the cobalt and nickel can be electrowon. Once the manganese reports to the electrolytes from which nickel or cobalt are electrowon, the manganese is oxidised at the anodes into a species (most probably Mn^{3+} or Mn^{4+}) that readily attacks the organic phase upon its return to the solvent-extraction circuit as part of the spent (or stripped) electrolyte.

When processing zinc ores, a certain level of manganese is tolerated, or even preferred, in the zinc electrolyte. The manganese in the zinc electrolyte is oxidised into a manganese oxide which coats the anodes and protects them from corrosion. However, the manganese concentration still needs to be controlled in the zinc electrolyte if the rate at which the manganese deposits onto the anodes is less than the rate at which the manganese enters the electrolyte. An example of a zinc ore body of which manganese is a significant constituent is the Gamsberg zinc deposit in South Africa. The manganese is such a significant part of the ore body that this ore will only be suitable for hydrometallurgical treatment if the method for removing the manganese from the circuit is effective and very selective for manganese over zinc.

The control of manganese concentrations in hydrometallurgical circuits, be it laterite processing or treatment of zinc ores, has proven to be difficult. Manganese does not readily precipitate out of solution using the standard method that is used for iron removal, namely goethite precipitation. In this process the iron is precipitated by sparging the leach solution with oxygen or air at elevated temperatures while controlling the pH with lime or limestone. The soluble manganese is largely unaffected in the pH range where the iron is normally precipitated (typically at pH values below 4). Figure 1-1 illustrates that it is possible to precipitate the manganese by using oxygen although the kinetics for doing so is very slow.

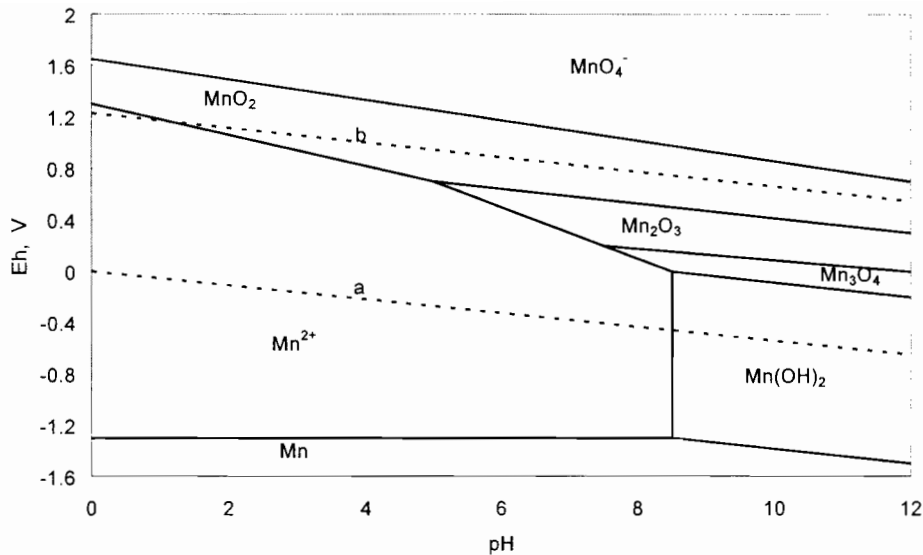


Figure 1-1: Eh – pH diagram of the Mn – H₂O system for 0.01M Mn(II) and 0.1M sulfate. Adapted from Zhang et al. (2002).

An insoluble manganese hydroxide does form at higher pH values (typically at pH values higher than 8), but this hydroxide formation is accompanied by large cobalt and nickel losses. Therefore, any process that removes the manganese from the cobalt-nickel solutions or the zinc solutions needs to accomplish this at pH values below where the cobalt, nickel or zinc would precipitate.

This thesis investigated the use of a sulfur dioxide - oxygen gas mixture to oxidatively precipitate the manganese as some form of manganese oxide. The use of an SO₂/O₂ gas mixture to form a highly oxidative species in solution has been known for decades although the only commercial application of this gas mixture is in the destruction of cyanide in effluent streams. The SO₂/O₂ gas mixture has also been extensively investigated as a means to remove iron from leach solutions, most notably by Krause (1988), Zhang et al. (2000) and Ferron et al. (1991). These authors found the SO₂/O₂ (or SO₂/air) gas mixtures to be much more effective than oxygen or air alone in removing iron from solution. However, there is no agreement in the literature on exactly how the chemical process works to oxidatively precipitate the iron when sparging a reducing gas (SO₂) and oxygen. It is because of this that a complete fundamental rate equation describing the precipitation of iron or manganese from solution has not yet been written in terms of the exact species responsible for the precipitation.

The aim of this thesis was to derive a rate equation to describe the manganese precipitation, not in terms of the actual aqueous species responsible for the oxidation, but in terms of easily measurable parameters identified from the literature as playing a role in the reaction kinetics:

- (i) Gas composition
- (ii) Dissolved sulfur dioxide and oxygen concentrations

- (iii) Temperature of the solution
- (iv) pH of the solution

To derive an empirical rate equation for the manganese precipitation, batch tests were used where one of the above-mentioned parameters was varied at a time. Once the rate equation for the removal of manganese with the gas mixture was obtained from the batch tests, the rate equation was tested on a continuous basis to determine if the rate equation holds for continuous reactors as well.

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2. LITERATURE REVIEW

2.1 Overview of the Manganese Problem in Hydrometallurgical Circuits

Manganese is an unwanted cation in leach solutions, especially when processing laterites. The soluble manganese (Mn^{2+}) needs to be removed from the solution prior to the electrowinning of the cobalt or nickel. If the manganese does report to the loaded electrolyte that enters the tank house, the manganese will be oxidised at the anodes into a higher valence state (Mn^{3+} or Mn^{4+}). These highly reactive manganese species will degrade the organic phase when the spent electrolyte returns to the solvent-extraction circuit (Cheng et al. (2000)). This manifests itself in slow phase-separating times and third phase formation in the solvent extraction circuit.

When processing zinc ores, a certain level of manganese is preferred in the zinc electrolyte for corrosion protection of the lead anodes. Manganese concentrations of approximately 5 g/l are common in zinc electrolytes to form a sufficient layer of manganese dioxide (MnO_2) on the anodes. However, there still needs to be some additional form of manganese removal from the zinc circuit to control the build-up of manganese in the zinc electrolyte if the rate of manganese precipitation on the lead anodes is insufficient.

The manganese in leach solutions cannot be controlled by using the same method of removing iron from leach solutions. As shown in figure 2-1, which was adapted from Zhang et al. (2002), the manganese does not respond to the method of sparging the solution with oxygen even while keeping the solution at a high pH and temperature.

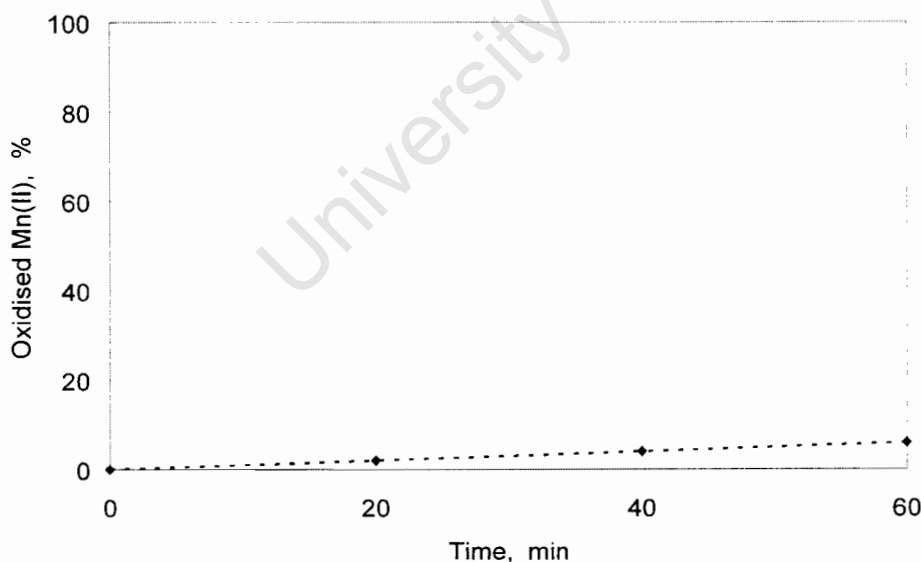


Figure 2-1: The inability of oxygen alone to precipitate manganese from a 0.1 M manganese(II) solution at 80 °C and at pH 6.0. Taken from Zhang et al. (2002).

Due to the slow reaction kinetics of the manganese precipitation with oxygen, numerous other methods have been developed to precipitate the manganese from leach solutions. These methods are discussed in the following section.

2.2 Existing Methods for Removing Manganese from Solutions

For the removal of manganese from solution by precipitation, there are patented technologies that use very strong oxidising agents such as ozone (Sherritt Gordon Mines Limited, 1983), ammonium persulfate (Newmont Exploration Limited, 1978) and Caro's acid (Hudson Bay Mining and Smelting Company, 1957). The drawbacks of these processes are the cost of the oxidising agents and the lack of selectivity of the oxidising agents for manganese over cobalt and nickel.

Mwema et al. (2002) investigated the use of air and sodium metabisulfite to oxidatively precipitate manganese from solution. Large amounts of cobalt (>10 %) were seen to co-precipitate with the manganese when conditions led to more than 90 % of the manganese being oxidised.

Other reagents which have been investigated for manganese precipitation include potassium perdisulfate (Nathsarma and Bhaskara Sarma (1987)) and sodium hypochlorite (Fonseca et al. (1990)). The use of potassium perdisulfate to precipitate the manganese had associated cobalt losses of as high as 27 %, while the sodium hypochlorite was used to simultaneously precipitate both cobalt and manganese from zinc solutions.

Sulfide precipitation (precipitating metals by sparging the solution with H_2S) has also been proposed to separate manganese from nickel and cobalt. In this instance the cobalt and nickel sulfides are thermodynamically more stable than the manganese sulfide, and thus the aim is to selectively precipitate the nickel and cobalt while leaving the manganese in the leach solution. This has the drawback of having to re-leach the valuable metals out of the formed sulfides.

Electro oxidation of manganese in electrowinning cells is another option for taking manganese out of hydrometallurgical circuits (Rodrigues and Dry (1990)). In this method, the manganous ion in solution is oxidised during electrowinning at the anodes into manganese dioxide (MnO_2). This process is the same as what occurs during zinc electrowinning as was discussed earlier, and this MnO_2 deposited onto the anodes is desirable as a form of corrosion protection. The MnO_2 might even be of economical value if the purity of the oxide is high enough. However, when using this method of removing manganese from the circuit it must be remembered that there will be soluble manganese present in the electrolyte which is returned to the solvent-extraction circuit if present. This is what makes this process unviable if there is a cobalt/nickel solvent-extraction circuit using Cytec's Cyanex 272 as the organic extractant (the most common organic extractant used in cobalt and nickel circuits). The higher valence manganese (Mn^{3+} or Mn^{4+}) attacks and degrades this organic extractant.

Solvent extraction has become an integral part of cobalt, copper and nickel processing, and has even found application for processing zinc ores such as the Skorpion zinc operation in Namibia. Unfortunately the extractant most commonly used for cobalt and nickel extraction is Cyanex 272 which is not very selective for cobalt over manganese. Thus, this is not a good extractant to use for the separation of manganese from cobalt, although it can be used to separate cobalt and manganese from nickel.

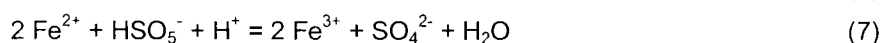
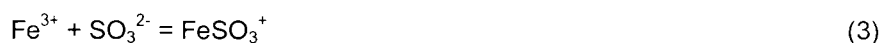
Zinc solvent extraction commonly uses di(2-ethylhexyl) phosphoric acid (DEHPA) as the extractant for zinc. DEHPA shows very good selectivity for zinc over manganese, although some manganese is extracted to eventually form the MnO_2 on the anodes during electrowinning of the zinc. Thus, although the zinc solvent-extraction process using DEHPA is successful in separating the manganese from the zinc, the manganese stays in the circuit because the raffinate from the solvent-extraction circuit normally has to be recycled to the leach circuit to close the water balance. This will cause the concentration of manganese in the leach solution to invariably increase to a point where it has to be removed.

2.3 Using a Gas Mixture of Sulfur Dioxide and Oxygen to Remove Manganese

An inexpensive technique to remove manganese from solution is the method of sparging the solution with a gas mixture of sulfur dioxide and oxygen. This technology has been patented for the removal of manganese from zinc solutions by Mintek (2003). Most of the literature available today concerns using the SO_2/O_2 gas mixture to remove iron from solution. However, the mechanisms and the influence of the operating parameters on manganese removal using the SO_2/O_2 gas mixture appear to be similar to those of removing iron with the gas mixture. Therefore, in the following sections the literature on iron removal with the gas mixture is used extensively to discuss manganese removal.

2.3.1 Proposed Mechanisms by which SO_2/O_2 Gas Mixtures Remove Iron from Solution

Sulfur dioxide is a reducing agent and is normally not suitable for use as an oxidant. However, when sulfur dioxide is diluted with air or oxygen and sparged into a solution containing manganese or iron, a highly oxidising aqueous species is formed that is responsible for the oxidation of the manganese or iron. Many researchers have speculated as to what this species is. The most recent work on the subject was that of Zhang et al. (2000) where a complicated mechanism was proposed whereby the SO_2/O_2 gas mixture oxidises soluble iron by forming peroxomonosulfate ($SO_5^{\cdot-}$) through the following steps:



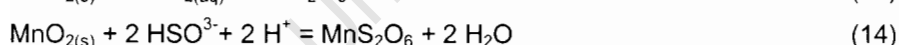
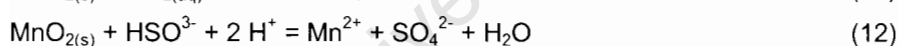


The evidence put forward for the existence of the $\text{SO}_5^{\cdot-}$ free radical was the high solution potential measured and the influence of hydroquinone on the rate of iron precipitation. Hydroquinone is a known free radical scavenger, and by the addition of hydroquinone the rate of iron precipitation decreased in the test work of Zhang et al. (2000). Berglund et al. (1994) also reported the oxidation of manganese(II) to manganese(III) by the $\text{SO}_5^{\cdot-}$ free radical.

Ferron et al. (1991) speculated on reactive intermediates such as HO_2^{\cdot} , OH^{\cdot} and HSO_3^{\cdot} being responsible for the oxidation of iron when using the SO_2/O_2 gas mixture. Whatever the true mechanism might be, the overall reaction for the precipitation of manganese or iron by the gas mixture appears to be described by the following two reactions (9) and (10):



The manganese precipitates as an oxide (MnO_2 , Mn_2O_3 or Mn_3O_4 depending on the pH), while the iron normally precipitates as a goethite. Competing with the above two reactions (9 and 10) is the reduction of the formed precipitates by aqueous sulfur dioxide. In the case of the manganese dioxide, Abbruzzese (1990) postulated that the MnO_2 could either be reduced to manganous sulfate at low pH values according to reactions (11) and (12), or to manganous dithionate at more neutral pH values according to reactions (13) and (14). These back reactions become more pronounced when using gas mixtures rich in sulfur dioxide.



The operating parameters such as the gas composition, temperature, pH, etc., will affect both the precipitation reactions and the dissolution reactions, affecting the resulting rate of manganese precipitation. From the literature the following operating parameters were identified as influencing the rate at which the manganese is precipitated from solution:

- (i) Gas composition
- (ii) Dissolved sulfur dioxide and oxygen concentrations
- (iii) Temperature of the solution
- (iv) pH of the solution

2.3.2 The Influence of the Gas Composition on the Rate of Manganese Precipitation

The gas composition of the SO_2/O_2 mixture has an indirect influence on the rate of manganese precipitation. The gas mixture does not directly precipitate the manganese, but rather an unknown chemical species (probably peroxomonosulfate) formed from the dissolved oxygen and dissolved sulfur dioxide is responsible for the oxidation. Therefore, the formation of the active oxidising species will depend not only on the gas composition but also on the mass transfer of the oxygen and the sulfur dioxide from the gas phase into the solution since sulfur dioxide is more soluble than oxygen in water. For example, using the same gas mixture in a reactor with poor gas mass transfer will result in a lower rate of manganese precipitation. But, if the mass transfer in the reactor is very good, then the influence of the gas composition alone on the rate of manganese precipitation can be shown as in figure 2-2, taken from Zhang et al. (2002).

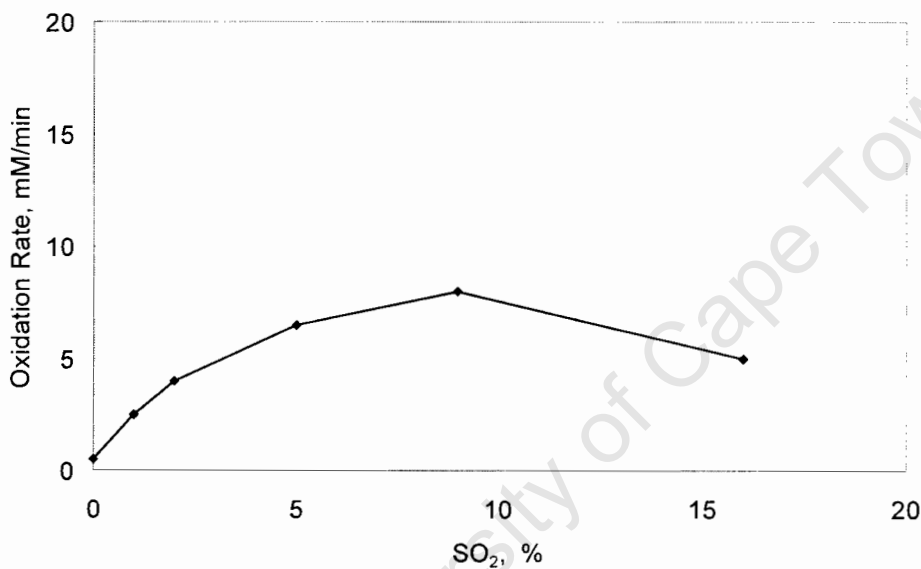


Figure 2-2: The influence of the gas composition on the rate of manganese precipitation (0.1 M manganese; pH 6.0 and 80 °C). Adapted from Zhang et al. (2002).

The rate of manganese precipitation increases with an increase in the SO_2 content of the gas mixture, up to some optimum value (approx. 10 % SO_2 in O_2). If the SO_2 in the gas mixture exceeds this optimum value, the rate of manganese removal decreases due to the back reactions of the dissolved sulfur dioxide with the manganese dioxide.

2.3.3 The Influence of the Dissolved Sulfur Dioxide and Oxygen Concentrations on the Rate of Manganese Precipitation

Krause (1988) postulated that it is not the actual gas mixture that controls the rate of manganese removal, but the dissolved species from the gas, i.e., the dissolved oxygen and the dissolved sulfur dioxide species. Since sulfur dioxide is orders of magnitude more soluble than oxygen, the dissolved oxygen concentration needs to be kept as high as possible for the system to remain oxidising. Therefore, a reactor with a high gas mass-transfer capability needs to be used for this technology. The effect of the agitation speed (i.e.,

mass transfer of the gas into the solution) on the rate of iron removal with the gas mixture is illustrated in figure 2-3, taken from Tiwari et al. (1979).

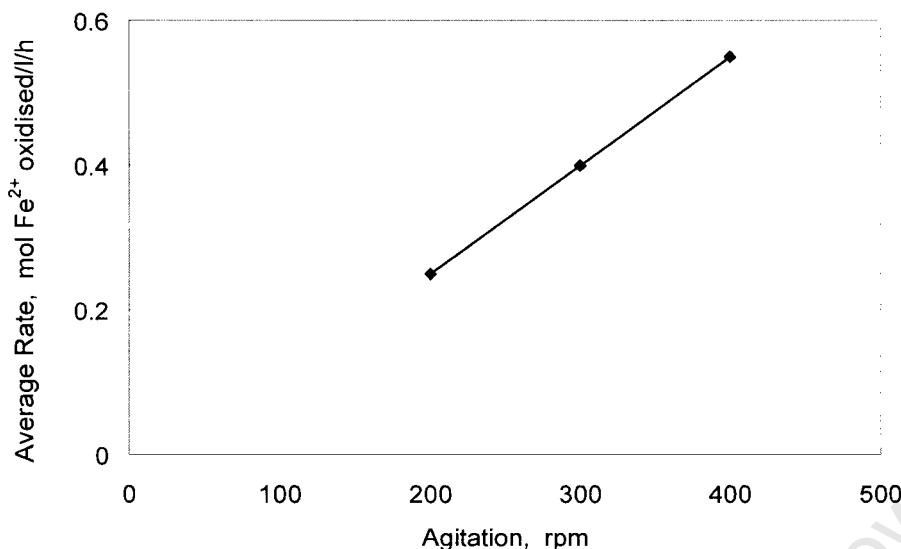


Figure 2-3: The influence of agitation on the removal rate of iron using a gas mixture of sulfur dioxide and oxygen (72 °C; 314 ml/min gas flow of which 8.2 % was SO₂). Adapted from Tiwari et al. (1979).

Figure 2-3 illustrates that if the mass-transfer conditions of the system become less favourable, the dissolved oxygen is most affected due to the large solubility of the sulfur dioxide. This once again shows that the rate of the manganese precipitation is not described by the gas composition alone, but also by the dissolved gas concentrations of the sulfur dioxide and oxygen in solution.

When the influence of temperature is discussed later, it can be seen that at too high a temperature, the rate of iron precipitation (and probably also the manganese precipitation) decreases, most probably due to the lower oxygen solubility.

2.3.4 The Influence of Temperature

The iron (and probably the manganese) removal rate increases with an increase in temperature, but as was the case for the sulfur dioxide in the gas mixture, the rate decreases when the temperature exceeds some optimum value, as was found by Zhang et al. (2000) for the precipitation of iron. This could be due to either or both of the following:

- i. At very high temperatures (>80 °C) an increase in the solution temperature enhances the dissolution reaction of the formed goethite (or manganese dioxide) by dissolved sulfur dioxide, more than it enhances the rate of precipitation;
- ii. An increase in temperature decreases the oxygen solubility of the solution, resulting in a more reducing system and hence a lower rate of precipitation.

Figure 2-4, adapted from the Arrhenius plots of Zhang et al. (2002 and 2000), shows the effect of temperature on the rate of manganese and iron removal. A decrease in the rate of manganese removal is expected at temperatures higher than 80 °C as was the case for the iron removal. It should also be noted that were the manganese removal and the iron removal conducted at the same pH and in the same reactor, the iron would be precipitated before the manganese.

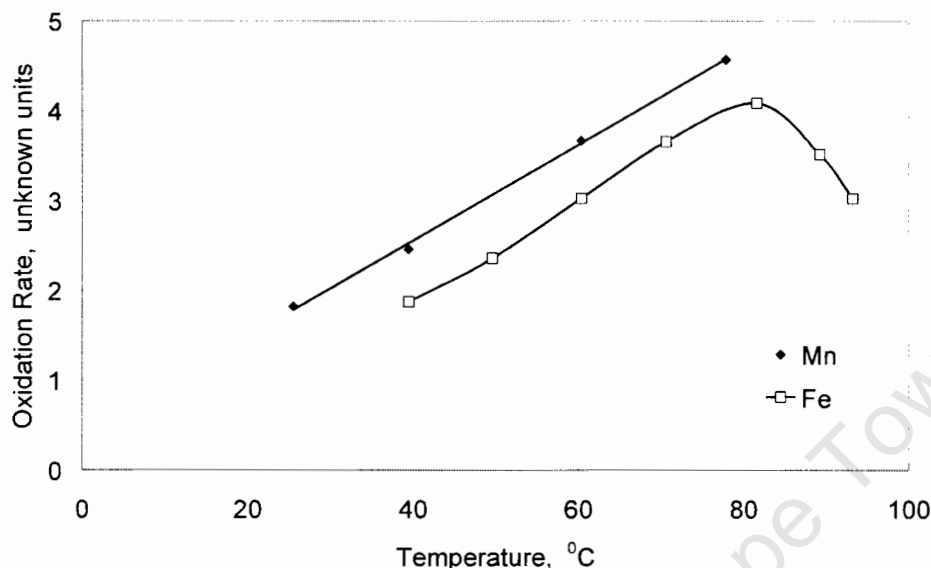


Figure 2-4: The influence of temperature on the rate of manganese and iron precipitation. (Manganese test at 0.1 M Mn(II); 2.0 % SO₂ and at pH 6.0) and (Iron test at 0.1 M Fe(II); 2.0 % SO₂ and pH 1.0). Adapted from Zhang et al. (2000 and 2002).

2.3.5 The Influence of pH

The rate at which a gas mixture of sulfur dioxide and oxygen removes iron or manganese from solution increases with an increase in pH. As can be seen from figure 2-5, which was adapted from Zhang et al. (2002 and 2000), the manganese precipitation only becomes pronounced above a pH of 3. This indicates the lower limit of the pH range in which the manganese can be precipitated from solution. It was also found by Zhang et al. (2002) that the gas mixture would start to oxidatively precipitate cobalt at a pH greater than 4.0, while nickel would start to precipitate above pH 6.5. Thus, there exists a window in the pH scale in which manganese can be selectively removed from cobalt and nickel solutions using the gas mixture.

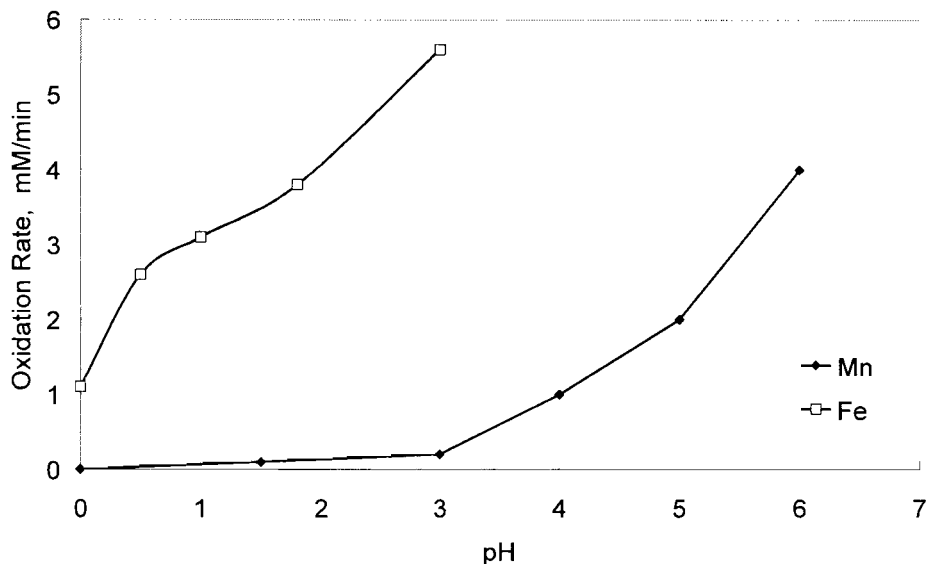


Figure 2-5: The influence of pH on the rate at which a gas mixture of sulfur dioxide and oxygen precipitates manganese and iron from solution. (Manganese test at 0.1 M Mn(II); 2.0 % SO₂ and at 80 °C) and (Iron test at 0.1 M Fe(II); 2.0 % SO₂ and at 80 °C). Adapted from Zhang et al. (2002 and 2000).

2.3.6 The Influence of Manganese Concentration

The effect of the ferrous ion concentration on the rate of iron precipitation with the SO₂/O₂ gas mixture was found to be insignificant in the test conditions studied by Zhang et al. (2000) (0.1 to 0.5 M Fe(II)). The ferric ion was seen to play a role in the initial rate of reaction, the rate being first order in relation to the ferric concentration up to 0.2 M Fe(III). Above this concentration of ferric ions, the rate of ferrous oxidation was unaffected by the ferric concentration.

2.4 Key Points from the Literature and the Aims of this Thesis

- (i) Manganese can be successfully removed from solution as a manganese oxide by using a gas mixture of SO₂/O₂.
- (ii) There is no conformity in the literature on the exact mechanism by which this gas mixture oxidises iron or manganese.
- (iii) The rate at which manganese precipitates is influenced by the following operating parameters:
 - (a) Gas composition
 - (b) Dissolved sulfur dioxide and oxygen concentrations
 - (c) Temperature of the solution
 - (d) pH of the solution

It was the aim of this thesis to derive a purely empirical rate equation that could describe the rate of manganese removal in terms of the easily measurable operating parameters, and not in terms of the exact chemical species (free radical) responsible for the manganese oxidation. To accomplish this, batch tests

were conducted by varying one of the above-mentioned operating parameters at a time while keeping the other operating parameters constant **or** by ensuring that the operating parameter change was equal for all of the batch tests. (This is applicable to the dissolved sulfur dioxide concentration which increased in the solution throughout each of the batch tests). In this manner a rate equation could be constructed one term at a time.

Once the rate equation was derived from the batch tests, it was used in the mass balance over a continuous reactor to determine if the equation still holds. The difference between a batch test and a continuous test is that the dissolved sulfur dioxide cannot be kept constant through the batch tests (the dissolved sulfur dioxide concentration will increase with time due to the high solubility of SO_2 in water), while the dissolved sulfur dioxide concentration will stabilise once steady state is achieved in a continuous reactor.

University of Cape Town

3. EXPERIMENTAL EQUIPMENT AND METHODS

3.1 The Experimental Equipment

A schematic representation of the experimental set-up appears in figure 3-1. This figure lists all of the equipment that was used for both the batch and the continuous testwork. A photograph of the experimental set-up is shown in figure 3-2.

The gas flow equipment consisted of two Bronkhorst flow meters, a type F-201C for the oxygen, and a type F-201D for the sulfur dioxide. The oxygen flow meter could deliver flows of up to 5000 ml/min, while the sulfur dioxide flow meter could deliver flows of up to 100 ml/min. The oxygen was mixed with the sulfur dioxide in a dispersion chamber prior to the gas mixture entering the reactor by means of a glass fritted sparge tube. A picture of the gas flow set-up can be seen in figure 3-3.

The reactor had a working volume of 3 litres and this varied slightly with the speed of agitation for the continuous tests (the solution left the reactor via an overflow port). The glass reactor had a water jacket for temperature control, and internal glass baffles to ensure that the flow of solution inside the reactor was as turbulent as possible to promote good gas mass transfer.

The agitation system consisted of a type A315 titanium impeller fitted onto a titanium shaft, with a polypropylene inductor situated just above the type A315 impeller. The type A315 impeller was used for its ability to keep gas bubbles from rising to the surface of the solution, while the high shear inductor was used to promote good gas dispersion. The high torque induced by the inductor and the required speed of agitation necessitated that a high powered motor with a variable speed drive be used to stir the contents of the reactor. An impeller speed of 800 rpm was used in the tests where the manganese was precipitated with the gas mixture.

A glass valve situated halfway up the side of the reactor was used to take kinetic samples during the tests. Two samples were taken at each time interval, one for manganese analysis and another sample for the total sulfur content of the solution. The samples taken for manganese analysis were acidified and sparged with nitrogen immediately after being taken from the reactor, while hydrogen peroxide was added to the samples taken for total sulfur analysis. By acidifying the samples taken for manganese analysis, further manganese precipitation inside the sample bottles was prevented. The hydrogen peroxide added to the samples taken for total sulfur analysis reacted with the sulfur dioxide to form sulfate (this was done to prevent the sulfur dioxide from diffusing out of the samples).

During the continuous tests where a solution of manganous sulfate was pumped into the reactor, an overflow port was used in order for the solution to flow out of the reactor at a rate equal to the solution

entering the reactor. The flow rate of the manganous sulfate was measured by following the rise of solution in the graduated overflow container.

Measurements recorded during each test included the solution potential, pH, dissolved oxygen concentration and the solution temperature. A Hamilton HT120 gel pH electrode was linked to a Mettler and Toledo autotitrator which kept the solution pH inside the reactor constant via the addition of a sodium hydroxide solution (see the data tables in the appendix for the concentrations used). The autotitrator recorded the consumption of the sodium hydroxide while temperature compensation of the pH was done automatically through the use of a temperature sensor which was also linked to the autotitrator.

The solution potential was measured using a silver/silver chloride gel electrode (the Hamilton Oxytrode gel electrode), while the dissolved oxygen concentration of the solution was measured using a Mettler and Toledo dissolved-oxygen sensor. The dissolved-oxygen sensor's working range was up to 60 °C and this limited the temperature range of the experiments.

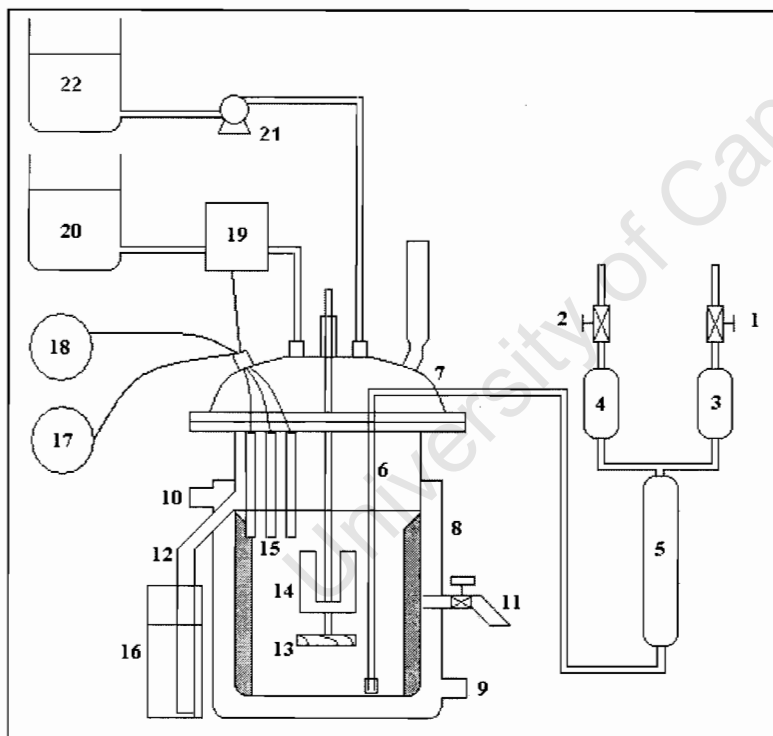


Figure 3-1: The experimental set-up for the batch and continuous tests

- 1 Sulfur dioxide flow control valve
- 2 Oxygen flow control valve
- 3 Flow meter for sulfur dioxide
- 4 Flow meter for oxygen
- 5 Gas dispersion chamber
- 6 Glass sparge tube with frit
- 7 Polypropylene reactor lid
- 8 Water-jacketed glass reactor with glass baffles
- 9 Water-jacket inlet for temperature control

- 10 Water-jacket outlet for temperature control
- 11 Sample port with glass valve
- 12 Slurry over-flow port used during the continuous tests
- 13 Titanium type A315 impeller fitted to a titanium shaft
- 14 Polypropylene inductor
- 15 Eh, pH, temperature and dissolved oxygen probes
- 16 Graduated solution overflow container used during the continuous tests
- 17 Eh meter
- 18 Dissolved oxygen meter
- 19 Autotitrator
- 20 Sodium hydroxide solution for pH control
- 21 Peristaltic pump for the manganous sulfate addition during the continuous tests
- 22 Manganous sulfate solution used during the continuous tests

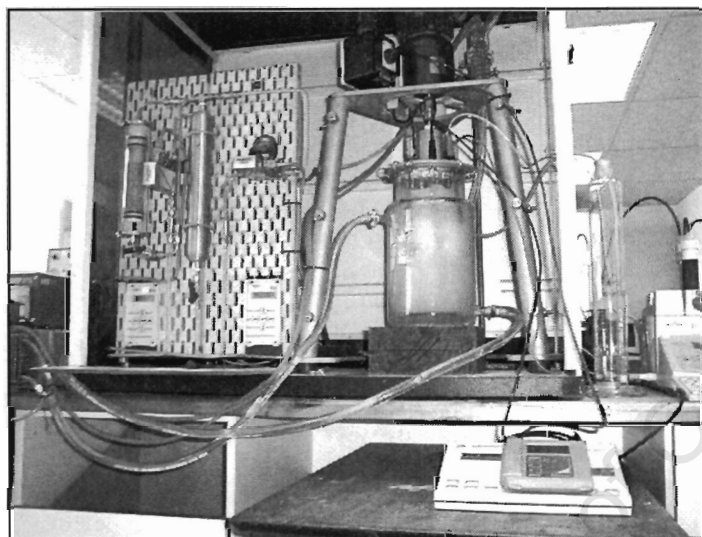


Figure 3-2: The experimental equipment from right to left: Autotitrator; Eh and dissolved oxygen meter; overhead stirrer and reactor; gas flow equipment; peristaltic pumps; and water bath behind pumps (not shown).



Figure 3-3: The gas flow set-up used to introduce the gas mixture of sulfur dioxide and oxygen. Peristaltic pumps and a water bath are situated to the left of the gas flow equipment.

Calibration of the oxygen flow meter was done by displacing a known volume of water from a submerged volumetric flask with oxygen. The same method was used to calibrate the sulfur dioxide flow meter although a different gas had to be used because of the high solubility of sulfur dioxide in water. Nitrogen was used to calibrate the sulfur dioxide flow meter, after which a conversion factor was used to translate the nitrogen flow rate into a sulfur dioxide flow rate. This conversion factor was calculated using the Fluidat® programme supplied by Bronkhorst Hi Tec.

3.2 The Experimental Flowchart and Method Used in Deriving an Empirical Rate Equation

A flow chart of the experimental work conducted for this thesis is given in figure 3-4. The empirical rate equation for the removal of the manganese was derived by performing batch tests varying the operating parameters identified as playing a role in the rate at which the gas mixture could precipitate the manganese. These included the gas composition; dissolved oxygen concentration; dissolved sulfur concentration attributed to the gas dissolution; manganese concentration; temperature and pH. To investigate the influence of one of the operating parameters on the rate at which the SO₂/O₂ gas mixture removed manganese from solution, one operating parameter was varied at a time. For this purpose, the base case test conditions were chosen to be:

Gas flow composition:	6 % SO ₂ in O ₂
Oxygen flow rate:	470 ml/min
Sulfur dioxide flow rate:	30 ml/min
Agitation speed:	800rpm
Solution volume:	3000 ml
Solution temperature:	30 °C
Solution pH:	4.0
Initial [Mn]:	1.5 g/l (added as manganous sulfate)

It should be noted that two of the above operating parameters are linked, namely the solution temperature and the dissolved oxygen concentration. As the temperature increases, the dissolved oxygen concentration will decrease. Table 3-1 lists the range of the operating parameters tested to derive the rate equation.

Table 3-1: The ranges for the operating parameters investigated to derive the rate equation

Gas composition*	3 % SO ₂ to 20 % SO ₂ in oxygen
Manganese concentration**	4.0 g/l to 250 mg/l Mn(II)
Temperature	20 °C to 50 °C
pH	3.5 to 6.0
Dissolved oxygen concentration	4 mg/l to 30 mg/l

**The overall gas flow rate was kept constant at 500 ml/min but the ratio of sulfur dioxide to oxygen was varied.*

*** The effect of introducing Mn^{3+} on the rate of removal was not investigated although it is expected to dictate the induction period before precipitation begins.*

Once the rate equation was derived from the batch data, the equation was tested on a continuous basis. The steady-state mass balance for manganese over a one-stage continuous reactor is described by the following reaction (15):

$$Mn_{in} = Mn_{ppt} + Mn_{out} \quad (15)$$

with Mn_{in} being the mass of soluble Mn entering the reactor

Mn_{ppt} being the mass of Mn precipitated

Mn_{out} being the mass of soluble Mn leaving the reactor

A solution of known manganese concentration was pumped with a peristaltic pump at a constant flow rate into the reactor (therefore Mn_{in} was known). Using the derived rate equation for the removal rate of manganese, Mn_{ppt} was calculated. Therefore, the Mn_{out} was calculated using equation (15) and compared with the actual Mn_{out} determined from samples taken from the reactor and the flow rate of the solution out of the reactor.

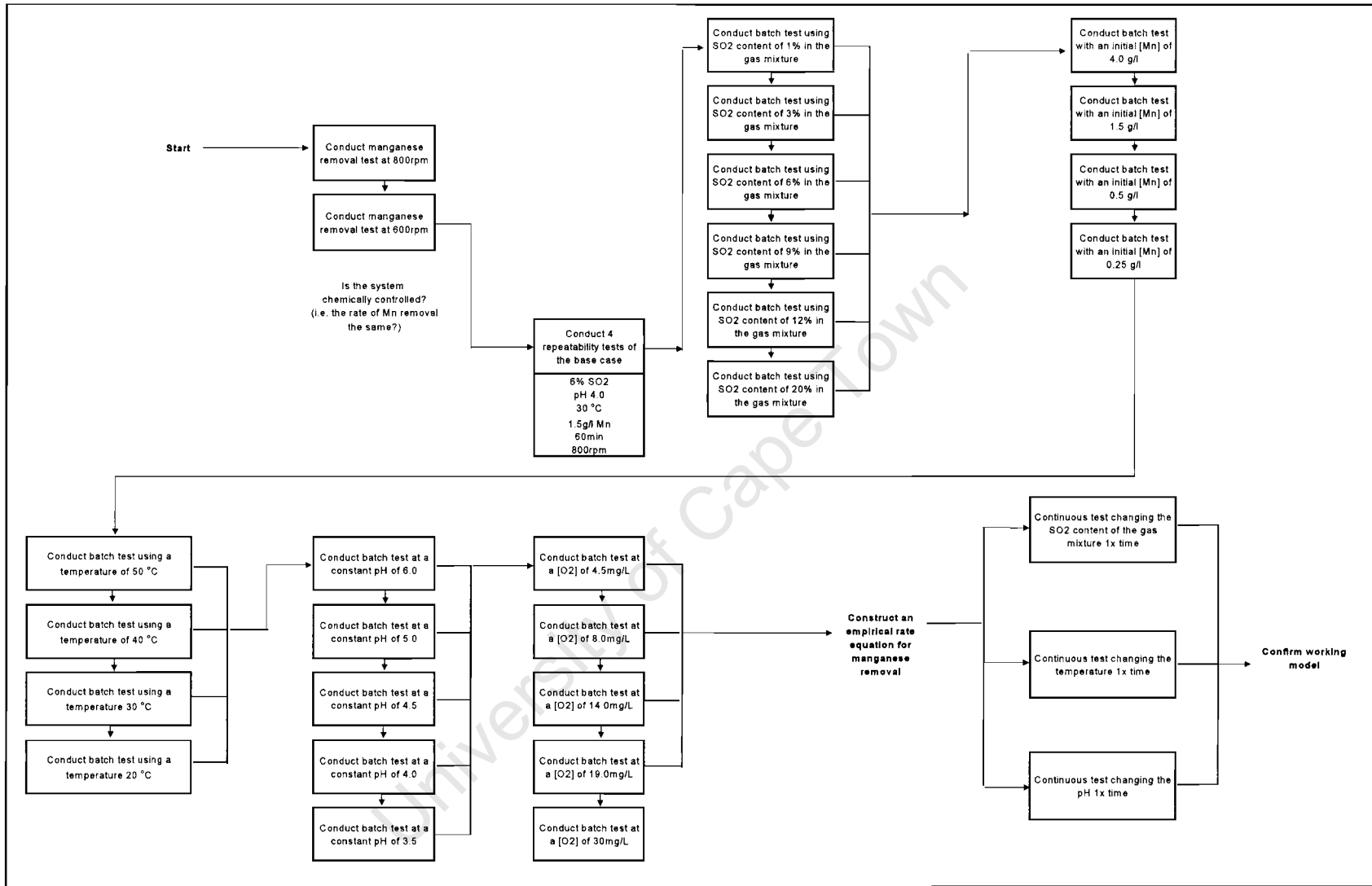


Figure 3-4: A flowchart of the experimental work to derive an empirical rate equation for the precipitation of manganese with SO_2/O_2 .

4. RESULTS AND DISCUSSION OF THE TEST WORK

4.1 The Repeatability of the Manganese Removal Experiments

The following conditions were chosen as the base case test for the batch precipitation tests:

Gas flow composition:	6 % SO ₂ in O ₂
Oxygen flow rate:	470 ml/min
Sulfur dioxide flow rate:	30 ml/min
Agitation speed:	800 rpm
Solution volume:	3000 ml
Solution temperature:	30 °C
Solution pH:	4.0
[Mn] as manganous sulfate:	1.5 g/l

To ensure confidence in the results of the testwork, the base case test was repeated four times to determine the variability of the data. It is clear from figure 4-1 that the test procedure and analyses showed excellent repeatability, the largest variance in the results of figure 4-1 being 3 % (the assays of the samples taken after 20 minutes).

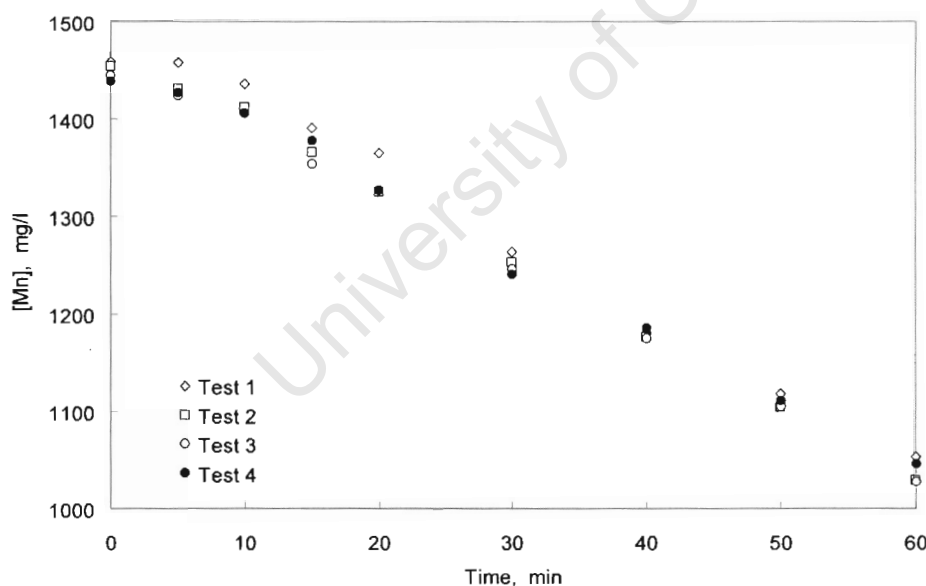


Figure 4-1: The repeatability of the experimental results. The base case test was repeated four times (6 % SO₂ in O₂; pH of 4.0; 30 °C; [Mn] of 1.5 g/l and 800 rpm).

4.2 Ensuring that the Manganese Removal is not Controlled by Transfer of the Gas into Solution

To ensure that the oxygen and sulfur dioxide transfer from the gas phase into solution were at their maximum rate and would therefore not be variables in the batch tests, precipitation tests at different

impeller speeds were conducted. From figure 4-2 it is clear that the uptake rate of sulfur dioxide and the rate of manganese precipitation were independent of the stirring rate. This means that the rate equation that was derived from the batch tests will not be specific only to the reactor used in these tests.

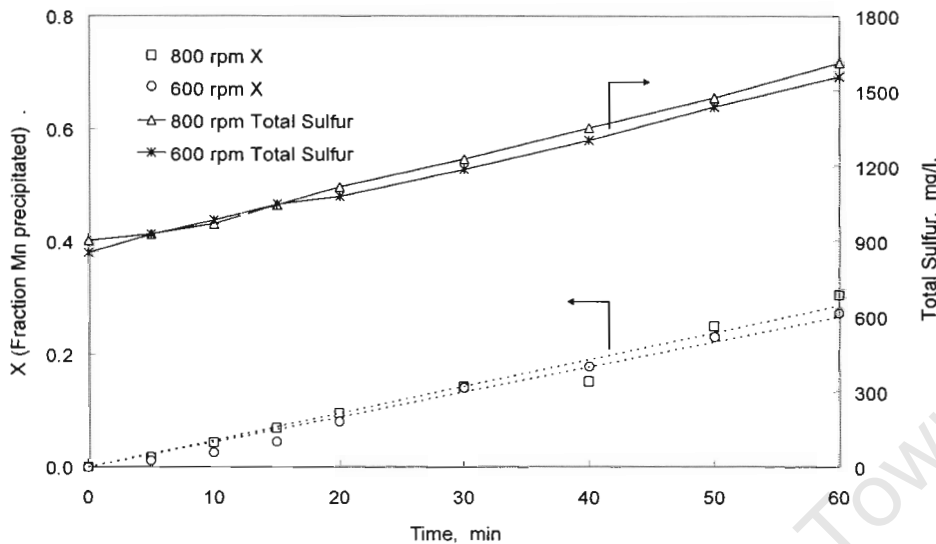


Figure 4-2: Graph showing the independence of the rate of manganese removal on the rate of agitation (6 % SO₂ in O₂; overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C; [Mn] of 1.5 g/l).

4.3 Deriving the Empirical Rate Equation from Batch Tests

Each of the operating parameters identified from the literature as having an influence on the rate of manganese removal was investigated separately in this section. The base case test conditions were used except for the operating parameter being investigated. Therefore, for each operating parameter a rate equation could be written as:

$$d[\text{Mn}]/dt = \text{Constant} \times f(\text{operating parameter}) \quad (16)$$

After all of the operating parameters had been investigated and rate equations such as equation (16) had been derived from the batch data, an overall rate equation could be written by combining the individual rate equations derived for each operating parameter and then calculating one rate constant.

4.3.1 Deriving an Empirical Rate Equation in Terms of Sulfur Dioxide

As was discussed earlier, the gas mixture is not expected to directly oxidise the manganese in solution. However, the gas composition will dictate the levels of dissolved sulfur dioxide and oxygen in the solution and will therefore be important. To be able to include the gas composition in the rate equation, the transfer of the gas into the solution may not be rate limiting. For example, using the same gas composition under very poor mass transfer conditions will result in a lower rate of manganese precipitation due to poor transfer of the gas phase (most probably oxygen transfer due to the high solubility of sulfur dioxide in

water). It has been shown in section 4.2 that the test conditions in this thesis are such that the transfer of the sulfur dioxide and oxygen into the solution should not play a role in the test results.

The influence of the gas composition on the rate of manganese precipitation in the batch tests is shown in figure 4-3. The rate of manganese removal increased with an increase in the sulfur dioxide content of the gas mixture up to 12 % SO₂. A further increase in the SO₂ content of the gas mixture led to a drop in the rate of manganese removal, probably due to the reduction of the product (manganese oxides) by the excess dissolved sulfur dioxide. This is consistent with the findings of Zhang et al. (2002).

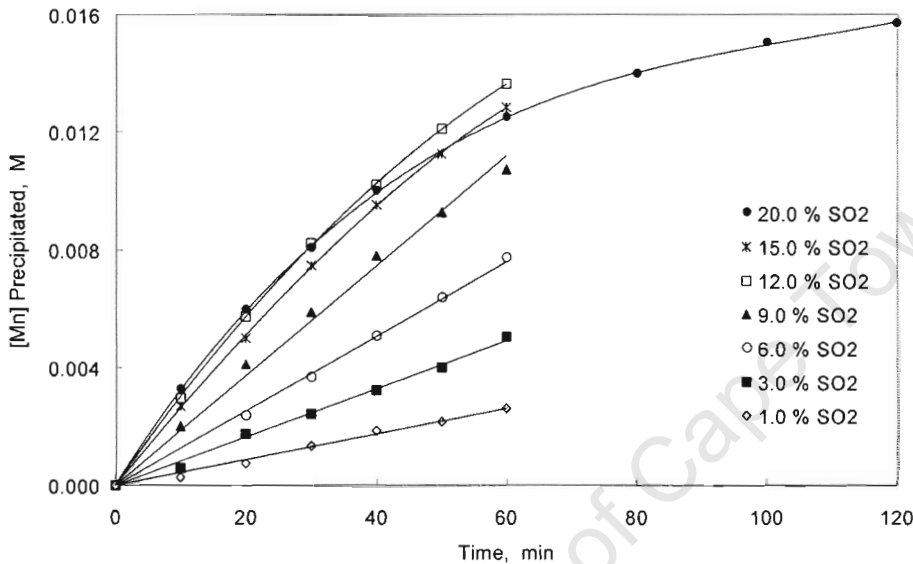


Figure 4-3: The influence of the gas composition on the rate of manganese removal. (Overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C and [Mn] of 1.5 g/l).

Figure 4-4 plots the average removal rate over the first 60 minutes of the batch tests when varying the gas composition. The rate of manganese removal increased linearly with an increase in the SO₂ content of the gas mixture up to 12 % SO₂, whereafter the rate dropped with a further increase in the SO₂ content of the gas mixture. Also shown in figure 4-4 is the total aqueous sulfur after 60 minutes attributed to the dissolution of the gas for each test. It should be noted that the term “[S from gas]” as it is used in this thesis, refers to all of the aqueous forms of sulfur attributed to the dissolution of the gas. Thus, “[S from gas]” excludes only the sulfur present in the solution at the start of the tests.

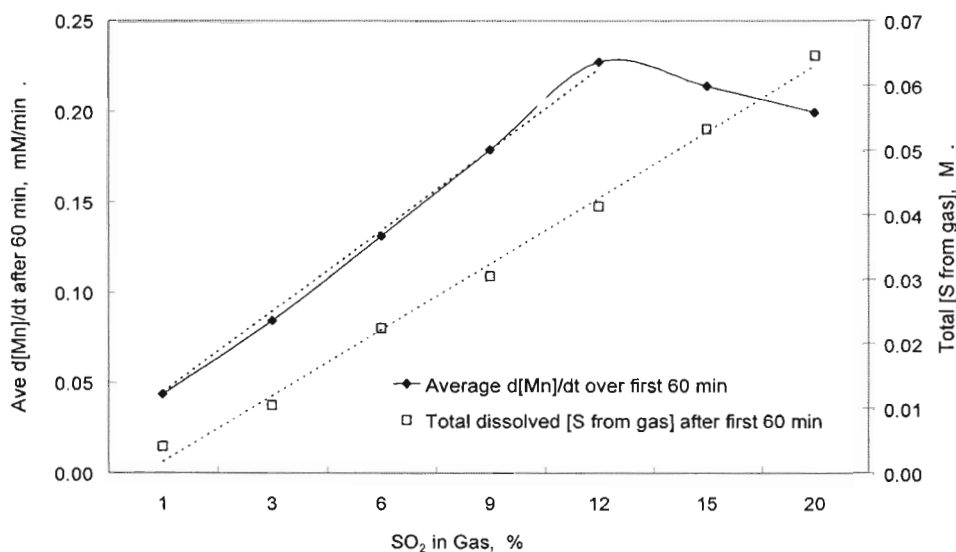


Figure 4-4: The influence of the gas composition on the average rate of manganese removal over the first 60 minutes of the batch tests (Overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C; [Mn] of 1.5 g/l).

As can be seen in figure 4-3, the rate of manganese removal slowly decreased over time as the dissolved sulfur dioxide increased in the solution. This effect was more pronounced in the tests which used a gas mixture rich in SO₂ and can be clearly seen in the test where a gas mixture of 20 % SO₂ was used. Thus, in figure 4-5 it is verified that the rate at which the gas mixture can precipitate the manganese is dependant on the dissolved sulfur attributed to the dissolution of the gas (the rate of manganese removal levelling off as the aqueous sulfur concentration attributed to the gas dissolution increased). This drop in the rate of manganese removal is accurately described by an exponential decay function as shown in figure 4-5.

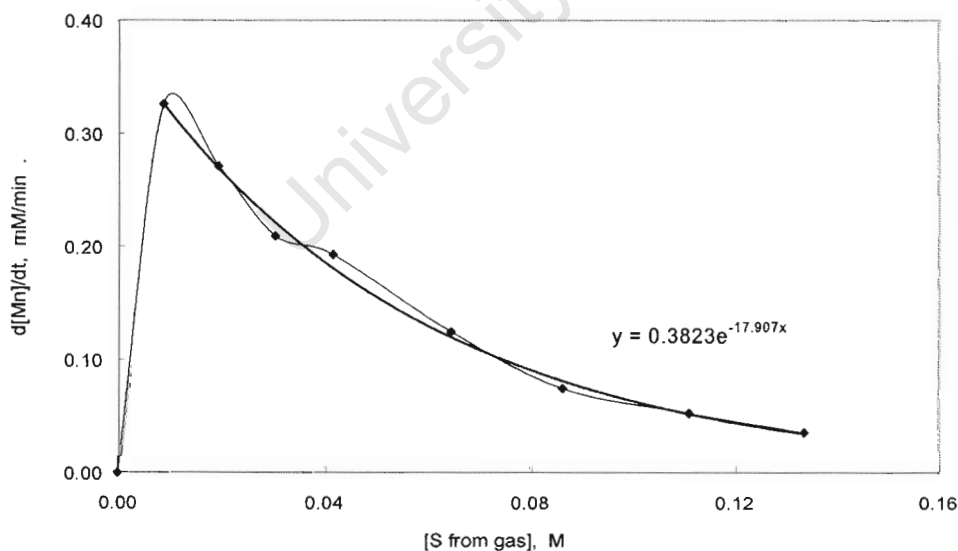


Figure 4-5: The effect of the aqueous sulfur obtained from the gas phase on the rate of manganese removal (using a 20 % SO₂ gas mixture; overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C and [Mn] of 1.5 g/l).

It should be noted that the manganese concentration was also a variable during the batch tests, and it could be argued that the exponential decay in the manganese removal rate noted in figure 4-5 was due to the lower manganese concentration and not due to the build-up of the aqueous sulfur dioxide. However, as will be shown in section 4.3.2, the rate of manganese precipitation was not significantly influenced by a change in the manganese concentration (except at manganese concentrations below 50 mg/l). Therefore, the relationship between “[S from gas]” and the precipitation rate shown in figure 4-5 was not influenced by the decrease in the manganese concentration.

From figure 4-6 it is clear that the rate of manganese removal cannot be described by the aqueous sulfur obtained from the gas phase alone. For example, at a [S from gas] of 0.02 M the rate of manganese removal is approximately double when using a 12 % SO₂ gas mixture as opposed to using a 6 % SO₂ gas mixture (the dissolved oxygen concentration being equal for both tests). A plot of the manganese removal rate versus [S(IV)] also results in graphs that are similar to figure 4-6.

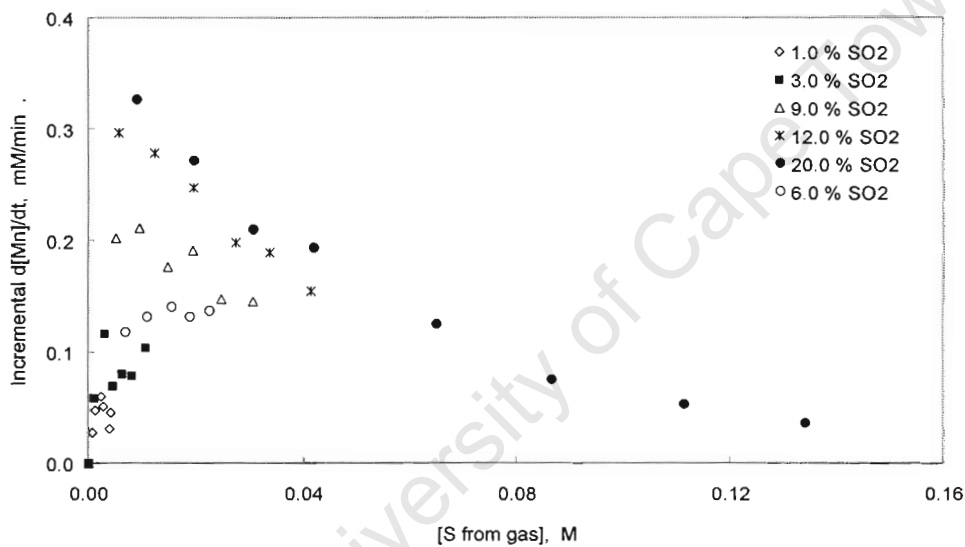


Figure 4-6: The effect of the aqueous sulfur obtained from the gas phase on the rate of manganese removal (using a range of different gas mixtures). (Overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C; [Mn] of 1.5 g/l).

The relationship between the rate of manganese removal and the solution potential is presented in figure 4-7. It is surprising that the manganese removal rate decreased with an increase in the solution potential, although the solution potential was still very high for all of the tests and varied in a narrow operating window (695 to 725 mV versus the Ag/AgCl electrode).

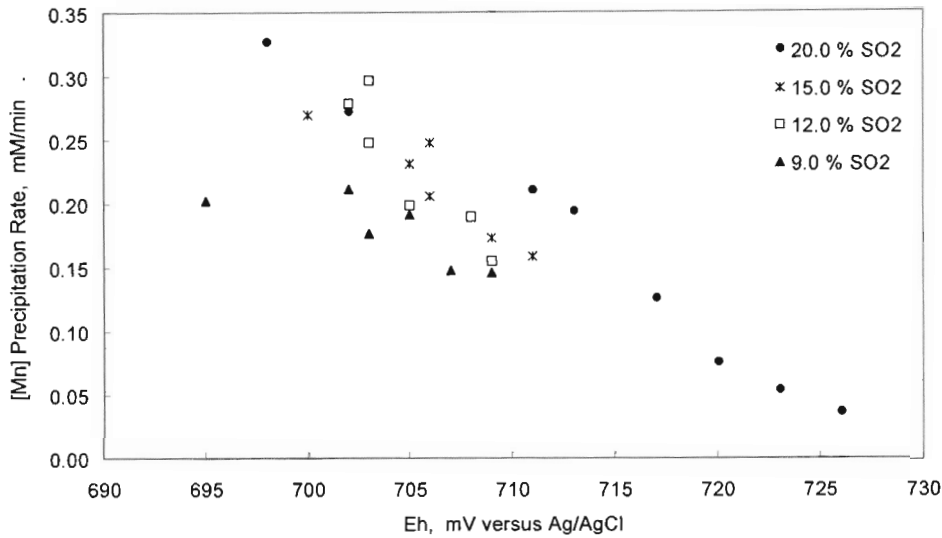


Figure 4-7: The effect of the dissolved sulfur from the gas phase on the solution potential and the subsequent influence on the rate of manganese removal (using a range of different gas mixtures). (Overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C; [Mn] of 1.5 g/l).

The rate of manganese removal can be described by a combination of the gas composition and the sulfur dissolved into the solution from the gas phase. It was hoped that the rate equation could be written in terms of the aqueous sulfur attributed to the dissolution of the gas phase, and not also in terms of the gas composition. However, as seen in figure 4-6, the manganese precipitation rate was not adequately described by the sulfur dissolved into the solution from the gas phase. Using the relationships in figure 4-4 and figure 4-5 a rate equation can be written as:

$$d[\text{Mn}]/dt = \underbrace{\text{Constant}_1 \times (P_{\text{SO}_2}/P_{\text{Total}})}_{\text{A}} \times \underbrace{\exp(-18[\text{S from gas}])}_{\text{B}} \quad (17)$$

with part **A** describing the linear relationship between the rate of manganese precipitation and the SO₂ content of the gas mixture up to 12 % SO₂ (figure 4-4); and part **B** describing the exponential decay in the manganese removal rate with the build-up of the aqueous sulfur in solution (figure 4-5). The term “[S from gas]” refers to the entire uptake of the sulfur dioxide into the solution and excludes only the sulfur present in the solution at the start of the tests (sulfate).

This relationship was plotted for the batch data (figure 4-8) and is seen to be an accurate way to describe the influence of the SO₂ (both in the gas and in solution) on the rate of manganese precipitation.

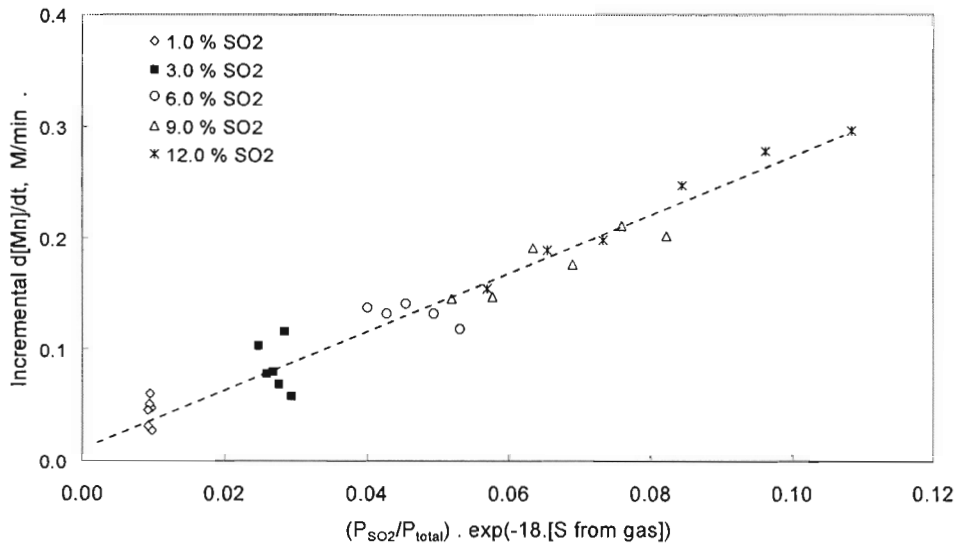


Figure 4-8: The effect of the dissolved sulfur from the gas phase and the gas mixture on the rate of manganese removal.

From the batch tests where the gas mixture was varied, the percentage of aqueous sulfur (obtained from the gas phase) which was used to precipitate manganese, was determined for each test. The assumption was made that one mole of sulfur dioxide was needed to precipitate one mole of manganese as per equation (9). The consumption of the dissolved sulfur dioxide as a percentage of the total sulfur in solution obtained from the gas phase is shown in figure 4-9. It is clear from figure 4-9 that as the sulfur dioxide content of the gas mixture increased, the utilisation of the sulfur dioxide to precipitate manganese decreased.

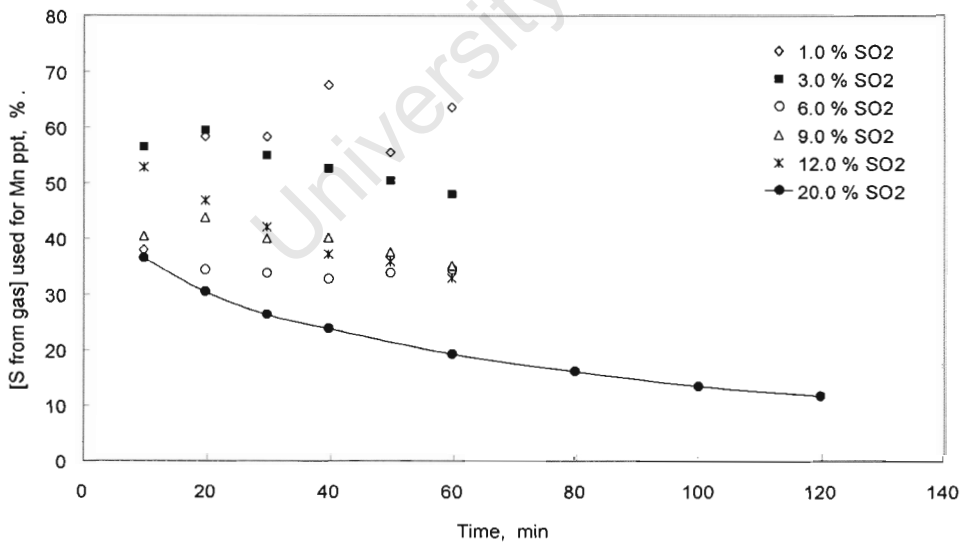


Figure 4-9: The influence of the gas composition on the utilisation of the dissolved sulfur dioxide to precipitate manganese.

4.3.2 Deriving an Empirical Rate Equation in Terms of the Manganese Concentration

The effect of the manganese concentration on the rate of the manganese removal rate was investigated by performing the base case test at different initial manganese concentrations. Figure 4-10 shows the decrease in the soluble manganese when starting out at the different initial manganese concentrations.

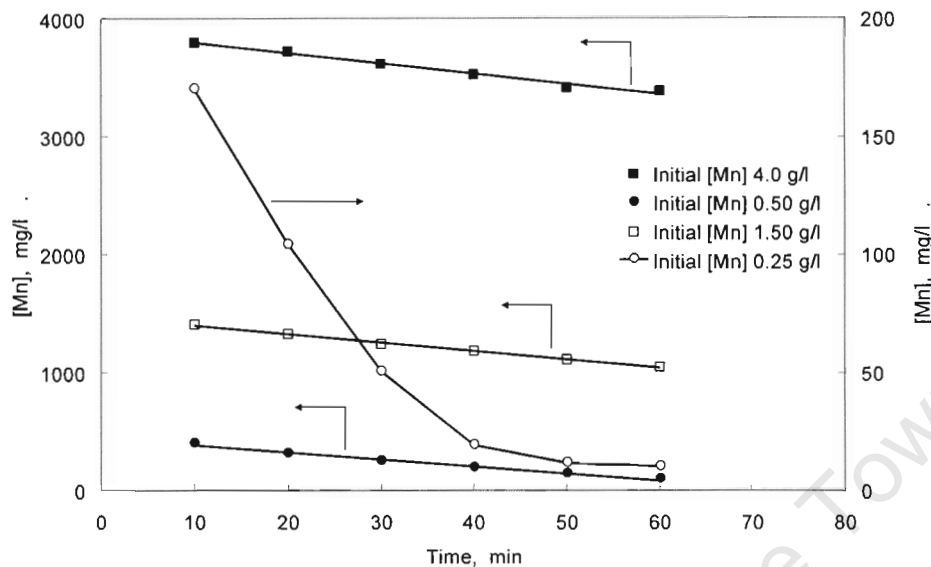


Figure 4-10: The effect of the initial manganese concentration on the rate of manganese removal (Overall gas flow of 500 ml/min, 6 % SO₂, pH 4.0 and at 30 °C).

As can be seen in figure 4-10, the rate of decrease in the manganese concentration was nearly identical over the whole range of manganese concentrations tested (except for manganese concentrations below 50 mg/l). This is also illustrated in figure 4-11 which plots the incremental manganese removal rate versus the manganese concentration for each test. It is clear that the manganese concentration does not significantly influence the rate of manganese precipitation, except at the very low concentrations (below 50 mg/l). According to Zhang et al (2000) the effect of Fe(II) on the rate of the iron oxidation was insignificant, but the concentration of the Fe(III) dictated the induction period before precipitation commenced – after the induction period the Fe(III) also did not play a role in dictating the rate of iron precipitation. Therefore, the results shown in figure 4-10 and figure 4-11 are quite similar to that of Zhang et al. (2000). This could be explained by assuming that the manganese acts as a catalyst only to form the free radical (i.e. a rise in manganese concentration does not equate to a rise in the free radical concentration).

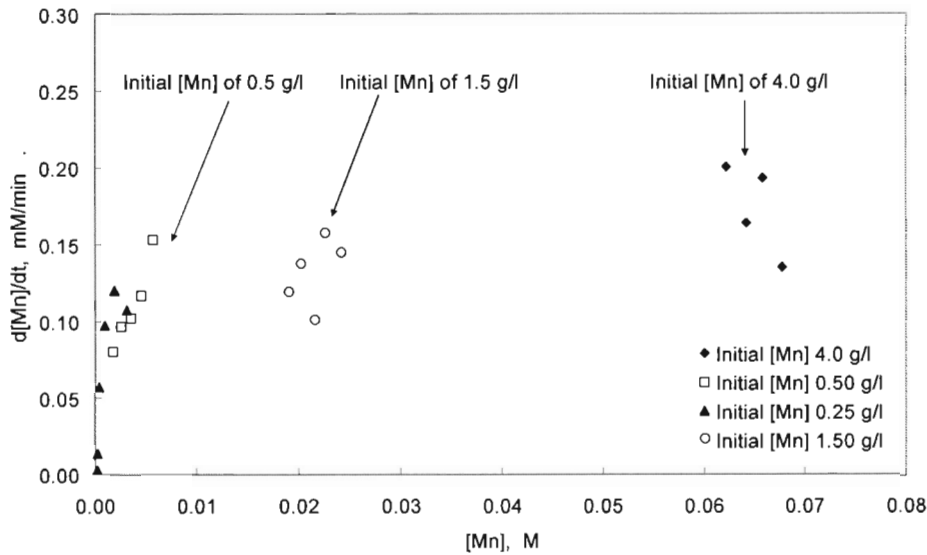


Figure 4-11: The effect of the manganese concentration on the rate of manganese removal (Overall gas flow of 500 ml/min, 6 % SO₂, pH 4.0 and at 30 °C).

Since the manganese concentration had such an insignificant influence on the rate of manganese precipitation with the gas mixture, the manganese concentration was not included in the overall rate equation describing the precipitation of manganese.

4.3.3 Deriving an Empirical Rate Equation in Terms of the Dissolved Oxygen

To determine the influence of the dissolved oxygen concentration on the rate of manganese removal, nitrogen was used to deoxygenate the manganous sulfate solution while conducting base case batch tests. The dissolved oxygen concentration was controlled by varying the flow rate of nitrogen into the solution. The results of these tests are plotted in figure 4-12, and clearly show that the manganese removal rate decreased with a decrease in the dissolved oxygen concentration.

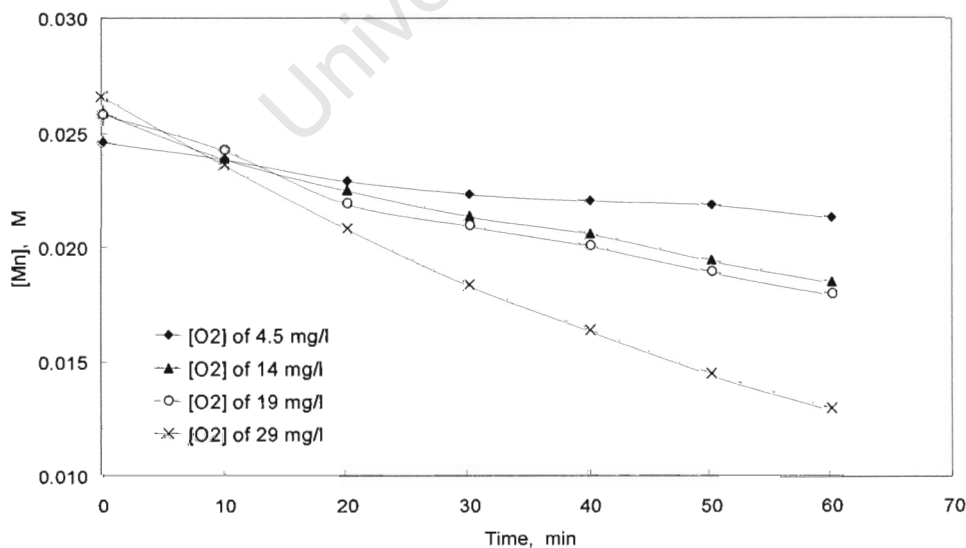


Figure 4-12: The influence of the dissolved oxygen concentration on the rate of manganese removal (12 % SO₂ in O₂; overall gas flow rate of 500 ml/min; pH of 4.0; 30 °C and [Mn] of 1.5 g/l).

To ensure that the flow of nitrogen only limited the concentration of dissolved oxygen and not also the transfer of sulfur dioxide from the gas into the solution, kinetic samples were taken during the tests and analysed for the total sulfur concentration. Figure 4-13 shows that the transfer of the sulfur dioxide was not hindered by the nitrogen flow in the experiments and therefore the rate of manganese precipitation decreased only due to the decrease in the dissolved oxygen concentration.

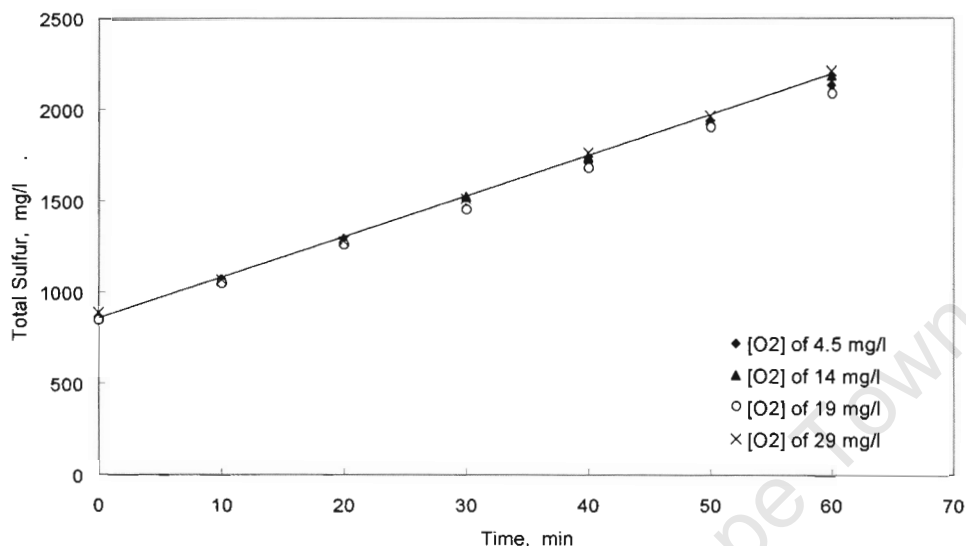


Figure 4-13: Graph showing that the nitrogen sparging only influenced the dissolved oxygen concentration and not the transfer of SO₂ into the solution.

The rate equation for the manganese removal in terms of the dissolved oxygen concentration is illustrated in figure 4-14. The rate is first order with respect to the dissolved oxygen concentration (equation 18).

$$d[\text{Mn}]/dt = \text{Constant}_2 \times [\text{O}_2] \quad (18)$$

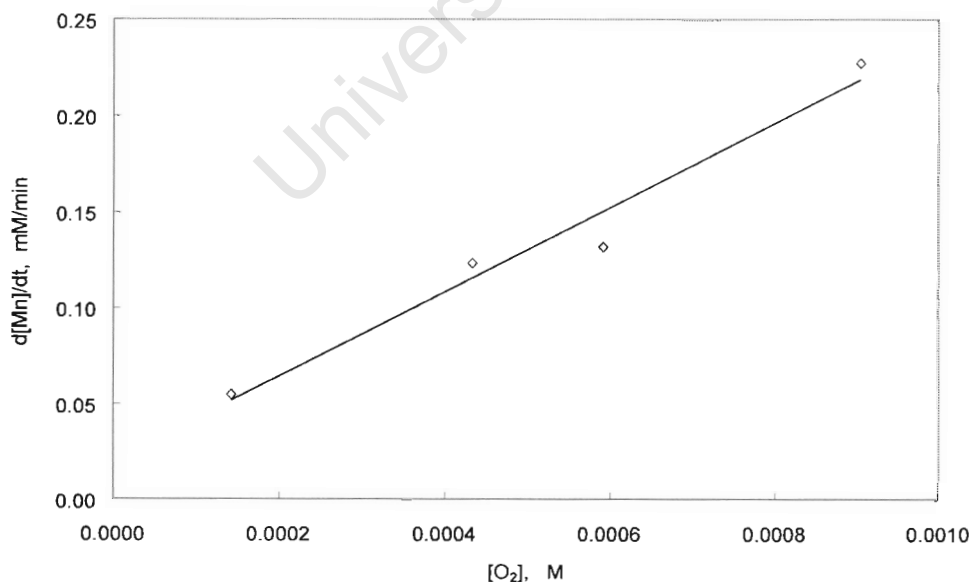


Figure 4-14: The influence of dissolved oxygen on the rate of manganese removal over the first 60 minutes of the batch tests.

From the batch tests where the dissolved oxygen concentration was varied, the percentage of the aqueous sulfur (obtained from the gas phase) which was used to precipitate the manganese was determined for each test. The assumption was made that one mole of sulfur dioxide was needed to precipitate one mole of manganese as per equation (9). The consumption of the dissolved sulfur dioxide as a percentage of the total sulfur in solution obtained from the gas phase is shown in figure 4-15. It is clear from figure 4-15 that as the dissolved oxygen concentration decreased, the utilisation of the sulfur dioxide to precipitate manganese also decreased.

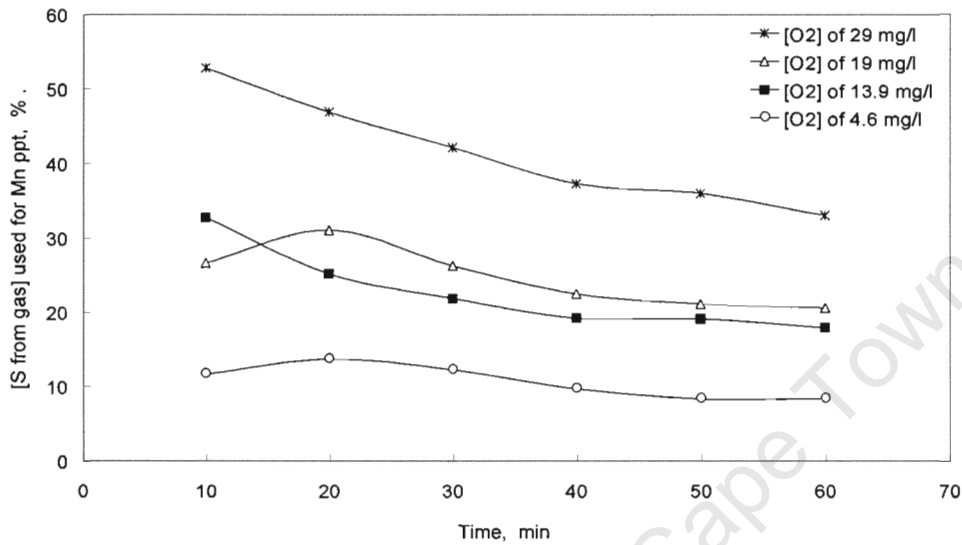


Figure 4-15: The influence of the dissolved oxygen concentration on the utilisation of the dissolved sulfur dioxide to precipitate manganese.

4.3.4 Deriving an Empirical Rate Equation in Terms of the Solution Temperature

The solution temperature was expected to influence the rate of manganese removal in two ways. From the work of Zhang et al. (2000), an increase in temperature increased the rate of iron removal. However, an increase in temperature will lead to a decrease in the solubility of the oxygen in the solution. As was seen in section 4.3.3, a decrease in the dissolved oxygen concentration will lead to a decrease in the rate of manganese precipitation.

To study the influence of temperature on the rate equation for the precipitation of the manganese, batch tests were conducted where the temperature of the solution was varied and the dissolved oxygen concentration recorded. Figure 4-16 shows the influence of temperature on the rate of manganese removal. The expected decrease in the rate of the manganese removal at the high temperatures (80 °C in the case of iron precipitation, Zhang et al. (2000)), was not investigated due to the working range of the dissolved oxygen probe being below 60 °C.

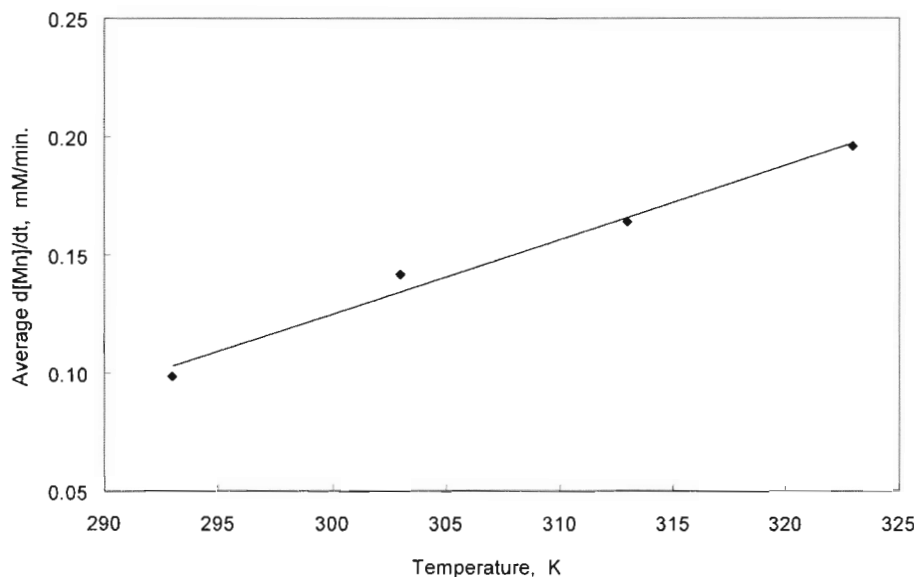


Figure 4-16: The effect of temperature on the average manganese removal rate over the first 60 minutes (6 % SO_2 in O_2 ; overall gas flow rate of 500 ml/min; pH of 4.0; and $[Mn]$ of 1.5 g/l).

An Arrhenius plot for the relationship between the manganese precipitation rate and the solution temperature is presented in figure 4-17. This plot assumes the dissolved oxygen concentration to be constant and part of the $\ln(A)$ term shown in figure 4-17. The activation energy calculated from the slope of the line in figure 4-17 is 23.5 kJ/mol and is similar to the activation energy calculated by Zhang et al. (2002) of 15 kJ/mol. However, since the dissolved oxygen concentration was not constant but varied from 35 mg/l to 22 mg/l in the temperature range tested, it should be taken out of the constant term, as was done in figure 4-18. In figure 4-18 the rate of precipitation was divided by the measured dissolved oxygen concentration to ensure that the only variable was the solution temperature.

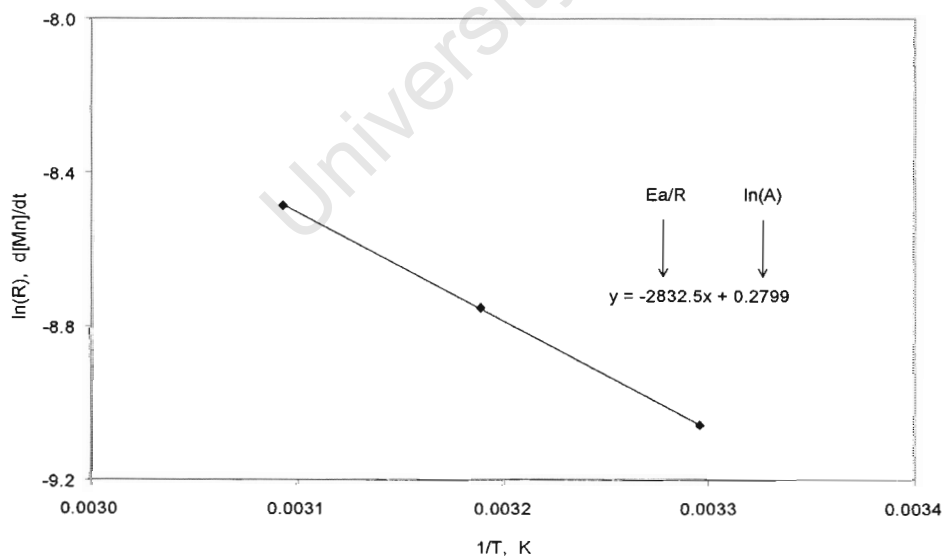


Figure 4-17: Arrhenius plot (not taking into account the influence of the changing dissolved oxygen concentration with the solution temperature).

The activation energy calculated from the slope of the line in figure 4-18 is 37 kJ/mol. However, the activation energy calculated from figure 4-17 was used in the rate equation as it proved to be more accurate in describing the batch data.

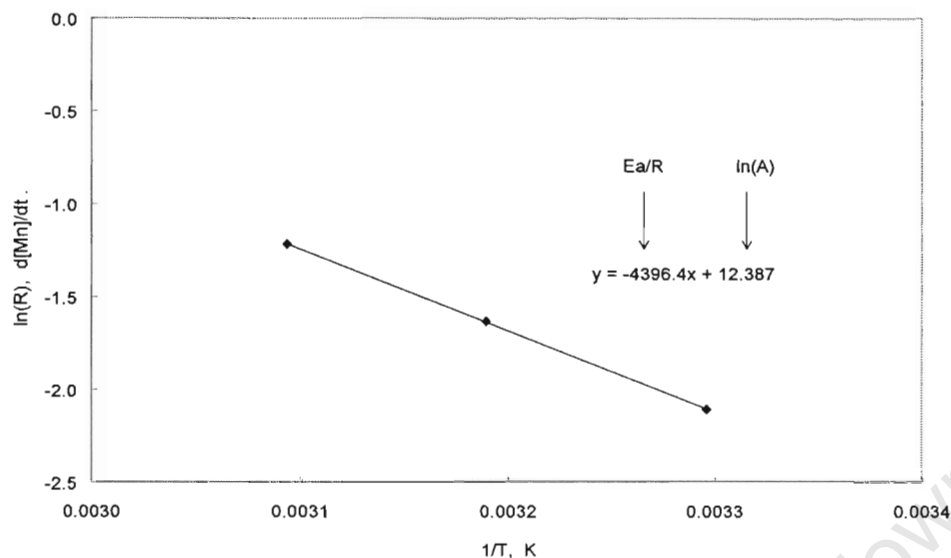


Figure 4-18: Arrhenius plot (taking into account the influence of the changing dissolved oxygen concentration with the solution temperature).

The rate equation for the manganese precipitation reaction in terms of the temperature was then described by the Arrhenius equation:

$$d[Mn]/dt = \text{Constant}_3 \times e^{(-E_a/RT)} \quad (19)$$

with $E_a = 23.5 \text{ kJ/mol}$
 $R = 8.314 \text{ kJ/K/mol}$

From the batch tests where the solution temperature was varied, the percentage of the aqueous sulfur (obtained from the gas phase) which was used to precipitate manganese was determined for each test. The assumption was made that one mole of sulfur dioxide was needed to precipitate one mole of manganese as per equation (9). The consumption of the dissolved sulfur dioxide as a percentage of the total sulfur in solution obtained from the gas phase is shown in figure 4-19. It is clear from figure 4-19 that as the solution temperature increased, the utilisation of the sulfur dioxide to precipitate manganese also increased.

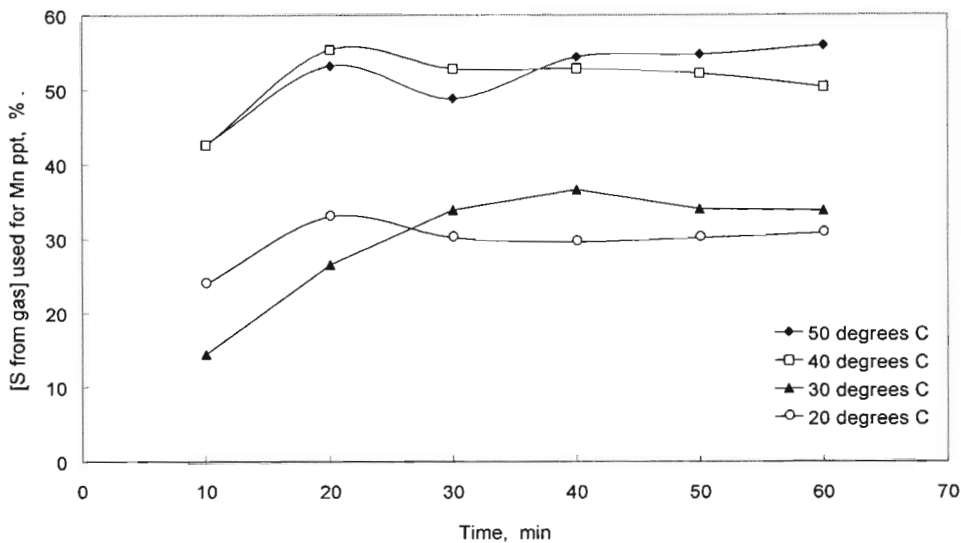


Figure 4-19: The influence of the solution temperature on the utilisation of the dissolved sulfur dioxide to precipitate manganese.

4.3.5 Deriving an Empirical Rate Equation in Terms of the Solution pH

From the literature, it was expected that the manganese precipitation rate would decrease with a decrease in the pH of the solution (with no manganese removed below a pH of 3). However, for this method of removing manganese to be a viable process, selectivity of manganese over other metals such as cobalt and nickel must be achieved. In the work of Zhang et al. (2002), cobalt started to precipitate with the gas mixture above a pH of 4.0 and nickel above a pH of 6.5. Therefore, the pH range investigated in this work was between 3.5 and 6.0.

Conducting batch tests and varying only the pH of the solution resulted in the data of figure 4-20. It is clear that the manganese precipitation rate was negatively influenced by a drop in the solution pH. Writing a rate equation for the removal of the manganese in terms of the hydronium concentration proved unsuccessful, and the only good fit to the data was to write the rate equation in terms of the pH. The batch data as illustrated in figure 4-21 shows a linear relationship between the rate of the manganese removal and the inverse of the pH.

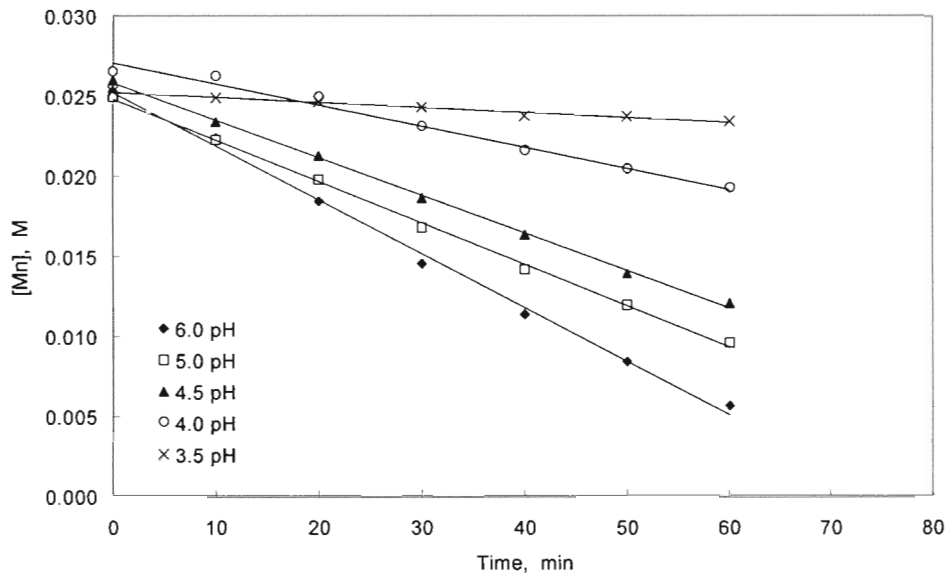


Figure 4-20: The influence of pH on the rate of manganese removal (6 % SO₂ in O₂; overall gas flow rate of 500 ml/min; 30 °C; and [Mn] of 1.5 g/l).

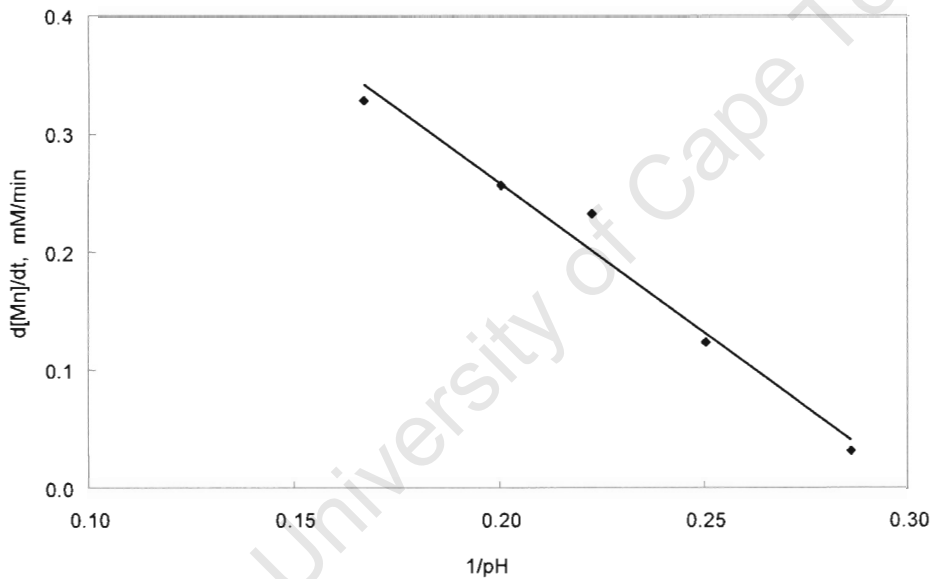


Figure 4-21: The influence of pH on the average rate of manganese removal over the first 60 minutes of the batch experiments.

Therefore, the rate equation in terms of the pH can be described by:

$$d[\text{Mn}]/dt = \text{Constant}_4 \times (1/\text{pH} - \text{Constant}_5) \quad (20)$$

with $\text{Constant}_5 = 0.3$ (where the line in figure 4-21 intersects the x-axis).

From the batch tests where the pH was varied, the percentage of the aqueous sulfur (attributed to the dissolution of the gas) which was used to precipitate manganese was determined for each test. The assumption was made that one mole of sulfur dioxide was needed to precipitate one mole of manganese as per equation (9). The consumption of the dissolved sulfur dioxide as a percentage of the total sulfur in

solution obtained from the gas phase is shown in figure 4-22. It is clear from figure 4-22 that as the pH increased, the utilisation of the sulfur dioxide to precipitate manganese also increased (up to 100% at pH 6.0).

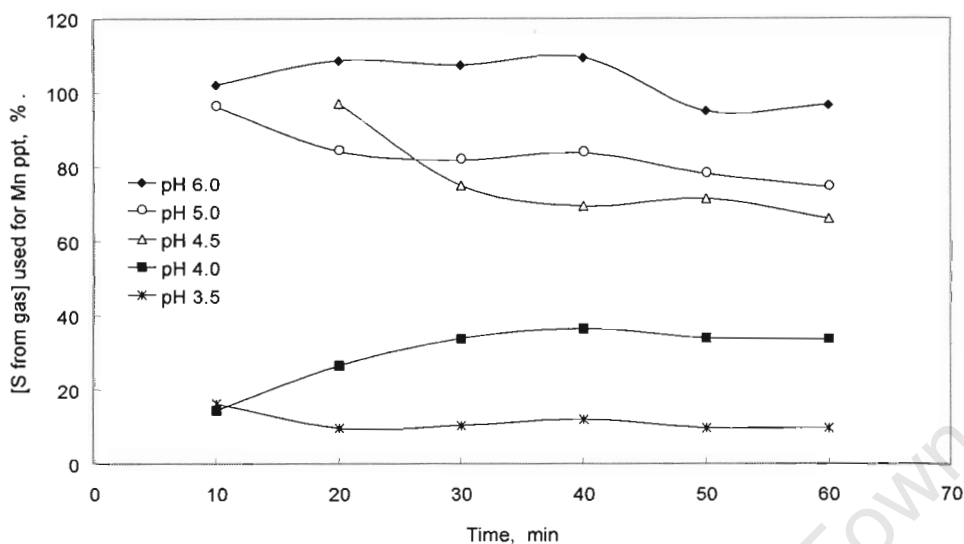


Figure 4-22: The influence of the pH on the utilisation of the dissolved sulfur dioxide to precipitate manganese.

4.3.6 Combining the Individual Rate Equations for the Operating Parameters into One Empirical Rate Equation

From the batch tests, where the operating parameters were varied on an individual basis, the rate equations in table 4-1 were obtained:

Table 4-1: The rate equations for each of the operating parameters

Operating Parameter	Rate Equation
Sulfur in the gas and solution	$d[Mn]/dt = \text{Constant}_1 \times (P_{SO_2}/P_{Total}) \times e^{(-18.[S \text{ from gas}])}$
Oxygen in the solution	$d[Mn]/dt = \text{Constant}_2 \times [O_2]$
Solution temperature	$d[Mn]/dt = \text{Constant}_3 \times e^{(-E_a/RT)}$
Solution pH	$d[Mn]/dt = \text{Constant}_4 \times (1/pH - \text{Constant}_5)$

Combining the rate equations listed in table 4-1 into one rate equation for the removal of manganese with a gas mixture of sulfur dioxide and oxygen resulted in equation (21). The value for the rate constant 'A' was then determined by substituting the data of the base case test into the equation, leaving 'A' as the only unknown.

$$d[Mn]/dt = A \cdot [O_2] \cdot (P_{SO_2}/P_{tot}) \cdot e^{(B.[S \text{ from gas}])} \cdot (1/pH + C) \cdot e^{(-E_a/RT)} \tag{21}$$

with $d[Mn]/dt$ in mol/litre/min
 $[O_2]$ in mol/litre
 P_{SO_2} in atmospheres

P_{tot} in atmospheres

[S from gas] in mol/litre

T in Kelvin

with $A = -6.8 \times 10^5$

$B = -18$

$C = -0.3$

$E_a = 23.5 \text{ kJ/mol}$

4.4 Comparing the Derived Rate Equation to the Actual Data of the Batch Tests

For the derived rate equation (21) to be of use it must be shown that it accurately describes the measured rate at which the manganese was precipitated in the batch tests, regardless of which operating parameter was varied. Therefore, the measured values for the operating parameters ($[O_2]$; P_{so_2} ; [S from gas]; pH and temperature) for every batch test conducted were inserted into the derived rate equation and the rate of manganese precipitation calculated. This calculated rate of manganese removal was used to calculate the manganese concentration in the solution for each test. Note that the starting concentration (or input) of the manganese for the rate equation was the assayed value after 10 minutes and not the initial concentration of the manganese at time zero. This was done to compare the rate equation with the actual measured rate without considering the induction period seen at the start of some of the batch tests.

Figure 4-23 shows the batch tests where the gas composition was varied. The assayed concentrations of the manganese are shown as well as the calculated manganese concentrations using the derived rate equation (dotted lines). Ignoring the induction period during the first few minutes of the batch experiments, the calculated rate of manganese removal is almost identical to the measured rate of the manganese removal. It should be remembered that the derived rate equation can only describe the rate of manganese precipitation for gas mixtures up to 12 % SO_2 in O_2 (this was due to the sudden deviation from the linear relationship between the rate of manganese removal and the sulfur dioxide content of the gas mixture above 12 % SO_2).

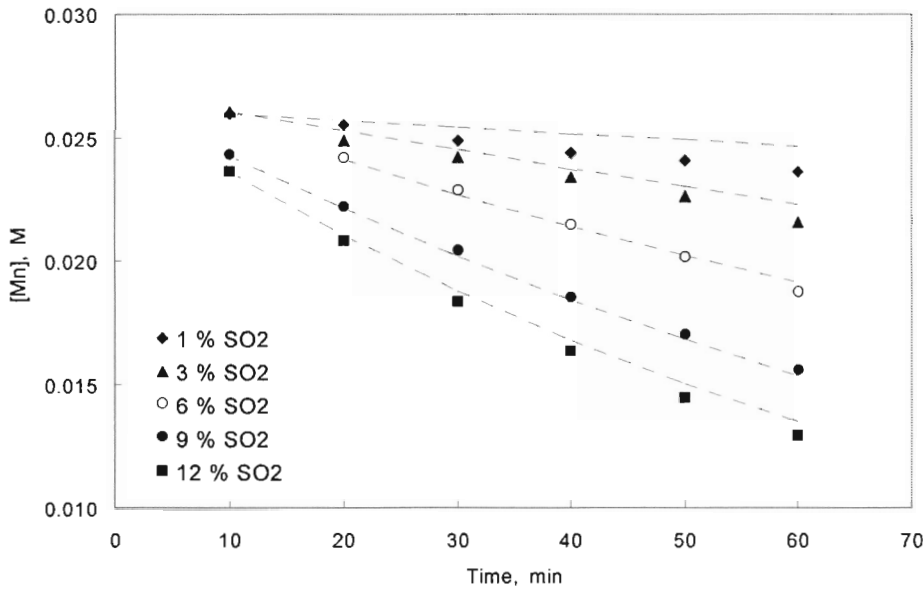


Figure 4-23: Comparing the manganese removal calculated by the derived empirical rate equation (dotted lines) with the actual data obtained from the batch tests where the gas composition was varied.

In figure 4-24 the manganese removal rate calculated by the empirical rate equation compares well with the measured rate of manganese precipitation when changing the dissolved oxygen concentration.

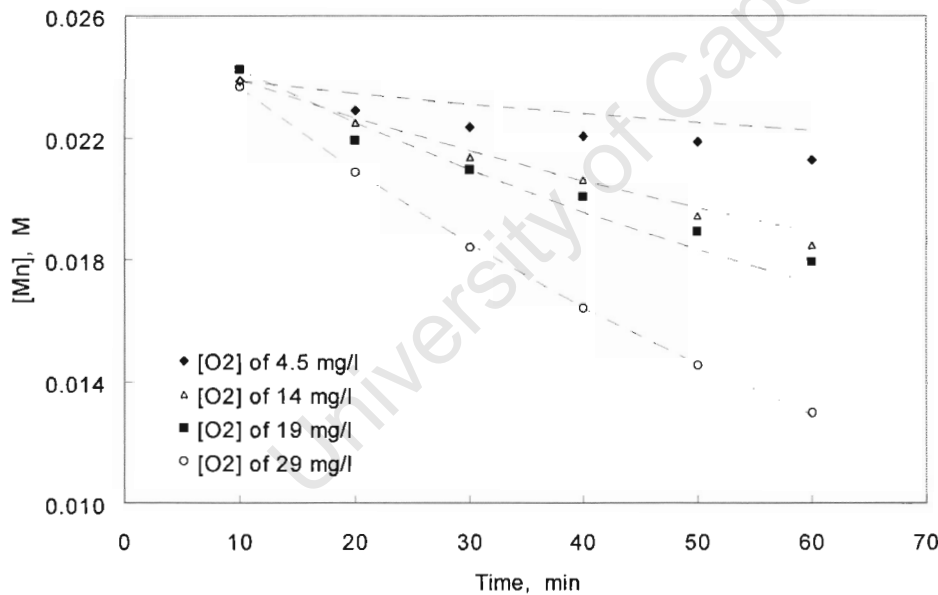


Figure 4-24: Comparing the manganese removal calculated by the derived empirical rate equation (dotted lines) with the actual data obtained from the batch tests where the dissolved oxygen was varied.

In figure 4-25 the manganese removal rate calculated by the empirical rate equation compares well with the measured rate of manganese precipitation over the entire temperature range tested. However, the rate equation does not cater for the high temperatures where the solubility of the oxygen becomes low enough to decrease the rate of manganese precipitation.

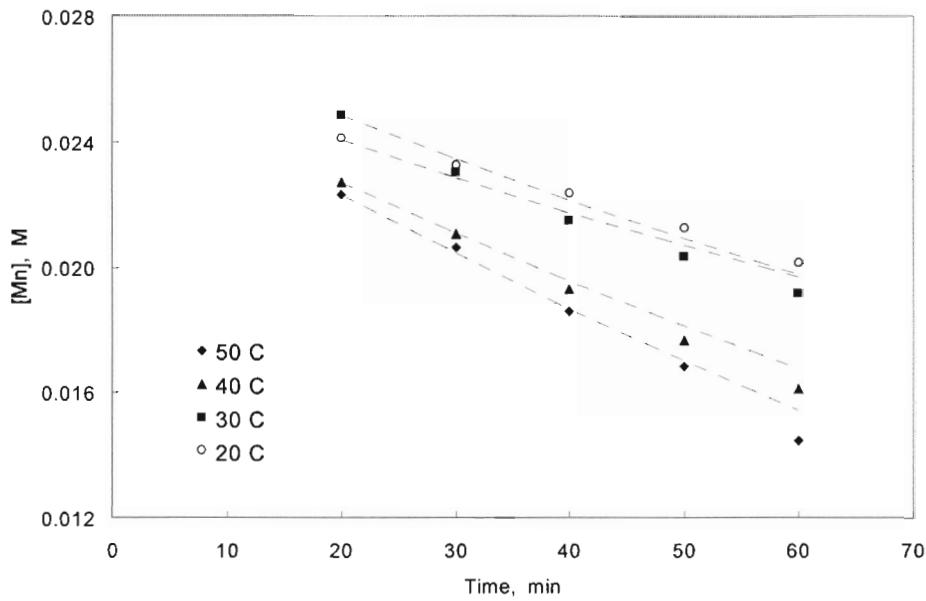


Figure 4-25: Comparing the manganese removal calculated by the derived empirical rate equation (dotted lines) with the actual data obtained from the batch tests where the temperature was varied.

In figure 4-26 the calculated rate of manganese precipitation with the SO_2/O_2 gas mixture is identical to the measured rate of manganese removal for the entire pH range tested (pH 3.5 to pH 6.0).

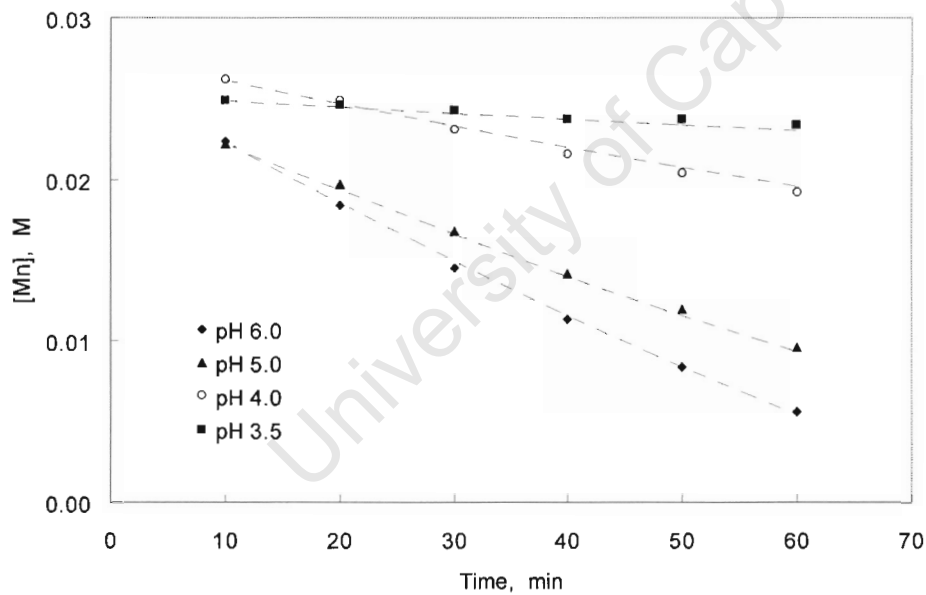


Figure 4-26: Comparing the manganese removal calculated by the derived empirical rate equation (dotted lines) with the actual data obtained from the batch tests where the pH was varied.

4.5 Testing the Derived Rate Equation on a Continuous Basis

In section 4.3 the relationships between the rate of manganese precipitation and each of the operating parameters were obtained. In section 4.3.6 these relationships were grouped into one rate equation (21) that was shown to accurately describe the rate at which the manganese was precipitated with the SO₂/O₂ gas mixtures in the batch tests.

If this rate equation for the removal of manganese from solution with the gas mixture is to be of use in the design of a reactor, the rate equation must also hold under continuous operation. The difference between the batch operation (which was how the rate equation was determined) and a continuous operation is the dissolved sulfur dioxide concentration of the solution. During the batch tests, the dissolved sulfur dioxide concentration increased during the tests due to the very high solubility of sulfur dioxide in water. In a continuous reactor, where there is manganese solution entering and leaving the reactor, the dissolved sulfur dioxide in the solution will stabilise once steady-state conditions are achieved. It was hoped that since the derived rate equation from the batch tests has a component that describes the rate of manganese removal according to the dissolved sulfur concentration attributed to the dissolution of the gas, that the derived rate equation would still be applicable. Therefore, the rate equation (equation 21) was used in the mass balance over a one-stage continuous reactor (equation 15) to determine if the rate equation verifies the measured concentration of manganese in the solution leaving the reactor under steady-state conditions. The inputs to the rate equation were the steady-state temperature, pH, [O₂], [S from gas] and the partial pressure of the SO₂ in the gas. To complete the mass balance over the continuous reactor, the flow rates of the solutions entering and leaving the reactor were also measured.

For the method of conducting the continuous tests, see section 3.2. Table 4-2 lists the operating conditions for each of the three continuous tests (in each continuous test the operating parameter investigated was changed once after 4 or 5 residence times).

Table 4-2: The operating conditions for the continuous testwork

	Continuous Test Varying the Gas Mixture	Continuous Test Varying the Temperature	Continuous Test Varying the pH
Gas Mixture (% SO ₂)	6 and 12	12	12
Solution Temperature (°C)	33	25 and 50	33
Solution pH (controlled with NaOH)	4.0	4.0	4.0 and 5.0
Total Gas Mixture Flowrate (ml/min)	500	500	500
Residence Time of Solution in Reactor (min)	60	60	60
[Mn] Entering the Reactor (g/l)	1.4	1.4	1.4
Stirring Speed (rpm)	800	800	800

In the first continuous test, the gas composition was changed once after 5 residence times (5 hours) from 6 % SO₂ to 12 % SO₂ in oxygen. As seen in figure 4-27, the concentration of the total dissolved sulfur and the manganese in the solution leaving the reactor stabilised at each of the gas mixtures used.

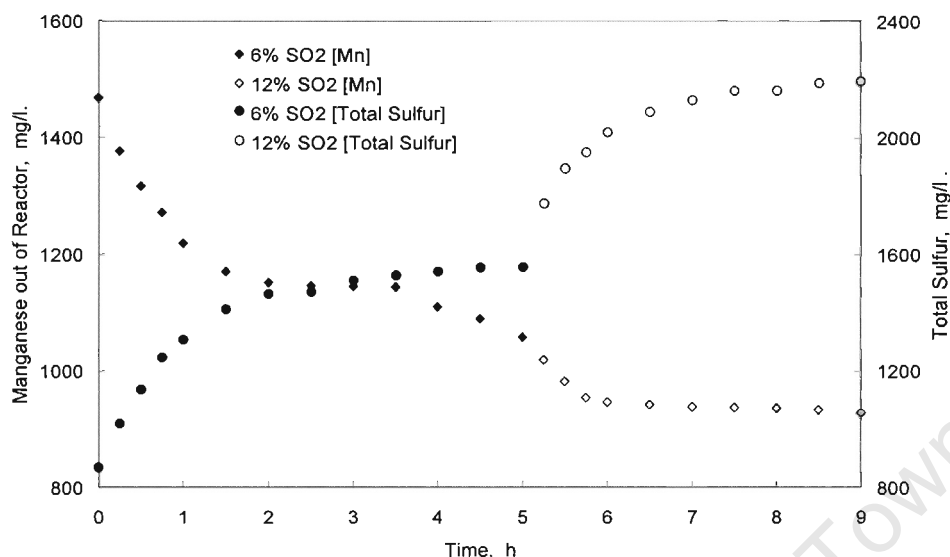


Figure 4-27: Graph of the concentrations of the manganese and the total sulfur in the continuous reactor (changing the gas mixture after 5 hours) (Overall gas flow rate of 500ml/min; pH of 4.0; 30 °C and [Mn] of 1.5 g/l).

Figure 4-28 shows the manganese concentration of the solution leaving the reactor and the calculated manganese concentrations when using both gas mixtures under steady-state conditions. The calculations for the calculated manganese concentration leaving the reactor can be seen in Table 8-13 in the appendix. The calculated manganese concentration compares very well with the assayed concentration under both gas compositions. In the case of the 6 % SO₂ gas mixture, the model calculated a steady-state manganese concentration of 1063 mg/l, which proved to be 99 % accurate (stated as the calculated manganese removal over the actual manganese removal). The model was 96 % accurate for the manganese removal when using a 12 % SO₂ gas mixture, with a calculated manganese concentration of 945 mg/l. This proves that the method of describing the rate of manganese removal with both the gas composition (P_{SO_2}) and the solution composition ([S from gas]) is viable for the continuous reactor in this test work.

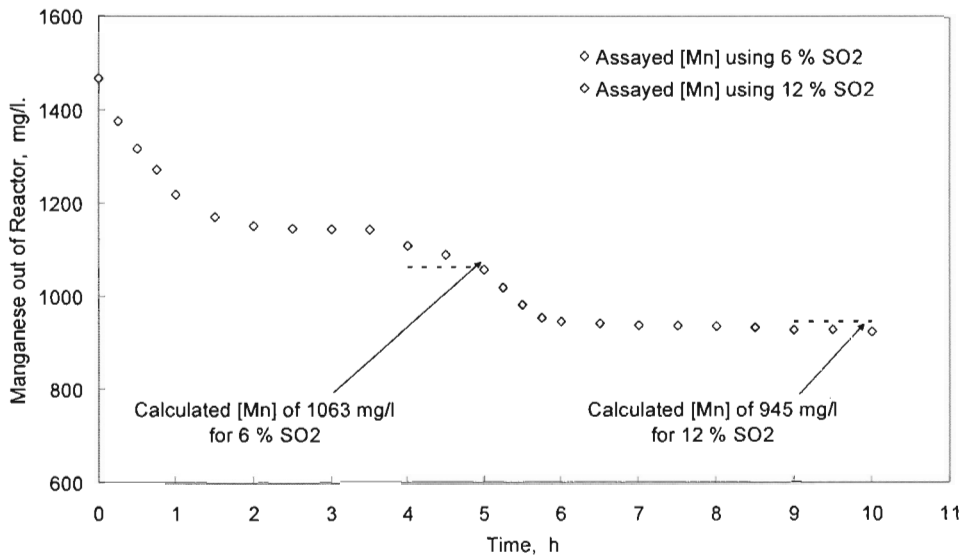


Figure 4-28: Graph showing the accuracy of the derived rate equation for the continuous reactor (changing the gas mixture after 5 hours).

A continuous test where the solution temperature was changed once after 5 residence times was conducted to evaluate the temperature term of the rate equation. Figure 4-29 shows that steady state conditions were achieved at both temperatures used (20 °C and 50 °C). The calculations for the calculated manganese concentration leaving the reactor can be seen in Table 8-14 in the appendix. As shown in figure 4-30, the model was slightly less accurate in calculating the steady-state manganese concentration at 20 °C (the calculated manganese concentration of 951 mg/l being 123 % accurate), than it was at calculating the steady state manganese concentration at 50 °C (the calculated manganese concentration of 761 mg/l being 111 % accurate). Nonetheless, the model is still accurate enough to use in the temperature range investigated (20 °C to 50 °C).

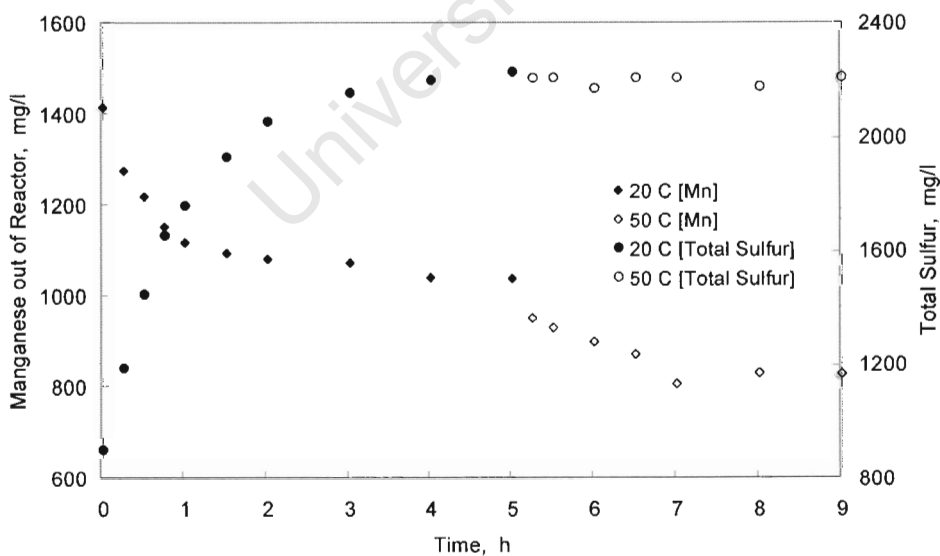


Figure 4-29: Graph of the concentrations of the manganese and total sulfur in the continuous reactor (changing the solution temperature after 5 hours) (12 % SO₂ in O₂; overall gas flow rate of 500 ml/min; pH of 4.0 and [Mn] of 1.4 g/l).

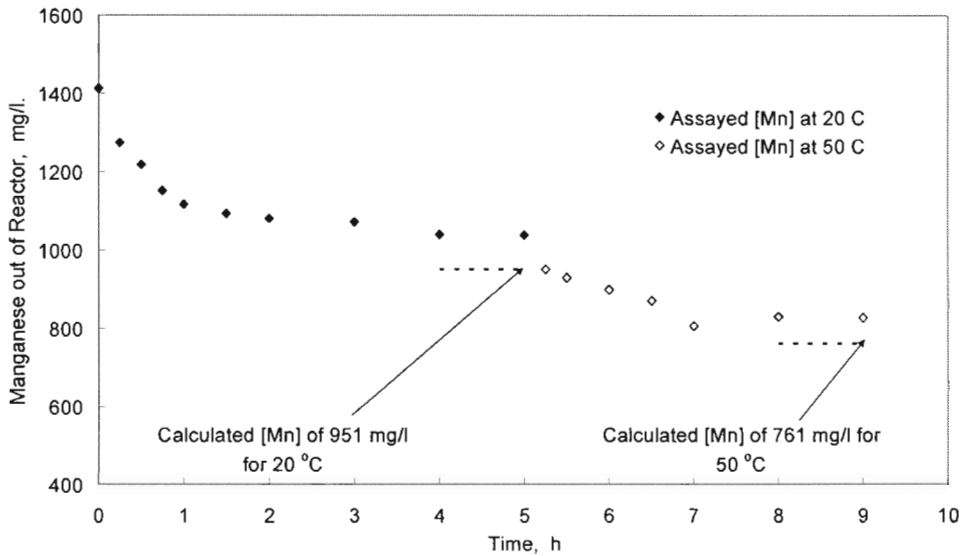


Figure 4-30: Graph showing the accuracy of the derived rate equation for the continuous reactor (changing the solution temperature after 5 hours).

In the last continuous test the applicability of the model when changing the solution pH under steady state conditions was investigated. Figure 4-31 shows that steady-state conditions were achieved at both pH 4.0 and at pH 5.0, and the calculations for the steady-state manganese concentrations can be seen in table 8-15 in the appendix. Four residence times were used for each test condition (a residence time of one hour was used).

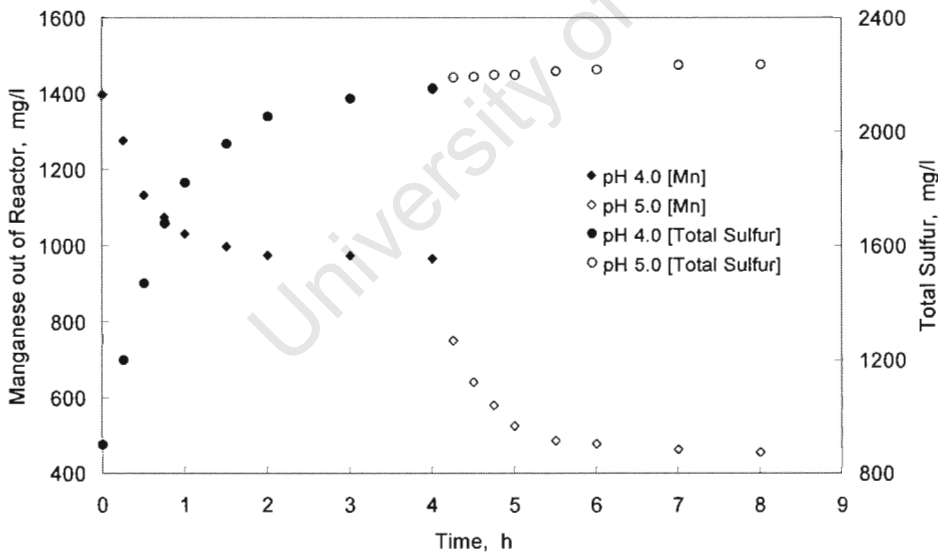


Figure 4-31: Graph of the concentrations of the manganese and total sulfur in the continuous reactor (changing the pH after 4 hours) (12 % SO₂ in O₂; overall gas flow rate of 500 ml/min; 30 °C and [Mn] of 1.4 g/l).

Figure 4-32 shows that the model was once again quite accurate when comparing the calculated steady-state manganese concentration against the assayed manganese concentration. The calculated

manganese concentration of 884 mg/l when controlling the solution pH at 4.0 was 118 % accurate, while the calculated manganese concentration of 445 mg/l when controlling the pH at 5.0 was 101 % accurate.

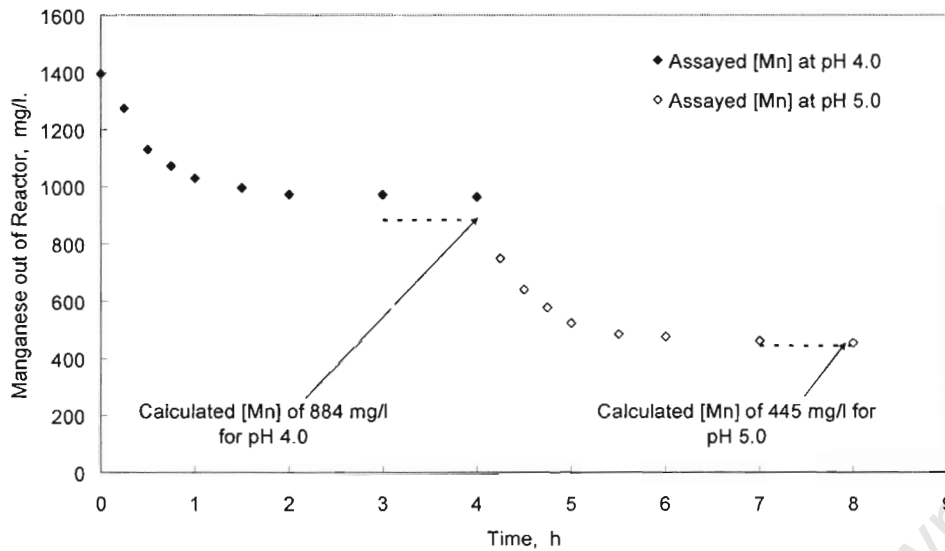


Figure 4-32: Graph showing the accuracy of the derived rate equation for the continuous reactor (changing the pH after 4 hours).

4.6 Using the Derived Rate Equation as a Predictive Tool

On its own, the derived rate equation cannot be used as a predictive tool since the dissolved oxygen concentration and the dissolved sulfur concentration need to be measured with time to calculate a manganese removal rate. To convert the rate equation into a predictive tool, the rate of oxygen mass transfer and the rate of sulfur dioxide mass transfer into the solution need to be combined with the manganese-precipitation rate equation. Thus, there will be three differential equations that must be solved simultaneously using a numerical method. The three equations needed to predict the rate of manganese precipitation are:

$$d[\text{Mn}]/dt = A \cdot [\text{O}_2]_{\text{bulk}} \cdot (P_{\text{SO}_2}/P_{\text{tot}}) \cdot e^{(B \cdot [\text{S from gas}])} \cdot (1/\text{pH} + C) \cdot e^{(-E_a/RT)} \quad (21)$$

$$d[\text{O}_2]/dt = K_L a_1 ([\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{bulk}}) \quad (22)$$

$$d[\text{S from gas}]/dt = K_L a_2 ([\text{S}_{\text{total}}]_{\text{sat}} - [\text{S from gas}]) \quad (23)$$

The standard method for determining a $K_L a$ value for oxygen is to conduct a sodium sulfite oxidation test. In this method, oxygen is sparged into a sodium sulfite solution under the agitation conditions envisaged for the precipitation tests. The dissolved oxygen reacts with the sulfite to form sulfate (this reaction is catalysed by a small addition of cobalt(II)). Kinetic samples are taken of the solution and the unreacted sulfite concentration is determined through a standard titration method involving iodine- and sodium thiosulfate solutions.

Unfortunately, the value of the mass transfer coefficient ($K_L a$) is dependent on the rate of reaction consuming the oxygen. The manganese precipitation reaction is much slower than the rate of the sulfite

oxidation, and thus to obtain a mass transfer coefficient using the sodium sulfite method would not have any value.

In this work it was found that the rate of oxygen transfer as well as the rate of sulfur dioxide transfer from the gas phase into solution were not influenced by the rate of the manganese precipitation reaction. Referring to the batch tests where the pH was varied, it is clear that the rate of oxygen transfer into the manganous sulfate solution was much larger than the consumption of the oxygen. This is proven by the very high bulk oxygen concentration measured for all of the precipitation tests (typically 30mg/l). Even when the rate of the precipitation reaction was very high (at pH 6.0), the dissolved oxygen concentration was the same as for the low pH tests where the manganese precipitation reaction was very slow.

The rate of the sulfur dioxide transfer from the gas into the solution was also independent of the manganese precipitation rate. As shown in figure 4-33 the increase in the concentration of the total sulfur in solution was not affected when using the same gas composition but at different precipitation rates (varying the pH).

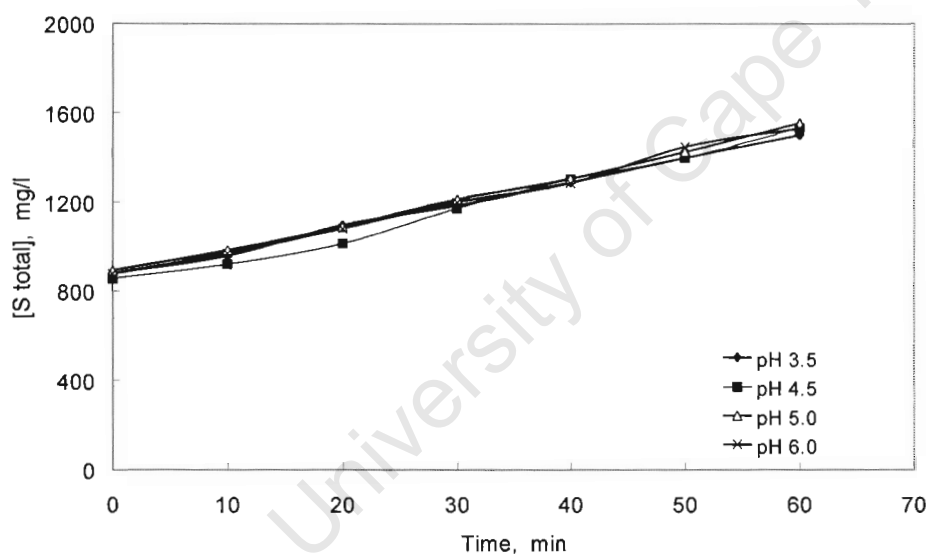


Figure 4-33: Graph showing the independence of the sulfur dioxide transfer rate on the rate of manganese precipitation.

Since neither the transfer of the oxygen, nor the transfer of the sulfur dioxide into the solution were influenced by a change in the rate of the precipitation reaction, the only consideration on the transfer rate was the physical adsorption of the oxygen and sulfur dioxide (assuming no reaction or very slow reaction in the solution).

To use the derived rate equation for manganese removal as a predictive tool, the mass transfer coefficients of equations (22) and (23) can be determined as follows:

- i. Determine the physical adsorption rate of the oxygen for the reactor. Use an oxygen probe with a very fast response time to measure the dissolved oxygen concentration increase when sparging oxygen into water (previously de-oxygenated with nitrogen). The slope of the line ($[O_2]$ versus time) can then be used to determine the $K_L a$ for the oxygen transfer.
- ii. Determine the physical adsorption of the sulfur dioxide for the reactor. Conduct an experiment where a gas mixture of nitrogen (to replace the oxygen component) and sulfur dioxide is sparged into water and take total sulfur samples of the solution with time. The slope of the line ($[S \text{ from gas}]$ versus time) can then be used to determine the $K_L a$ for the sulfur dioxide transfer in the reactor.

Note that this method might not apply to process solutions where there are side reactions influencing the rate of oxygen and sulfur dioxide transfer from the gas phase into the solution.

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5. CONCLUSIONS

The relationships between the rate of manganese precipitation and each of the operating parameters were determined using batch tests. From the batch data the following relationships between the rate of manganese removal and the operating parameters were obtained:

$$d[\text{Mn}]/dt = \text{Constant}_1 \times (P_{\text{SO}_2}/P_{\text{Total}}) \times \exp(-18 \cdot [\text{S from gas}])$$

$$d[\text{Mn}]/dt = \text{Constant}_2 \times [\text{O}_2]$$

$$d[\text{Mn}]/dt = \text{Constant}_3 \times e^{(-E_a/RT)}$$

$$d[\text{Mn}]/dt = \text{Constant}_4 \times (1/\text{pH} - \text{Constant}_5)$$

The relationship between the sulfur dioxide and the rate of manganese precipitation was described by both the sulfur dioxide content of the gas mixture, as well as by the dissolved sulfur obtained in solution from the gas phase. The rate of manganese precipitation was found to be first order with respect to the dissolved oxygen concentration. An Arrhenius relationship was used to relate the solution temperature to the rate of manganese precipitation, with an activation energy of 23.5 kJ/mol. The rate of manganese precipitation was found to be inversely proportional to the pH of the solution. The rate of manganese removal was found to be largely unaffected by the manganese concentration except at very low concentrations (less than 50 mg/l manganese).

The rate equations stated for each of the operating parameters were combined into one rate equation for the precipitation of manganese by using a sulfur dioxide – oxygen gas mixture:

$$d[\text{Mn}]/dt = A \cdot [\text{O}_2] \cdot (P_{\text{SO}_2}/P_{\text{tot}}) \cdot e^{(B \cdot [\text{S from gas}])} \cdot (1/\text{pH} + C) \cdot e^{(-E_a/RT)}$$

with $d[\text{Mn}]/dt$ in mol/litre/min

$[\text{O}_2]$ in mol/litre

P_{SO_2} in atmospheres

P_{tot} in atmospheres

$[\text{S from gas}]$ in mol/litre

T in Kelvin

with $A = -6.8 \times 10^5$

$B = -18$

$C = -0.3$

$E_a = 23.5$ kJ/mol

Ignoring the induction period noticed at the start of some of the batch tests, this rate equation was found to accurately describe all of the batch data.

Continuous tests were performed in the same reactor in which the rate equation was derived, to compare the actual steady-state concentration of the manganese with that calculated by the rate equation. The rate equation was found to still apply in a continuous environment, the accuracy of the calculated manganese removal in most cases being close to 100 % (the least accurate calculated removal rate being 123 %) of the actual manganese removal rate.

An empirical rate equation was thus produced in this work that is useful in describing the rate at which manganese precipitates from solution by using a gas mixture of sulfur dioxide and oxygen, both under batch and continuous operation.

On its own, the rate equation cannot be used as a predictive tool since the dissolved oxygen concentration and the dissolved sulfur concentration need to be measured with time to calculate a manganese removal rate. To convert the rate equation into a predictive tool, the rate of oxygen mass transfer and the rate of sulfur dioxide mass transfer into the solution need to be combined with the rate equation for the manganese precipitation. Thus, there will be three differential equations that must be solved simultaneously using a numerical method. The three equations needed to predict the rate of manganese precipitation are:

$$d[\text{Mn}]/dt = A \cdot [\text{O}_2]_{\text{bulk}} \cdot (P_{\text{SO}_2}/P_{\text{tot}}) \cdot e^{(B \cdot [\text{S from gas}])} \cdot (1/pH + C) \cdot e^{(-E_a/RT)}$$

$$d[\text{O}_2]/dt = K_L a_1 ([\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{bulk}})$$

$$d[\text{S from gas}]/dt = K_L a_2 ([\text{S}_{\text{total}}]_{\text{sat}} - [\text{S from gas}])$$

In this work it was found that the rate of oxygen transfer as well as the rate of sulfur dioxide transfer from the gas phase into solution were not influenced by the rate of the manganese precipitation reaction. Therefore, the rate of oxygen transfer and the rate of sulfur dioxide transfer could be described by assuming that no reaction was taking place in solution and that physical dissolution alone described the rate at which oxygen and sulfur dioxide were absorbed by the solution.

6. RECOMMENDATIONS AND POSSIBLE FUTURE TESTWORK

The derived rate equation for the removal of manganese from solution using a gas mixture of sulfur dioxide and oxygen can be used as a first approximation for the design of a circuit using this technology. The rate equation will be very useful in large reactors where the conditions inside the reactor are not uniform (most probably in height). The rate equation can be used to define the rate of manganese removal at different heights in the reactor according to the aqueous sulfur obtained from the gas phase and the dissolved oxygen concentrations.

The rate equation was also derived from pure manganous sulfate solutions and it would be of value to investigate the accuracy of the rate equation when the manganese is removed from typical leach solutions containing cobalt and nickel.

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8. APPENDIX

(DATA TABLES FOR THE TESTWORK)

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Table 8-1: Sulfur Dioxide Uptake in Hydrogen Peroxide

Temperature	ambient °C	Gas Range:	N ₂ Flow:	470 ml/min
pH	-		SO ₂ Flow Rate:	30 ml/min
Peroxide Solution (30%)	270 ml			
Distilled Water	2.83 litres			
Percent peroxide in solution	8.7 % (v/v)			
Starting Volume	3015 ml			
Impeller Speed	varies rpm			

Test Number:	A5	(batch)			
N ₂ Flow Rate:	470	ml/min	actual flow	346	ml/min meter reading 1.0 Bar
SO ₂ Flow Rate:	30	ml/min	actual flow	22.7	ml/min meter reading 1.4 Bar
SO ₂ in Gas Mixture:	6.0	%			
Stirrer Speed	800	rpm			

vs. Ag/AgCl

Time (min)	Temperature (°C)	pH (-)	EMF (mV)	N ₂ Flow (ml/min)	SO ₂ Flow (ml/min)
0	17.5			470	30
5	17.9			470	30
10	18.2			470	30
20	19.1			470	30
30	19.8			470	30
40	20.5			470	30
50	21.2			470	30
60	21.8			470	30

Test Number:	A6	(batch)			
N ₂ Flow Rate:	470	ml/min	actual flow	346	ml/min meter reading 1.0 Bar
SO ₂ Flow Rate:	30	ml/min	actual flow	22.7	ml/min meter reading 1.0 Bar
SO ₂ in Gas Mixture:	6.0	%			
Stirrer Speed	800 rep	rpm			

vs. Ag/AgCl

Time (min)	Temperature (°C)	pH (-)	EMF (mV)	N ₂ Flow (ml/min)	SO ₂ Flow (ml/min)
0	16.8			470	30
5	17.2			470	30
10	17.6			470	30
20	18.4			470	30
30	19.1			470	30
40	19.8			470	30
50	20.5			470	30
60	21.0			470	30

Test Number:	A7	(batch)			
N ₂ Flow Rate:	470	ml/min	actual flow	346	ml/min meter reading 1.0 Bar
SO ₂ Flow Rate:	30	ml/min	actual flow	22.7	ml/min meter reading 1.1 Bar
SO ₂ in Gas Mixture:	6.0	%			
Stirrer Speed	600	rpm			

vs. Ag/AgCl

Time (min)	Temperature (°C)	pH (-)	EMF (mV)	N ₂ Flow (ml/min)	SO ₂ Flow (ml/min)
0	18.4			470	30
5	18.7			470	30
10	19.1			470	30
20	19.7			470	30
30	20.2			470	30
40	20.6			470	30
50	21.1			470	30
60	21.6			470	30

Table 8-1: Sulfur Dioxide Uptake in Hydrogen Peroxide (Continued)

Test A5

ml Volume of Sample	g/l Conc STB Sodium Tetra Borate	ml Volume of Sodium Tetra Borate	g STB Mass of Sodium Tetra Borate	moles STB Moles of Sodium Tetra Borate	moles of H2SO4 in sample	moles/litre acid	reactor volume (ml)	moles acid moles SO2 in reactor	SO2 ml that went into the reactor	moles SO2 In gas	Utilization of SO2	[S(IV)] mole/litre	Time (min)
25	12.8	0.10	0.0013	6.36E-08	6.36E-06	2.54E-04	3015	0.001	0		(%)		
20	12.8	0.40	0.0051	2.54E-05	2.54E-05	1.27E-03	3015	0.004	150	0.007		0.001	5
10	12.8	0.50	0.0064	3.18E-05	3.18E-05	3.18E-03	3015	0.010	300	0.013	72	0.003	10
10	12.8	1.00	0.0128	6.36E-05	6.36E-05	6.36E-03	3015	0.019	800	0.027	72	0.006	20
10	12.8	1.50	0.0192	9.54E-05	9.54E-05	9.54E-03	3015	0.029	900	0.040	72	0.010	30
10	12.8	2.20	0.0282	1.40E-04	1.40E-04	1.40E-02	3015	0.042	1200	0.054	79	0.014	40
10	12.8	2.60	0.0333	1.65E-04	1.65E-04	1.65E-02	3015	0.050	1500	0.067	74	0.017	50
10	12.8	3.25	0.0416	2.07E-04	2.07E-04	2.07E-02	3015	0.062	1800	0.080	78	0.021	60

Test A6

ml Volume of Sample	g/l Conc STB Sodium Tetra Borate	ml Volume of Sodium Tetra Borate	g STB Mass of Sodium Tetra Borate	moles STB Moles of Sodium Tetra Borate	moles of H2SO4 in sample	moles/litre acid	reactor volume (ml)	moles acid moles SO2 in reactor	SO2 ml that went into the reactor	moles SO2 In gas	Utilization of SO2	Dissolved SO2 mole/litre	Time (min)
25	12.8	0.10	0.0013	6.36E-08	6.36E-06	2.54E-04	3015	0.001	0		(%)		
25	12.8	0.70	0.0090	4.45E-05	4.45E-05	1.78E-03	3015	0.005	150	0.007	80	0.002	5
20	12.8	1.10	0.0141	7.00E-05	7.00E-05	3.50E-03	3015	0.011	300	0.013	79	0.003	10
20	12.8	2.10	0.0269	1.34E-04	1.34E-04	6.88E-03	3015	0.020	600	0.027	75	0.007	20
20	12.8	3.30	0.0422	2.10E-04	2.10E-04	1.05E-02	3015	0.032	900	0.040	79	0.010	30
20	12.8	4.40	0.0563	2.80E-04	2.80E-04	1.40E-02	3015	0.042	1200	0.054	79	0.014	40
20	12.8	5.50	0.0704	3.50E-04	3.50E-04	1.75E-02	3015	0.053	1500	0.067	79	0.017	50
20	12.8	6.70	0.0858	4.26E-04	4.26E-04	2.13E-02	3015	0.064	1800	0.080	80	0.021	60

Test A7

ml Volume of Sample	g/l Conc STB Sodium Tetra Borate	ml Volume of Sodium Tetra Borate	g STB Mass of Sodium Tetra Borate	moles STB Moles of Sodium Tetra Borate	moles of H2SO4 in sample	moles/litre acid	reactor volume (ml)	moles acid moles SO2 in reactor	SO2 ml that went into the reactor	moles SO2 In gas	Utilization of SO2	Dissolved SO2 mole/litre	Time (min)
25	12.8	0.20	0.0026	1.27E-05	1.27E-05	5.09E-04	3015	0.002	0		(%)		
25	12.8	0.70	0.0090	4.45E-05	4.45E-05	1.78E-03	3015	0.005	150	0.007	80	0.002	5
20	12.8	1.10	0.0141	7.00E-05	7.00E-05	3.50E-03	3015	0.011	300	0.013	79	0.003	10
20	12.8	2.10	0.0269	1.34E-04	1.34E-04	6.88E-03	3015	0.020	600	0.027	75	0.007	20
20	12.8	3.30	0.0422	2.10E-04	2.10E-04	1.05E-02	3015	0.032	900	0.040	79	0.010	30
20	12.8	4.50	0.0578	2.88E-04	2.88E-04	1.43E-02	3015	0.043	1200	0.054	81	0.014	40
20	12.8	5.50	0.0704	3.50E-04	3.50E-04	1.75E-02	3015	0.053	1500	0.067	79	0.017	50
20	12.8	6.60	0.0845	4.20E-04	4.20E-04	2.10E-02	3015	0.063	1800	0.080	79	0.021	60

Table 8-2: Batch Data for the Removal of Manganese at Two Different Impeller Speeds

Temperature	30 °C	Gas Range:	O ₂ Flow:	470 ml/min	
pH	4.0 -		SO ₂ Flow:	30 ml/min	6.0 % SO ₂
Mn Solution Conc.	1.5 g/l				
NaOH Solution Conc.	2 M				
Starting Volume	3015 ml				
Impeller Speed	varies rpm				

Test Number:	B1	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ in Gas Mixture:	6.0	%
Stirrer Speed	800	rpm

actual flow	346	ml/min	meter reading
actual flow	22.7	ml/min	meter reading

Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl		Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	(A.T.) Cumulative		Mn (mg/l)	X (fraction)	Mn ppt rate (moles/min)	S total (mg/l)	Total S uptake (moles)	Total Mn removed (moles)
			EMF (mV)	NaOH Used (ml)											
0	30.8		445	6.74	0	0	0.0	1448	0.00	0.00E+00	904				
5	30.5		645	22.5	470	30	5.7	1423	0.02	2.74E-04	930				
10	30.8		692	28.0	470	30	12.9	1385	0.04	4.17E-04	971				
15	30.7		692	29.8	470	30	20.0	1348	0.07	4.08E-04	1046				
20	30.7		690	30.1	470	30	28.0	1310	0.10	4.17E-04	1118				
30	30.6		699	30.3	470	30	42.3	1242	0.14	3.73E-04	1230				
40	30.5		701	30.4	470	30	56.5	1228	0.15	7.88E-05	1354				
50	30.2		702	30.5	470	30	70.2	1086	0.25	7.79E-04	1475				
60	30.1		703	30.6	470	30	83.7	1006	0.31	4.39E-04	1613	6.68E-02	2.42E-02		

Test Number:	B2	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ in Gas Mixture:	6.0	%
Stirrer Speed	600	rpm

actual flow	346	ml/min	meter reading
actual flow	22.7	ml/min	meter reading

Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl		Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	(A.T.) Cumulative		Mn (mg/l)	X (fraction)	Mn ppt rate (moles/min)	S total (mg/l)	Total S uptake (moles)	Total Mn removed (moles)
			EMF (mV)	NaOH Used (ml)											
0	30.1		484	6.53	0	0	0.0	1439	0.00	0.00E+00	855				
5	30.9		712	24.8	470	30	7.3	1426	0.01	1.43E-04	928				
10	31.2		710	28.3	470	30	14.2	1405	0.02	2.30E-04	985				
15	31.4		708	29.1	470	30	21.1	1377	0.04	3.07E-04	1049				
20	31.4		706	29.1	470	30	28.2	1326	0.08	5.60E-04	1080				
30	31.4		706	29.2	470	30	42.1	1240	0.14	4.72E-04	1189				
40	31.2		707	29.3	470	30	55.6	1185	0.18	3.02E-04	1305				
50	31.0		707	29.4	470	30	68.9	1110	0.23	4.11E-04	1439				
60	30.7		710	29.8	470	30	82.4	1045	0.27	3.57E-04	1559	6.62E-02	2.16E-02		

Table 8-3: Batch Data to Ensure Repeatability of the Testwork

Temperature	30 °C	Gas Range:	O ₂ Flow:	470 ml/min	
pH	4.0 -		SO ₂ Flow:	30 ml/min	6.0 % SO ₂
Mn Solution Conc.	1.5 g/l				
NaOH Solution Conc.	2 M				
Starting Volume	3015 ml				
Impeller Speed	800 rpm				

Test Number:	R 1	(batch)
O ₂ Flow Rate:	470	m ³ /min
SO ₂ Flow Rate:	30	m ³ /min
SO ₂ in Gas Mixture:	6.0	%
Stirrer Speed	800	rpm

actual flow
actual flow

346	m ³ /min	meter reading
22.7	m ³ /min	meter reading

Average Mn precipitation rate:	3.71E-04	moles/min
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vs. Ag/AgCl			Cumulative										NaOH used to neutralize H ₂ SO ₄ from Mn reaction		NaOH used in total		Percentage of dissolved SO ₂ used to ppt Mn
Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Total S uptake (moles)	Total Mn removed (moles)	NaOH used to neutralize H ₂ SO ₄ from Mn reaction (moles)		NaOH used in total (moles)		Percentage of dissolved SO ₂ used to ppt Mn	
0	29.9	484	8.8	470	30	0.0	1459	0.00	923								
5	30.4	700	25.2	470	30	5.0	1458	0.00	968	4.04E-03	5.49E-05	2.19E-04	1.00E-02		1.4		
10	30.6	701	29.0	470	30	11.7	1436	0.02	1016	8.74E-03	1.26E-03	5.05E-03	2.33E-02		14.4		
15	30.7	701	29.8	470	30	18.8	1391	0.05	1074	1.42E-02	3.73E-03	1.46E-02	3.76E-02		26.3		
20	30.7	700	30.0	470	30	25.8	1365	0.06	1130	1.95E-02	5.16E-03	2.06E-02	5.17E-02		26.5		
30	30.6	701	30.2	470	30	39.6	1284	0.13	1259	3.16E-02	1.07E-02	4.28E-02	7.93E-02		33.9		
40	30.5	702	30.3	470	30	53.1	1181	0.19	1367	4.17E-02	1.53E-02	6.10E-02	1.06E-01		36.5		
50	30.3	703	30.5	470	30	66.6	1118	0.23	1509	5.51E-02	1.87E-02	7.48E-02	1.33E-01		34.0		
60	30.2	705	30.6	470	30	79.8	1053	0.28	1626	6.61E-02	2.23E-02	8.91E-02	1.60E-01		33.7		

Test Number:	R 2	(batch)
O ₂ Flow Rate:	470	m ³ /min
SO ₂ Flow Rate:	30	m ³ /min
SO ₂ in Gas Mixture:	8.0	%
Stirrer Speed	800	rpm

actual flow
actual flow

346	m ³ /min	meter reading
22.7	m ³ /min	meter reading

Average Mn precipitation rate:	3.89E-04	moles/min
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vs. Ag/AgCl			Cumulative										NaOH used to neutralize H ₂ SO ₄ from Mn reaction		NaOH used in total		Percentage of dissolved SO ₂ used to ppt Mn
Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Total S uptake (moles)	Total Mn removed (moles)	NaOH used to neutralize H ₂ SO ₄ from Mn reaction (moles)		NaOH used in total (moles)		Percentage of dissolved SO ₂ used to ppt Mn	
0	30.5	499	8.53	470	30	0.0	1454	0.00	904								
5	30.9	650	25.00	470	30	5.3	1431	0.02	983	5.55E-03	1.28E-03	5.05E-03	1.06E-02		40.9		
10	31.0	701	28.70	470	30	12.1	1412	0.03	1015	1.04E-02	2.30E-03	9.22E-03	2.43E-02		29.8		
15	31.1	702	29.40	470	30	18.9	1388	0.06	1083	1.88E-02	4.83E-03	1.93E-02	3.78E-02		33.9		
20	31.1	701	29.50	470	30	25.7	1325	0.09	1123	2.06E-02	7.08E-03	2.83E-02	5.15E-02		39.1		
30	31.1	703	29.70	470	30	39.6	1253	0.14	1251	3.28E-02	1.10E-02	4.41E-02	7.91E-02		36.7		
40	31.1	703	29.80	470	30	53.3	1178	0.19	1399	4.65E-02	1.53E-02	6.10E-02	1.07E-01		34.7		
50	31.0	705	29.90	470	30	66.4	1104	0.24	1507	5.67E-02	1.92E-02	7.68E-02	1.33E-01		35.5		
60	30.8	706	30.00	470	30	80.0	1029	0.29	1624	6.77E-02	2.33E-02	9.33E-02	1.60E-01		35.8		

Table 8-3: Batch Data to Ensure Repeatability of the Testwork (Continued)

Test Number:	R 3	(batch)																
O ₂ Flow Rate:	470	mL/min	actual flow															
SO ₂ Flow Rate:	30	mL/min	actual flow															
SO ₂ in Gas Mixture:	6.0	%																
Stirrer Speed	800	rpm																
			vs. Ag/AgCl															
Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (mL/min)	SO ₂ Flow (mL/min)	Cumulative NaOH Used (mL)	Mn (mg/L)	X (fraction)	S total (mg/L)	Total S uptake (moles)	Total Mn removed (moles)	NaOH used to neutralize H ₂ SO ₄ from Mn reaction (moles)	NaOH used in total (moles)	Percentage of dissolved SO ₂ used to ppt Mn				
0	29.9	538	6.6	470	30	0.0	1445	0.00	900									
5	30.6	675	26.2	470	30	4.6	1423	0.02	972	6.77E-03	1.21E-03	4.83E-03	9.18E-03	42.9				
15	31.3	700	29.4	470	30	18.6	1353	0.06	1080	1.69E-02	5.05E-03	2.02E-02	3.72E-02	39.4				
20	31.4	700	29.6	470	30	25.5	1326	0.08	1113	2.00E-02	6.53E-03	2.61E-02	5.11E-02	40.9				
30	31.6	700	29.7	470	30	39.1	1245	0.14	1225	3.05E-02	1.10E-02	4.39E-02	7.81E-02	41.4				
40	31.5	700	29.8	470	30	53.1	1174	0.19	1350	4.23E-02	1.49E-02	5.95E-02	1.06E-01	39.0				
50	31.5	703	29.8	470	30	66.2	1104	0.24	1482	5.47E-02	1.87E-02	7.48E-02	1.32E-01	37.1				
60	31.4	704	29.6	470	30	79.6	1027	0.29	1581	6.40E-02	2.29E-02	9.17E-02	1.59E-01	38.3				

Average Mn precipitation rate:	3.82E-04	moles/min
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Test Number:	R 4	(batch)																
O ₂ Flow Rate:	470	mL/min	actual flow															
SO ₂ Flow Rate:	30	mL/min	actual flow															
SO ₂ in Gas Mixture:	6.0	%																
Stirrer Speed	800	rpm																
			vs. Ag/AgCl															
Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (mL/min)	SO ₂ Flow (mL/min)	Cumulative NaOH Used (mL)	Mn (mg/L)	X (fraction)	S total (mg/L)	Total S uptake (moles)	Total Mn removed (moles)	NaOH used to neutralize H ₂ SO ₄ from Mn reaction (moles)	NaOH used in total (moles)	Percentage of dissolved SO ₂ used to ppt Mn				
0	30.1	484	8.53	0	0	0.0	1439	0.00	855									
5	30.9	712	24.6	470	30	7.3	1426	0.01	928	6.66E-03	7.13E-04	2.85E-03	1.46E-02	38.2				
10	31.2	710	28.3	470	30	14.2	1405	0.02	985	1.22E-02	1.87E-03	7.46E-03	2.84E-02	50.8				
15	31.4	708	29.1	470	30	21.1	1377	0.04	1049	1.82E-02	3.40E-03	1.36E-02	4.22E-02	38.0				
20	31.4	708	29.1	470	30	28.2	1326	0.08	1080	2.11E-02	6.20E-03	2.48E-02	5.64E-02	49.4				
30	31.4	708	29.2	470	30	42.1	1240	0.14	1189	3.14E-02	1.09E-02	4.37E-02	8.41E-02	48.1				
40	31.2	707	29.3	470	30	55.6	1185	0.18	1305	4.23E-02	1.39E-02	5.57E-02	1.11E-01	41.9				
50	31.0	707	29.4	470	30	68.9	1110	0.23	1439	5.49E-02	1.80E-02	7.22E-02	1.38E-01	39.5				
60	30.7	710	29.6	470	30	82.4	1045	0.27	1559	6.62E-02	2.18E-02	8.65E-02	1.65E-01	38.0				

Average Mn precipitation rate:	3.60E-04	moles/min
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Table 8-4: Batch Data Varying the Gas Mixture

	30 °C	Gas Range:	SO ₂ Flow:	O ₂ Flow:			Average Mn	Average Mn	Total Dissolved
							precipitation rate	precipitation rate	SO ₂
							over the first 60min	over the first 60min	
Temperature	30 °C						M/min	mM/min	(moles/litre)
pH	4.0 -		5	495	ml/min	1.0 % SO ₂	4.37E-05	4.37E-02	4.12E-03
Mn Solution Conc.	1.5 g/l		15	485	ml/min	3.0 % SO ₂	8.43E-05	8.43E-02	1.05E-02
NaOH Solution Conc.	2 M		30	470	ml/min	6.0 % SO ₂	1.31E-04	1.31E-01	2.25E-02
Starting Volume	3015 ml		45	465	ml/min	9.0 % SO ₂	1.79E-04	1.79E-01	3.05E-02
Impeller Speed	800 rpm		60	440	ml/min	12.0 % SO ₂	2.28E-04	2.28E-01	4.14E-02
			75	425	ml/min	15.0 % SO ₂	2.14E-04	2.14E-01	5.33E-02
			100	400	ml/min	20.0 % SO ₂	2.00E-04	2.00E-01	6.47E-02

Test Number:	C1	(batch)
O ₂ Flow Rate:	495	m/min actual flow
SO ₂ Flow Rate:	5	ml/min actual flow
SO ₂ in Gas :	1.0	% SO ₂

365	ml/min	meter reading
4.5	ml/min	meter reading

Average Mn precipitation rate:	4.37E-05	d[Mn]/dt (M/min)
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Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn Conc (mg/l)	Mn Precipitated (moles/litre)	Mn Removed (X)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	PSO ₂ /Ptot x exp(-18x[S from gas])	Percentage of dissolved SO ₂ used to ppt Mn
0	29.9	519	6.6	0	0	0.0	1443	0.00E+00	0.00	888	0.00E+00	0.00E+00	2.83E-02	0	0	0	0
10	30.0	701	29.4	495	5	2.4	1428	2.73E-04	0.01	911	2.73E-05	3.27E-04	2.80E-02	0.0010	7.17E-04	9.87E-03	35.1
20	30.0	694	30.2	495	5	5.6	1402	7.46E-04	0.03	929	4.73E-05	3.74E-04	2.55E-02	0.0018	1.28E-03	9.77E-03	58.4
30	30.0	692	30.2	495	5	8.5	1369	1.35E-03	0.05	962	6.01E-05	9.05E-04	2.49E-02	0.0023	2.31E-03	9.59E-03	58.4
40	29.9	692	30.2	495	5	11.7	1341	1.86E-03	0.07	976	6.10E-05	8.10E-04	2.44E-02	0.0019	2.74E-03	9.62E-03	67.7
50	30.1	691	30.3	495	5	15.0	1324	2.17E-03	0.08	1013	3.09E-05	1.41E-03	2.41E-02	0.0012	3.90E-03	9.32E-03	55.6
60	30.7	691	30.1	495	5	18.1	1299	2.62E-03	0.10	1020	4.55E-05	1.11E-03	2.36E-02	0.0017	4.12E-03	9.29E-03	63.7

Test Number:	C2	(batch)
O ₂ Flow Rate:	485	m/min actual flow
SO ₂ Flow Rate:	15	ml/min actual flow
SO ₂ in Gas :	3.0	% SO ₂

358	ml/min	meter reading
11.8	ml/min	meter reading

Average Mn precipitation rate:	8.43E-05	d[Mn]/dt (M/min)
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Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	Mn Removed (X)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	PSO ₂ /Ptot x exp(-18x[S from gas])	Percentage of dissolved SO ₂ used to ppt Mn
0	29.8	521	6.6	0	0	0.0	1465	0.00E+00	0.00	905	0.00E+00	0.00E+00	2.87E-02	0	0	0	0
10	30.2	700	29.5	485	15	6.0	1433	5.82E-04	0.02	938	5.82E-05	2.98E-05	2.81E-02	0.0022	1.03E-03	2.94E-02	56.8
20	30.4	695	30.0	485	15	13.7	1389	1.75E-03	0.07	999	1.16E-04	6.65E-04	2.49E-02	0.0044	2.93E-03	2.85E-02	59.6
30	30.4	695	30.0	485	15	21.4	1331	2.44E-03	0.09	1047	6.92E-05	8.78E-04	2.42E-02	0.0026	4.43E-03	2.77E-02	55.1
40	30.4	698	30.2	485	15	28.9	1287	3.24E-03	0.12	1102	8.01E-06	1.35E-03	2.34E-02	0.0030	6.14E-03	2.69E-02	52.7
50	30.3	698	30.2	485	15	38.6	1244	4.02E-03	0.15	1180	7.83E-05	1.89E-03	2.29E-02	0.0029	7.95E-03	2.60E-02	50.6
60	30.3	698	30.3	485	15	44.2	1187	5.08E-03	0.19	1242	1.04E-04	3.19E-03	2.16E-02	0.0039	1.05E-02	2.48E-02	48.1

Test Number:	C3	(batch)
O ₂ Flow Rate:	455	m/min actual flow
SO ₂ Flow Rate:	45	ml/min actual flow
SO ₂ in Gas :	9.0	% SO ₂

334	ml/min	meter reading
33.7	ml/min	meter reading

Average Mn precipitation rate:	1.79E-04	d[Mn]/dt (M/min)
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Time (min)	Temperature (°C)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	Mn Removed (X)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	PSO ₂ /Ptot x exp(-18x[S from gas])	Percentage of dissolved SO ₂ used to ppt Mn
0	30.0	490	6.6	0	0	0.0	1444	0.00E+00	0.00	878	0.00E+00	0.00E+00	2.83E-02	0	0	0	0
10	30.4	695	29.0	455	45	17.9	1333	2.02E-03	0.08	1038	2.02E-04	2.03E-03	2.43E-02	0.0077	4.99E-03	8.23E-02	40.5
20	30.6	702	30.0	455	45	37.7	1217	4.13E-03	0.16	1180	2.11E-04	3.18E-03	2.22E-02	0.0080	9.42E-03	7.60E-02	43.9
30	30.7	703	30.1	455	45	57.5	1120	5.90E-03	0.22	1350	1.77E-04	5.19E-03	2.04E-02	0.0067	1.47E-02	6.91E-02	40.1
40	30.7	705	30.1	455	45	76.9	1015	7.81E-03	0.30	1500	1.91E-04	6.66E-03	1.85E-02	0.0073	1.94E-02	6.35E-02	40.3
50	30.7	707	30.1	455	45	96.2	934	9.28E-03	0.35	1669	1.47E-04	8.72E-03	1.70E-02	0.0056	2.47E-02	5.77E-02	37.6
60	30.7	709	30.2	455	45	116.6	854	1.07E-02	0.41	1857	1.46E-04	1.12E-02	1.55E-02	0.0055	3.05E-02	5.19E-02	35.2

Table 8-4: Batch Data Varying the Gas Mixture (Continued)

Test Number:	R 2	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ In Gas :	6.0	% SO ₂

actual flow
actual flow

346	ml/min	meter reading
22.7	ml/min	meter reading

Average Mn precipitation rate:	1.31E-04	d[Mn]/dt	(M/min)
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Time (min)	Temperature (°C)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	Mn Removed X	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	PSO ₂ /Ptot x exp(-18x[S from gas])	Percentage of dissolved SO ₂ used to ppt Mn
0	30.5	499	5.5	470	30	0.0	1454	0.00E+00	0.00	904	0.00E+00	0.00E+00	2.65E-02	0	0	0	0
20	31.1	701	29.5	470	30	25.7	1325	2.35E-03	0.09	1123	1.17E-04	2.57E-03	2.41E-02	0.0044	6.83E-03	5.31E-02	34.4
30	31.1	703	29.7	470	30	39.6	1253	3.66E-03	0.14	1251	1.31E-04	4.27E-03	2.28E-02	0.0050	1.08E-02	4.84E-02	33.8
40	31.1	703	29.8	470	30	53.3	1176	5.06E-03	0.19	1399	1.40E-04	6.61E-03	2.14E-02	0.0063	1.54E-02	4.64E-02	32.8
50	31.0	705	29.9	470	30	66.4	1104	6.37E-03	0.24	1507	1.31E-04	7.81E-03	2.01E-02	0.0050	1.88E-02	4.28E-02	33.9
60	30.8	706	30.0	470	30	80.0	1029	7.74E-03	0.29	1624	1.37E-04	9.20E-03	1.87E-02	0.0052	2.25E-02	4.01E-02	34.5

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Table 8-5: Batch Data Varying the Initial Manganese Concentration

Temperature	30 °C	Gas Range:	O2 Flow:	470 ml/min
pH	4.0 -		SO2 Flow:	30 ml/min
Mn Solution Conc.	varies g/l			6.0 % SO2
NaOH Solution Conc.	2 M			
Starting Volume	3015 ml			
Impeller Speed	800 rpm			

Initial Mn conc (mM)	Average Mn precipitation rate: d[Mn]/dt
72.81	0.1450
9.10	0.1129
4.55	0.0955
27.30	0.1195

Test Number:	D1	(batch)
O2 Flow Rate:	470 ml/min	actual flow
SO2 Flow Rate:	30 ml/min	actual flow
SO2 in Gas Mixture:	6.0 %	
Initial [Mn]	4.0 g/l	

346 ml/min	meter reading
22.7 ml/min	meter reading

Average Mn precipitation rate:	0.1450	d[Mn]/dt	(mM/min)
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Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O2 (ppm)	O2 Flow (ml/min)	SO2 Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)
0	29.5		455	6.7	0	0	0.0	3855	0.00E+00	0.00	2396	0.00E+00	0.00E+00	7.04E-02	0.00E+00	0
10	30.4		880	29.5	470	30	10.1	3797	1.24E-03	0.02	2487	1.24E-04	1.18E-03	8.91E-02	1.76E-03	2.84E-03
20	30.7		880	30.1	470	30	23.0	3723	2.58E-03	0.04	2564	1.35E-04	1.43E-03	6.78E-02	1.91E-03	5.24E-03
30	30.7		878	30.2	470	30	35.8	3817	4.51E-03	0.08	2685	1.93E-04	3.09E-03	6.58E-02	2.74E-03	9.01E-03
40	30.6		878	30.3	470	30	48.9	3527	6.15E-03	0.09	2777	1.64E-04		6.42E-02		1.19E-02
50	30.5		681	30.3	470	30	82.2	3417	8.15E-03	0.12	2871	2.00E-04	4.51E-03	6.22E-02	2.85E-03	1.48E-02
60	30.3		682	30.4	470	30	75.4	3387	8.70E-03	0.12	3037	5.46E-05	7.49E-03	6.17E-02	7.76E-04	2.00E-02

Test Number:	D3	(batch)
O2 Flow Rate:	470 ml/min	actual flow
SO2 Flow Rate:	30 ml/min	actual flow
SO2 in Gas Mixture:	6.0 %	
Initial [Mn]	0.50 g/l	

346 ml/min	meter reading
22.7 ml/min	meter reading

Average Mn precipitation rate:	0.1129	d[Mn]/dt	(mM/min)
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Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O2 (ppm)	O2 Flow (ml/min)	SO2 Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)
0	29.5		504	6.6	0	0	0.0	488	0.00E+00	0.00	304	0.00E+00	0.00E+00	8.52E-03	0.00E+00	0
10	29.9		707	28.8	470	30	14.8	397	1.29E-03	0.15	409	1.29E-04	8.28E-04	7.23E-03	1.52E-02	3.27E-03
20	30.1		706	29.7	470	30	28.9	313	2.82E-03	0.33	567	1.53E-04		5.70E-03	1.79E-02	8.20E-03
30	30.1		712	29.8	470	30	42.5	249	3.99E-03	0.47	645	1.18E-04	3.59E-03	4.53E-03	1.37E-02	1.08E-02
40	30.1		717	29.8	470	30	58.3	193	5.01E-03	0.59	757	1.02E-04	4.80E-03	3.51E-03	1.20E-02	1.41E-02
50	30.0		723	30.0	470	30	69.3	140	5.97E-03	0.70	877	9.95E-05	6.39E-03	2.55E-03	1.13E-02	1.79E-02
60	29.9		729	30.1	470	30	81.5	96	6.77E-03	0.79	1027	8.01E-05	9.05E-03	1.75E-03	9.40E-03	2.25E-02

Test Number:	D4	(batch)
O2 Flow Rate:	470 ml/min	actual flow
SO2 Flow Rate:	30 ml/min	actual flow
SO2 in Gas Mixture:	6.0 %	
Initial [Mn]	0.25 g/l	

346 ml/min	meter reading
22.7 ml/min	meter reading

over 40 minutes	Average Mn precipitation rate:	0.0955	d[Mn]/dt	(mM/min)
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Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O2 (ppm)	O2 Flow (ml/min)	SO2 Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	Mn Precipitated (moles/litre)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)
0	29.5		530	6.6	0	0	0.0	229	0.00E+00	0.00	151	0.00E+00	0.00E+00	4.17E-03	0.00E+00	0
10	29.9		724	28.7	470	30	12.2	170	1.07E-03	0.28	249	1.07E-04	1.03E-03	3.09E-03	2.58E-02	3.08E-03
20	30.1		727	29.7	470	30	25.9	104	2.28E-03	0.55	373	1.20E-04	2.82E-03	1.89E-03	2.88E-02	6.92E-03
30	30.1		737	29.8	470	30	39.1	51	3.25E-03	0.78	484	9.74E-05	3.90E-03	9.19E-04	2.34E-02	1.04E-02
40	30.1		750	29.9	470	30	51.0	19	3.82E-03	0.92	604	5.72E-05	5.67E-03	3.48E-04	1.37E-02	1.41E-02
50	30.0		760	30.0	470	30	61.9	12	3.98E-03	0.95	748	1.37E-05	8.30E-03	2.11E-04	3.28E-03	1.88E-02
60	29.8		781	30.1	470	30	71.7	10	3.98E-03	0.98	888	2.73E-06	1.11E-02	1.84E-04	6.55E-04	2.30E-02

Table 8-6: Batch Data Varying the Solution Temperature

Temperature	varies °C	Gas Range:	O ₂ Flow:	470 ml/min	Temperature	Average Mn precipitation rate:	Temperature	lnR	lnR (divided by [O ₂])	1/T	exp(-Ea/RT)
pH	4.0 -		SO ₂ Flow:	30 ml/min	degrees C	M/min	Kelvin	ln(d[Mn]/dt)		1/Kelvin	
Mn Solution Conc.	1.5 g/l				40.5	0.00016	314	-8.485	-1.216	0.0031	0.0002
NaOH Solution Conc.	2 M				22.5	0.00011	298	-8.751	-1.631	0.0032	0.0001
Starting Volume	3015 ml				30.4	0.00012	303	-9.114	-2.284	0.0034	0.0001
Impeller Speed	800 rpm							-9.058	-2.105	0.0033	0.0001

slope = (Ea/R) = 2832
 Activation Energy = 23.5 kJ/mol [O₂] taken as constant

slope = (Ea/R) = 4396
 Activation Energy = 36.5 kJ/mol [O₂] not a constant

Test Number:	E1	(batch)
O ₂ Flow Rate:	470	ml/min actual flow
SO ₂ Flow Rate:	30	ml/min actual flow
SO ₂ in Gas:	6.0	%
Temperature	50	degrees C

346	ml/min	meter reading
22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00021	d[Mn]/dt in M/min	40 - 60min
Average Mn precipitation rate:	0.29848	d[Mn]/dt/[O ₂]	40 - 60min

Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	Mn Removed (moles/litre)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
0	50.4		481	4.9	0	0	0.0	1400	0.00E+00	0.00	887	0.00E+00	0.00E+00	2.55E-02	0.00E+00	0	0
10	50.4		864	21.9	470	30	13.8	1332	1.24E-03	0.06	980	1.24E-04	6.44E-04	2.42E-02	4.86E-03	2.90E-03	42.7
20	50.4		861	22.2	470	30	29.0	1226	3.19E-03	0.13	1079	1.95E-04	1.18E-03	2.23E-02	7.64E-03	5.99E-03	53.2
30	50.0		864	22.5	470	30	44.2	1134	4.84E-03	0.19	1205	1.86E-04	2.59E-03	2.08E-02	6.50E-03	9.92E-03	48.8
40	50.1		865	22.4	470	30	59.7	1021	6.90E-03	0.27	1294	2.06E-04	2.81E-03	1.88E-02	8.07E-03	1.27E-02	54.4
50	50.2		868	22.3	470	30	73.6	925	8.65E-03	0.34	1394	1.75E-04	3.61E-03	1.68E-02	6.86E-03	1.58E-02	54.7
60	50.2		870	22.3	470	30	87.7	794	1.10E-02	0.43	1520	2.38E-04	5.21E-03	1.45E-02	9.36E-03	1.97E-02	55.9

[O₂] in moles/l: 0.00089876

Test Number:	E2	(batch)
O ₂ Flow Rate:	470	ml/min actual flow
SO ₂ Flow Rate:	30	ml/min actual flow
SO ₂ in Gas:	6.0	%
Temperature	40	degrees C

346	ml/min	meter reading
22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00016	d[Mn]/dt in M/min	40 - 60min
Average Mn precipitation rate:	0.19566	d[Mn]/dt/[O ₂]	40 - 60min

Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	Mn Removed (moles/litre)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
0	40.6		492	6.6	0	0	0.0	1432	0.00E+00	0.00	880	0.00E+00	0.00E+00	2.81E-02	0.00E+00	0	0
10	40.8		874	24.8	470	30	13.0	1370	1.13E-03	0.04	986	1.13E-04	4.98E-04	2.49E-02	4.33E-03	2.85E-03	42.8
20	40.6		875	25.5	470	30	27.8	1247	3.37E-03	0.13	1075	2.24E-04	1.47E-03	2.27E-02	8.59E-03	6.08E-03	55.4
30	40.6		878	25.6	470	30	42.7	1169	5.02E-03	0.19	1185	1.66E-04	2.43E-03	2.10E-02	6.35E-03	9.51E-03	52.8
40	40.8		878	25.6	470	30	57.3	1060	6.77E-03	0.28	1291	1.75E-04	3.32E-03	1.93E-02	6.70E-03	1.28E-02	52.8
50	40.5		882	25.7	470	30	71.1	970	8.41E-03	0.32	1397	1.64E-04	4.34E-03	1.77E-02	6.28E-03	1.61E-02	52.2
60	40.0		885	25.9	470	30	85.8	886	9.94E-03	0.38	1513	1.63E-04	5.56E-03	1.61E-02	5.87E-03	1.97E-02	50.3

[O₂] in moles/l: 0.00089876

Table 8-6: Batch Data Varying the Solution Temperature (Continued)

Test Number: E4 (batch)			actual flow		346 ml/min meter reading		actual flow		22.7 ml/min meter reading		Average Mn precipitation rate: 0.00011 d[Mn]/dt in M/min 40 - 60min		Average Mn precipitation rate: 0.10185 d[Mn]/dV[O2] 40 - 60min					
O ₂ Flow Rate: 470 ml/min																		
SO ₂ Flow Rate: 30 ml/min																		
SO ₂ In Gas: 6.0 %																		
Temperature: 20 degrees C																		
			vs. Ag/AgCl		(A.T.)		Cumulative				Incremental Mn		Incremental Mn		Percentage of			
Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	Mn Removed (moles/litre)	X (fraction)	S total (mg/l)	Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn	
0	21.5		487	7.7	0	0	0.0	1430	0.00E+00	0.00	884	0.00E+00	0.00E+00	2.80E-02	0.00E+00	0	0	
10	22.1		674	33.8	470	30	11.1	1389	7.46E-04	0.03	984	7.46E-05	1.28E-03	2.53E-02	2.87E-03	3.12E-03	23.9	
20	22.5		703	34.8	470	30	24.0	1321	1.98E-03	0.08	1077	1.24E-04	2.05E-03	2.40E-02	4.76E-03	6.02E-03	33.0	
30	22.7		710	34.8	470	30	36.5	1274	2.84E-03	0.11	1186	8.66E-05	3.38E-03	2.32E-02	3.29E-03	9.42E-03	30.2	
40	22.8		713	34.7	470	30	49.4	1225	3.73E-03	0.14	1289	8.92E-05	4.45E-03	2.23E-02	3.43E-03	1.26E-02	29.5	
50	23.0		712	34.6	470	30	61.8	1164	4.84E-03	0.19	1400	1.11E-04	5.84E-03	2.12E-02	4.27E-03	1.61E-02	30.1	
60	23.1		712	34.6	470	30	74.4	1104	5.93E-03	0.23	1503	1.09E-04	6.98E-03	2.01E-02	4.20E-03	1.93E-02	30.7	
			[O ₂] in moles/l:		0.00108126													

Test Number: R 1 (batch)			actual flow		346 ml/min meter reading		actual flow		22.7 ml/min meter reading		Average Mn precipitation rate: 0.00012 d[Mn]/dt in M/min 40 - 60min		Average Mn precipitation rate: 0.12182 d[Mn]/dV[O2] 40 - 60min					
O ₂ Flow Rate: 470 ml/min																		
SO ₂ Flow Rate: 30 ml/min																		
SO ₂ In Gas: 6.0 %																		
Temperature: 30 degrees C																		
			vs. Ag/AgCl		(A.T.)		Cumulative				Incremental Mn		Incremental Mn		Percentage of			
Time (min)	Temperature (°C)	pH (A.T.) (-)	EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	NaOH Used (ml)	Mn (mg/l)	Mn Removed (moles/litre)	X (fraction)	S total (mg/l)	Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn	
0	29.9		464	6.6	470	30	0.0	1459	0.00E+00	0.00	923	0.00E+00	0.00E+00	2.66E-02	0.00E+00	0	0	
10	30.6		701	29.0	470	30	11.7	1436	4.19E-04	0.02	1016	4.19E-05	8.69E-04	2.81E-02	1.58E-03	2.90E-03	14.4	
20	30.7		700	30.0	470	30	25.8	1365	1.71E-03	0.06	1130	1.29E-04	2.17E-03	2.48E-02	4.87E-03	6.46E-03	26.6	
30	30.6		701	30.2	470	30	39.6	1264	3.56E-03	0.13	1259	1.84E-04	3.91E-03	2.30E-02	6.82E-03	1.05E-02	33.9	
40	30.5		702	30.3	470	30	53.1	1181	5.06E-03	0.19	1367	1.51E-04	5.05E-03	2.15E-02	5.69E-03	1.38E-02	36.5	
50	30.3		703	30.5	470	30	66.6	1118	6.21E-03	0.23	1509	1.16E-04	7.24E-03	2.04E-02	4.32E-03	1.83E-02	34.0	
60	30.2		705	30.6	470	30	79.8	1053	7.39E-03	0.28	1626	1.18E-04	8.71E-03	1.92E-02	4.46E-03	2.19E-02	33.7	
			[O ₂] in moles/l:		0.00096626													

Table 8-7: Batch Data Varying the pH of the Solution

Temperature	30 °C	Gas Range:	O ₂ Flow:	470 ml/min
pH	varies -		SO ₂ Flow:	30 ml/min
Mn Solution Conc.	1.5 g/l			
NaOH Solution Conc.	2 M			
Starting Volume	3015 ml			
Impeller Speed	800 rpm			

pH	Average Mn precipitation		
	rate:	1/pH	1/pH - 0.3
-	M/min	-	-
8.0	0.00033	0.167	-0.133
5.0	0.00026	0.200	-0.100
4.5	0.00023	0.222	-0.078
3.5	0.00003	0.286	-0.014
4.0	0.00012	0.250	-0.050

Test Number:	F1	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ in Gas Mixture:	6.0	%
pH	6.0	pH

actual flow	346	ml/min	meter reading
actual flow	22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00033	d[Mn]/dt	M/min
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Time (min)	Temperature (°C)	pH (A.T.) (-)	(A.T.) vs. Ag/AgCl											Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
			EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)									
0	29.8		368	6.4	0	0	0.0	1389	0.00	879	0.00E+00	0.00E+00	2.53E-02	0.00E+00	0	0			
10	30.3		437	28.8	470	30	19.3	1228	0.12	971	2.93E-04	-3.35E-04	2.24E-02	1.18E-02	2.87E-03	102.1			
20	30.6		427	28.9	470	30	39.4	1011	0.27	1082	3.95E-04	-2.01E-04	1.84E-02	1.58E-02	6.33E-03	108.7			
30	30.7		432	29.0	470	30	60.0	788	0.43	1200	3.88E-04	6.69E-05	1.45E-02	1.53E-02	1.00E-02	107.5			
40	30.6		437	29.0	470	30	79.5	624	0.55	1287	3.17E-04	-4.55E-04	1.14E-02	1.25E-02	1.27E-02	109.4			
50	30.6		442	29.0	470	30	98.0	461	0.67	1449	2.97E-04	1.53E-03	8.39E-03	1.17E-02	1.78E-02	95.0			
60	30.5		447	29.1	470	30	115.2	309	0.78	1531	2.77E-04	1.24E-03	5.62E-03	1.09E-02	2.03E-02	96.7			

Test Number:	F2	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ in Gas Mixture:	6.0	%
pH	5.0	pH

actual flow	346	ml/min	meter reading
actual flow	22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00026	d[Mn]/dt	M/min
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Time (min)	Temperature (°C)	pH (A.T.) (-)	(A.T.) vs. Ag/AgCl											Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
			EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)									
0	29.6		415	6.5	0	0	0.0	1370	0.00	893	0.00E+00	0.00E+00	2.49E-02	0.00E+00	0	0			
10	30.2		565	28.4	470	30	17.5	1220	0.11	984	2.73E-04	-7.02E-05	2.22E-02	1.09E-02	2.84E-03	96.2			
20	30.4		565	29.2	470	30	35.9	1084	0.21	1091	2.48E-04	2.24E-04	1.97E-02	9.93E-03	6.17E-03	84.3			
30	30.4		568	29.3	470	30	54.2	921	0.33	1213	2.97E-04	1.00E-03	1.68E-02	1.19E-02	8.98E-03	81.9			
40	30.4		570	29.3	470	30	70.8	777	0.43	1308	2.62E-04	1.18E-03	1.41E-02	1.05E-02	1.29E-02	83.8			
50	30.4		574	29.4	470	30	87.7	658	0.52	1428	2.20E-04	2.08E-03	1.19E-02	8.83E-03	1.66E-02	78.2			
60	30.3		574	29.4	470	30	104.1	526	0.62	1554	2.37E-04	3.36E-03	9.57E-03	9.49E-03	2.06E-02	74.5			

Test Number:	F3	(batch)
O ₂ Flow Rate:	470	ml/min
SO ₂ Flow Rate:	30	ml/min
SO ₂ in Gas Mixture:	6.0	%
pH	4.5	pH

actual flow	346	ml/min	meter reading
actual flow	22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00023	d[Mn]/dt	M/min
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Time (min)	Temperature (°C)	pH (A.T.) (-)	(A.T.) vs. Ag/AgCl											Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
			EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)									
0	29.6		448	6.7	0	0	0.0	1427	0.00	857	0.00E+00	0.00E+00	2.60E-02	0.00E+00	0	0			
10	30.2		631	29.5	470	30	15.5	1283	0.10	921	2.62E-04	-5.78E-04	2.34E-02	1.01E-02	2.00E-03				
20	30.4		627	30.2	470	30	33.0	1186	0.18	1014	2.13E-04	-5.68E-04	2.12E-02	8.20E-03	4.90E-03	97.0			
30	30.4		628	30.3	470	30	50.2	1022	0.28	1172	2.62E-04	1.51E-03	1.88E-02	1.01E-02	9.82E-03	75.0			
40	30.4		632	30.4	470	30	66.8	898	0.37	1303	2.29E-04	2.83E-03	1.63E-02	8.83E-03	1.39E-02	69.5			
50	30.3		632	30.4	470	30	82.7	763	0.47	1399	2.42E-04	3.19E-03	1.39E-02	9.32E-03	1.69E-02	71.5			
60	30.2		641	30.5	470	30	98.9	662	0.54	1533	1.84E-04	4.69E-03	1.20E-02	7.08E-03	2.11E-02	66.1			

Table 8-7: Batch Data Varying the pH of the Solution (Continued)

Test Number:	F4	(batch)
O ₂ Flow Rate:	470	ml/min actual flow
SO ₂ Flow Rate:	30	ml/min actual flow
SO ₂ in Gas Mixture:	6.0	%
pH	3.5	pH

346	ml/min	meter reading
22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00003	d[Mn]/dt	M/min
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Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl		Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
			EMF (mV)	(A.T.)													
0	29.5		516	6.51	0	0	0.0	1388	0.00	880	0.00E+00	0.00E+00	2.53E-02	0.00E+00	0	0	
10	30.2		688	28.5	470	30	9.8	1388	0.02	959	4.00E-05	8.65E-04	2.49E-02	1.59E-03	2.48E-03	18.3	
20	30.5		715	29.2	470	30	20.8	1352	0.03	1097	2.55E-05	3.32E-03	2.46E-02	1.01E-03	8.77E-03	9.7	
30	30.6		722	29.2	470	30	31.7	1334	0.04	1185	3.28E-05	4.28E-03	2.43E-02	1.30E-03	9.51E-03	10.3	
40	30.5		723	29.3	470	30	42.5	1304	0.06	1289	5.46E-05	5.71E-03	2.37E-02	2.18E-03	1.28E-02	12.0	
50	30.5		728	29.4	470	30	52.8	1302	0.06	1399	3.64E-05	7.44E-03	2.37E-02	1.44E-04	1.82E-02	9.7	
60	30.4		728	29.4	470	30	83.3	1285	0.07	1501	3.09E-05	8.88E-03	2.34E-02	1.22E-03	1.94E-02	9.7	

Test Number:	R 1	(batch)
O ₂ Flow Rate:	470	ml/min actual flow
SO ₂ Flow Rate:	30	ml/min actual flow
SO ₂ in Gas Mixture:	6.0	%
pH	4.0	pH

346	ml/min	meter reading
22.7	ml/min	meter reading

Average Mn precipitation rate:	0.00012	d[Mn]/dt	M/min
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Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl		Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn
			EMF (mV)	(A.T.)													
0	29.9		464	6.6	0	0	0.0	1459	0.00	923	0.00E+00	0.00E+00	2.66E-02	0.00E+00	0	0	
10	30.6		701	29.0	470	30	11.7	1438	0.02	1016	4.19E-05	9.68E-04	2.61E-02	1.58E-03	2.90E-03	14.4	
20	30.7		700	30.0	470	30	25.8	1385	0.06	1130	1.29E-04	2.17E-03	2.48E-02	4.87E-03	6.46E-03	26.5	
30	30.8		701	30.2	470	30	39.6	1264	0.13	1259	1.84E-04	3.91E-03	2.30E-02	6.92E-03	1.05E-02	33.9	
40	30.5		702	30.3	470	30	53.1	1181	0.19	1367	1.51E-04	5.05E-03	2.15E-02	5.69E-03	1.38E-02	36.5	
50	30.3		703	30.5	470	30	66.6	1118	0.23	1509	1.15E-04	7.24E-03	2.04E-02	4.32E-03	1.83E-02	34.0	
60	30.2		705	30.6	470	30	79.8	1053	0.28	1626	1.18E-04	8.71E-03	1.92E-02	4.46E-03	2.19E-02	33.7	

Table 8-8: Batch Data Varying the Dissolved Oxygen Concentration by Sparging Nitrogen

Temperature	30 °C	Gas Range:	O2 Flow:	440 ml/min
pH	varies -		SO2 Flow:	60 ml/min
Mn Solution Conc.	1.5 g/l			
NaOH Solution Conc.	3 M			
Starting Volume	3015 ml			
Impeller Speed	800 rpm			

Test Number:	O1	(batch)
O2 Flow Rate:	440	ml/min
SO2 Flow Rate:	60	ml/min
SO2 in Gas Mixture:	12.0	%
N2 Flow Rate:	1770	ml/min

actual flow
actual flow

323	ml/min	meter reading
44.6	ml/min	meter reading

Average Mn precipitation rate:	0.000055	M/min
	0.0552	mM/min

Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl EMF (mV)	Dissolved O2 (ppm)	O2 Flow (ml/min)	SO2 Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles /l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO2 used to ppt Mn
0	30.2		-	6.6	0	0	0.0	1352	0.00	867	0.00E+00	0.00E+00	2.46E-02	0.00E+00	0	0
10	31.1		-	4.2	440	60	14.3	1311	0.03	1072	7.46E-05	4.02E-03	2.39E-02	3.03E-03	6.39E-03	11.7
20	31.4		-	4.3	440	60	28.9	1258	0.07	1268	9.65E-05	7.72E-03	2.29E-02	3.92E-03	1.25E-02	13.7
30	31.4		611	4.4	440	60	43.3	1227	0.09	1463	5.84E-05	1.14E-02	2.23E-02	2.29E-03	1.86E-02	12.2
40	31.4		609	4.4	440	60	57.3	1211	0.10	1714	2.91E-05	1.69E-02	2.20E-02	1.18E-03	2.64E-02	9.7
50	31.3		605	4.5	440	60	70.4	1201	0.11	1919	1.82E-05	2.12E-02	2.19E-02	7.40E-04	3.28E-02	8.4
60	31.3		602	4.6	440	60	83.8	1170	0.13	2135	5.64E-05	2.57E-02	2.13E-02	2.29E-03	3.95E-02	8.4

0.00014 steady state [O2] moles/l

Test Number:	O3	(batch)
O2 Flow Rate:	440	ml/min
SO2 Flow Rate:	60	ml/min
SO2 in Gas Mixture:	12.0	%
N2 Flow Rate:	430	ml/min

actual flow
actual flow

323	ml/min	meter reading
44.6	ml/min	meter reading

Average Mn precipitation rate:	0.000123	d[Mn]/dt
	0.1235	mM/min

Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl EMF (mV)	Dissolved O2 (ppm)	O2 Flow (ml/min)	SO2 Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles /l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO2 used to ppt Mn
0	30.5		454	6.5	0	0	0.0	1422	0.00	864	0.00E+00	0.00E+00	2.59E-02	0.00E+00	0	0
10	31.3		623	13.3	440	60	16.2	1312	0.06	1080	2.00E-04	3.43E-03	2.39E-02	7.74E-03	6.11E-03	32.8
20	31.6		622	13.4	440	60	33.2	1236	0.13	1295	1.38E-04	7.94E-03	2.25E-02	5.34E-03	1.34E-02	25.2
30	31.6		619	13.6	440	60	47.9	1174	0.17	1526	1.13E-04	1.27E-02	2.14E-02	4.36E-03	2.08E-02	21.9
40	31.6		615	13.7	440	60	62.8	1132	0.20	1746	7.64E-05	1.71E-02	2.08E-02	2.95E-03	2.75E-02	19.2
50	31.5		615	13.8	440	60	78.0	1088	0.25	1946	1.16E-04	2.08E-02	1.94E-02	4.50E-03	3.37E-02	19.1
60	31.5		615	13.9	440	60	93.0	1015	0.29	2189	9.65E-05	2.59E-02	1.85E-02	3.73E-03	4.13E-02	17.9

0.00043 steady state [O2] moles/l

Table 8-8: Batch Data Varying the Dissolved Oxygen Concentration by Sparging Nitrogen (Continued)

Test Number:	O4	(batch)																
O ₂ Flow Rate:	440	ml/min	actual flow			323	ml/min	meter reading										
SO ₂ Flow Rate:	60	ml/min	actual flow			44.6	ml/min	meter reading										
SO ₂ in Gas Mixture:	12.0	%																
N ₂ Flow Rate:	220	ml/min																
												Average Mn precipitation rate:		0.000132	d[Mn]/dt			
														0.1320	mM/min			
Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn		
0	29.6		450	6.5	0	0	0.0	1420	0.00	850	0.00E+00	0.00E+00	2.58E-02	0.00E+00	0	0		
10	30.7		571	18.8	440	60	14.8	1332	0.06	1043	1.60E-04	3.57E-03	2.42E-02	6.20E-03	6.02E-03	26.6		
20	31.2		573	18.9	440	60	30.3	1204	0.15	1256	2.33E-04	7.64E-03	2.19E-02	9.01E-03	1.27E-02	31.1		
30	31.4		575	18.9	440	60	45.9	1151	0.18	1448	9.65E-05	1.10E-02	2.10E-02	3.73E-03	1.88E-02	26.3		
40	31.4		578	18.9	440	60	60.9	1102	0.22	1876	8.92E-05	1.57E-02	2.01E-02	3.45E-03	2.58E-02	22.5		
50	31.4		583	18.9	440	60	75.7	1040	0.27	1900	1.13E-04	2.02E-02	1.89E-02	4.37E-03	3.27E-02	21.1		
60	31.4		588	19.0	440	60	90.1	985	0.31	2084	1.00E-04	2.36E-02	1.79E-02	3.87E-03	3.85E-02	20.6		

0.00059 steady state [O₂] moles/l

Test Number:	R 1	(batch)																
O ₂ Flow Rate:		ml/min	actual flow			323	ml/min	meter reading										
SO ₂ Flow Rate:		ml/min	actual flow			44.6	ml/min	meter reading										
SO ₂ in Gas Mixture:	12.0	%																
N ₂ Flow Rate:	0	ml/min																
												Average Mn precipitation rate:		0.000228	d[Mn]/dt			
														0.2275	mM/min			
Time (min)	Temperature (°C)	pH (A.T.) (-)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	(A.T.) Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	Mn Conc (moles/l)	Incremental Mn Removal Rate (dX/dt)	[S from gas] (moles/litre)	Percentage of dissolved SO ₂ used to ppt Mn		
0	29.8		490	6.6	0	0	0.0	1461	0.00	888	0.00E+00	0.00E+00	2.66E-02	0.00E+00	0	0		
10	31.0		703	27.8	440	60	12.8	1298	0.11	1088	2.97E-04	3.49E-03	2.36E-02	1.12E-02	5.61E-03	52.9		
20	31.7		702	28.9	440	60	28.4	1145	0.22	1281	2.78E-04	7.89E-03	2.08E-02	1.05E-02	1.23E-02	46.9		
30	31.9		703	28.9	440	60	39.4	1009	0.31	1514	2.48E-04	1.30E-02	1.84E-02	9.31E-03	1.95E-02	42.1		
40	32.0		705	28.9	440	60	51.2	900	0.38	1766	1.88E-04	1.89E-02	1.64E-02	7.46E-03	2.74E-02	37.3		
50	32.0		708	28.9	440	60	63.2	796	0.46	1967	1.89E-04	2.32E-02	1.45E-02	7.12E-03	3.36E-02	36.0		
60	32.0		709	29.0	440	60	75.2	711	0.51	2214	1.55E-04	2.89E-02	1.29E-02	5.82E-03	4.14E-02	33.0		

0.00091 steady state [O₂] moles/l

Table 8-9: Testing the Model for the Different Gas Mixtures (Batch Data)

-6.80E+06 Rate Constant (K _r)										
Test number C1										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00020	1.0	0.00E+00	4.0	303	0		0.0263		
10	0.00092	1.0	7.17E-04	4.0	303	0.000027	0.000027	0.0260	0.0260	
20	0.00094	1.0	1.28E-03	4.0	303	0.000047	0.000027	0.0255	0.0257	
30	0.00094	1.0	2.31E-03	4.0	303	0.000060	0.000027	0.0249	0.0255	
40	0.00094	1.0	2.74E-03	4.0	303	0.000051	0.000027	0.0244	0.0252	
50	0.00095	1.0	3.90E-03	4.0	303	0.000031	0.000026	0.0241	0.0249	
60	0.00094	1.0	4.12E-03	4.0	303	0.000046	0.000026	0.0236	0.0247	
Test number C2										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00021	3.0	0.00E+00	4.0	303	0		0.0267		
10	0.00092	3.0	1.03E-03	4.0	303	0.00006	0.00006	0.0261	0.0261	
20	0.00094	3.0	2.93E-03	4.0	303	0.00012	0.00008	0.0249	0.0253	
30	0.00094	3.0	4.43E-03	4.0	303	0.00007	0.00008	0.0242	0.0245	
40	0.00094	3.0	6.14E-03	4.0	303	0.00008	0.00008	0.0234	0.0238	
50	0.00094	3.0	7.95E-03	4.0	303	0.00008	0.00007	0.0226	0.0230	
60	0.00095	3.0	1.05E-02	4.0	303	0.00010	0.00007	0.0216	0.0223	
Test number C3										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00021	9.0	0.00E+00	4.0	303	0		0.0263		
10	0.00091	9.0	4.99E-03	4.0	303	0.00020	0.00020	0.0243	0.0243	
20	0.00094	9.0	9.42E-03	4.0	303	0.00021	0.00021	0.0222	0.0222	
30	0.00094	9.0	1.47E-02	4.0	303	0.00018	0.00019	0.0204	0.0202	
40	0.00094	9.0	1.94E-02	4.0	303	0.00019	0.00018	0.0185	0.0185	
50	0.00094	9.0	2.47E-02	4.0	303	0.00015	0.00016	0.0170	0.0168	
60	0.00094	9.0	3.05E-02	4.0	303	0.00015	0.00015	0.0155	0.0154	
Test number C4										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00020	12.0	0.00E+00	4.0	303	0		0.0266		
10	0.00087	12.0	5.61E-03	4.0	303	0.00030	0.00030	0.0236	0.0236	
20	0.00090	12.0	1.23E-02	4.0	303	0.00028	0.00026	0.0208	0.0210	
30	0.00090	12.0	1.95E-02	4.0	303	0.00025	0.00023	0.0184	0.0188	
40	0.00090	12.0	2.74E-02	4.0	303	0.00020	0.00020	0.0164	0.0168	
50	0.00090	12.0	3.36E-02	4.0	303	0.00019	0.00018	0.0145	0.0151	
60	0.00091	12.0	4.14E-02	4.0	303	0.00015	0.00015	0.0129	0.0135	
Test number C5										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00021	15.0	0.00E+00	4.0	303	0		0.0264		
10	0.00087	15.0	7.55E-03	4.0	303	0.00027	0.00027	0.0237	0.0237	
20	0.00092	15.0	1.62E-02	4.0	303	0.00023	0.00031	0.0214	0.0207	
30	0.00092	15.0	2.51E-02	4.0	303	0.00025	0.00026	0.0189	0.0181	
40	0.00092	15.0	3.49E-02	4.0	303	0.00021	0.00022	0.0169	0.0159	
50	0.00093	15.0	4.44E-02	4.0	303	0.00017	0.00019	0.0152	0.0140	
60	0.00093	15.0	5.33E-02	4.0	303	0.00016	0.00016	0.0136	0.0124	
Test number C6										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00021	20.0	0.00E+00	4.0	303	0		0.0260		
10	0.00088	20.0	8.92E-03	4.0	303	0.00033	0.00033	0.0227	0.0227	
20	0.00091	20.0	1.96E-02	4.0	303	0.00027	0.00038	0.0200	0.0189	
30	0.00092	20.0	3.06E-02	4.0	303	0.00021	0.00031	0.0179	0.0158	
40	0.00092	20.0	4.18E-02	4.0	303	0.00019	0.00026	0.0160	0.0132	
60	0.00093	20.0	6.47E-02	4.0	303	0.00012	0.00017	0.0135	0.0086	
80	0.00093	20.0	8.64E-02	4.0	303	0.00007	0.00012	0.0120	0.0051	
100	0.00093	20.0	1.11E-01	4.0	303	0.00005	0.00007	0.0109	0.0026	
120	0.00093	20.0	1.34E-01	4.0	303	0.00004	0.00005	0.0102	0.0006	
Test number R 2										
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]	
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)	(moles/l)
0	0.00020	6.0	0.00E+00	4.0	303	0		0.0265		
20	0.00092	6.0	6.83E-03	4.0	303	0.00012	0.00012	0.0241	0.0241	
30	0.00093	6.0	1.08E-02	4.0	303	0.00013	0.00014	0.0228	0.0227	
40	0.00093	6.0	1.54E-02	4.0	303	0.00014	0.00013	0.0214	0.0214	
50	0.00093	6.0	1.88E-02	4.0	303	0.00013	0.00012	0.0201	0.0202	
60	0.00094	6.0	2.25E-02	4.0	303	0.00014	0.00011	0.0187	0.0192	

Table 8-10: Testing the Model for the Different Solution Temperatures (Batch Data)

-6.80E+06 Rate Constant (K ₁)									
Test number E1									
Time (min)	[O ₂] (moles/l)	P _{SO₂} /P _{tot} (%)	[S from gas] (moles/l)	pH	Temperature (Kelvin)	Measured d[Mn]/dt (moles/l/min)	Model d[Mn]/dt (moles/l/min)	Measured [Mn] (moles/l)	Model [Mn] (moles/l)
0	0.00015	6.0	0.00E+00	4.0	323	0		0.0255	
10	0.00068	6.0	2.90E-03	4.0	323	0.00012		0.0242	
20	0.00069	6.0	5.99E-03	4.0	323	0.00019	0.00019	0.0223	0.0223
30	0.00070	6.0	9.92E-03	4.0	323	0.00017	0.00019	0.0206	0.0204
40	0.00070	6.0	1.27E-02	4.0	323	0.00021	0.00018	0.0186	0.0187
50	0.00070	6.0	1.58E-02	4.0	323	0.00017	0.00017	0.0168	0.0170
60	0.00070	6.0	1.97E-02	4.0	323	0.00024	0.00016	0.0145	0.0154
Test number E2									
Time (min)	[O ₂] (moles/l)	P _{SO₂} /P _{tot} (%)	[S from gas] (moles/l)	pH	Temperature (Kelvin)	Measured d[Mn]/dt (moles/l/min)	Model d[Mn]/dt (moles/l/min)	Measured [Mn] (moles/l)	Model [Mn] (moles/l)
0	0.00017	6.0	0.00E+00	4.0	313	0		0.0261	
10	0.00078	6.0	2.65E-03	4.0	313	0.00011		0.0249	
20	0.00080	6.0	6.08E-03	4.0	313	0.00022	0.00022	0.0227	0.0227
30	0.00080	6.0	9.51E-03	4.0	313	0.00017	0.00016	0.0210	0.0211
40	0.00080	6.0	1.28E-02	4.0	313	0.00017	0.00015	0.0193	0.0196
50	0.00080	6.0	1.61E-02	4.0	313	0.00016	0.00014	0.0177	0.0181
60	0.00081	6.0	1.97E-02	4.0	313	0.00015	0.00014	0.0161	0.0168
Test number E4									
Time (min)	[O ₂] (moles/l)	P _{SO₂} /P _{tot} (%)	[S from gas] (moles/l)	pH	Temperature (Kelvin)	Measured d[Mn]/dt (moles/l/min)	Model d[Mn]/dt (moles/l/min)	Measured [Mn] (moles/l)	Model [Mn] (moles/l)
0	0.00024	6.0	0.00E+00	4.0	293	0		0.0260	
10	0.00106	6.0	3.12E-03	4.0	293	0.00007		0.0253	
20	0.00109	6.0	6.02E-03	4.0	293	0.00012	0.00012	0.0240	0.0240
30	0.00109	6.0	9.42E-03	4.0	293	0.00009	0.00012	0.0232	0.0229
40	0.00108	6.0	1.26E-02	4.0	293	0.00009	0.00011	0.0223	0.0217
50	0.00108	6.0	1.61E-02	4.0	293	0.00011	0.00010	0.0212	0.0207
60	0.00108	6.0	1.93E-02	4.0	293	0.00011	0.00010	0.0201	0.0197
Test number R 1									
Time (min)	[O ₂] (moles/l)	P _{SO₂} /P _{tot} (%)	[S from gas] (moles/l)	pH	Temperature (Kelvin)	Measured d[Mn]/dt (moles/l/min)	Model d[Mn]/dt (moles/l/min)	Measured [Mn] (moles/l)	Model [Mn] (moles/l)
0	0.00021	6.0	0.00E+00	4.0	303	0		0.0266	
10	0.00091	6.0	2.90E-03	4.0	303	0.00004		0.0261	
20	0.00094	6.0	6.46E-03	4.0	303	0.00013	0.00013	0.0248	0.0248
30	0.00094	6.0	1.05E-02	4.0	303	0.00018	0.00014	0.0230	0.0235
40	0.00095	6.0	1.38E-02	4.0	303	0.00015	0.00013	0.0215	0.0221
50	0.00095	6.0	1.83E-02	4.0	303	0.00011	0.00012	0.0204	0.0209
60	0.00096	6.0	2.19E-02	4.0	303	0.00012	0.00011	0.0192	0.0198

Table 8-11: Testing the Model for the Different pH Values (Batch Data)

-6.80E+06 Rate Constant (K₁)

Test number F1									
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	6.0	0.00E+00	6.0	303	0		0.0253	
10	0.00090	6.0	2.87E-03	6.0	303	0.00029	0.00029	0.0224	0.0224
20	0.00090	6.0	6.33E-03	6.0	303	0.00039	0.00038	0.0184	0.0185
30	0.00091	6.0	1.00E-02	6.0	303	0.00039	0.00036	0.0145	0.0149
40	0.00091	6.0	1.27E-02	6.0	303	0.00032	0.00034	0.0114	0.0115
50	0.00091	6.0	1.78E-02	6.0	303	0.00030	0.00031	0.0084	0.0084
60	0.00091	6.0	2.03E-02	6.0	303	0.00028	0.00030	0.0056	0.0054
Test number F2									
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	6.0	0.00E+00	5.0	303	0		0.0249	
10	0.00089	6.0	2.84E-03	5.0	303	0.00027	0.00027	0.0222	0.0222
20	0.00091	6.0	6.17E-03	5.0	303	0.00025	0.00029	0.0197	0.0194
30	0.00092	6.0	9.98E-03	5.0	303	0.00030	0.00027	0.0168	0.0166
40	0.00092	6.0	1.29E-02	5.0	303	0.00026	0.00026	0.0141	0.0140
50	0.00092	6.0	1.66E-02	5.0	303	0.00022	0.00024	0.0119	0.0116
60	0.00092	6.0	2.06E-02	5.0	303	0.00024	0.00023	0.0096	0.0093
Test number F3									
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00021	6.0	0.00E+00	4.5	303	0		0.0260	
10	0.00092	6.0	2.00E-03	4.5	303	0.00026	0.00026	0.0234	0.0234
20	0.00094	6.0	4.90E-03	4.5	303	0.00021	0.00024	0.0212	0.0210
30	0.00095	6.0	9.82E-03	4.5	303	0.00026	0.00022	0.0186	0.0188
40	0.00095	6.0	1.39E-02	4.5	303	0.00023	0.00020	0.0163	0.0167
50	0.00095	6.0	1.69E-02	4.5	303	0.00024	0.00019	0.0139	0.0148
60	0.00095	6.0	2.11E-02	4.5	303	0.00018	0.00018	0.0120	0.0130
Test number F4									
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	6.0	0.00E+00	3.5	303	0		0.0253	
10	0.00089	6.0	2.46E-03	3.5	303	0.00004	0.00004	0.0249	0.0249
20	0.00091	6.0	6.77E-03	3.5	303	0.00003	0.00004	0.0246	0.0245
30	0.00091	6.0	9.51E-03	3.5	303	0.00003	0.00004	0.0243	0.0241
40	0.00092	6.0	1.28E-02	3.5	303	0.00005	0.00004	0.0237	0.0237
50	0.00092	6.0	1.62E-02	3.5	303	0.00000	0.00003	0.0237	0.0233
60	0.00092	6.0	1.94E-02	3.5	303	0.00003	0.00003	0.0234	0.0230
Test number R 1									
Time	[O ₂]	P _{SO₂} /P _{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00021	6.0	0.00E+00	4.0	303	0		0.0266	
10	0.00091	6.0	2.90E-03	4.0	303	0.00004	0.00004	0.0261	0.0261
20	0.00094	6.0	6.46E-03	4.0	303	0.00013	0.00015	0.0248	0.0247
30	0.00094	6.0	1.05E-02	4.0	303	0.00018	0.00014	0.0230	0.0233
40	0.00095	6.0	1.38E-02	4.0	303	0.00015	0.00013	0.0215	0.0219
50	0.00095	6.0	1.83E-02	4.0	303	0.00011	0.00012	0.0204	0.0207
60	0.00096	6.0	2.19E-02	4.0	303	0.00012	0.00011	0.0192	0.0196

Table 8-12: Testing the Model for Different Dissolved Oxygen Concentrations (Batch Data)

-6.80E+06 Rate Constant (K ₁)									
Test number O1									
4.5									
Time	[O₂]	P_{SO₂}/P_{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00021	12.0	0.00E+00	4.0	303	0		0.0246	
10	0.00013	12.0	6.39E-03	4.0	304	0.00007	0.00007	0.0239	0.0239
20	0.00013	12.0	1.25E-02	4.0	304	0.00010	0.00004	0.0229	0.0235
30	0.00014	12.0	1.86E-02	4.0	304	0.00006	0.00004	0.0223	0.0231
40	0.00014	12.0	2.64E-02	4.0	304	0.00003	0.00003	0.0220	0.0228
50	0.00014	12.0	3.28E-02	4.0	304	0.00002	0.00003	0.0219	0.0225
60	0.00014	12.0	3.95E-02	4.0	304	0.00006	0.00003	0.0213	0.0222
Test number O3									
14									
Time	[O₂]	P_{SO₂}/P_{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	12.0	0.00E+00	4.0	304	0		0.0259	
10	0.00042	12.0	6.11E-03	4.0	304	0.00020	0.00020	0.0239	0.0239
20	0.00042	12.0	1.34E-02	4.0	305	0.00014	0.00012	0.0225	0.0227
30	0.00042	12.0	2.06E-02	4.0	305	0.00011	0.00011	0.0214	0.0216
40	0.00043	12.0	2.75E-02	4.0	305	0.00008	0.00010	0.0206	0.0206
50	0.00043	12.0	3.37E-02	4.0	305	0.00012	0.00009	0.0194	0.0197
60	0.00043	12.0	4.13E-02	4.0	305	0.00010	0.00008	0.0185	0.0189
Test number O4									
19									
Time	[O₂]	P_{SO₂}/P_{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	12.0	0.00E+00	4.0	303	0		0.0258	
10	0.00059	12.0	6.02E-03	4.0	304	0.00016	0.00016	0.0242	0.0242
20	0.00059	12.0	1.27E-02	4.0	304	0.00023	0.00017	0.0219	0.0225
30	0.00059	12.0	1.86E-02	4.0	304	0.00010	0.00016	0.0210	0.0209
40	0.00059	12.0	2.58E-02	4.0	304	0.00009	0.00014	0.0201	0.0196
50	0.00059	12.0	3.27E-02	4.0	304	0.00011	0.00012	0.0189	0.0183
60	0.00059	12.0	3.85E-02	4.0	304	0.00010	0.00011	0.0179	0.0172
Test number R 1									
29									
Time	[O₂]	P_{SO₂}/P_{tot}	[S from gas]	pH	Temperature	Measured d[Mn]/dt	Model d[Mn]/dt	Measured [Mn]	Model [Mn]
(min)	(moles/l)	(%)	(moles/l)		(Kelvin)	(moles/l/min)	(moles/l/min)	(moles/l)	(moles/l)
0	0.00020	12.0	0.00E+00	4.0	303	0		0.0266	
10	0.00087	12.0	5.61E-03	4.0	304	0.00030	0.00030	0.0236	0.0236
20	0.00090	12.0	1.23E-02	4.0	305	0.00028	0.00027	0.0208	0.0209
30	0.00090	12.0	1.95E-02	4.0	305	0.00025	0.00024	0.0184	0.0185
40	0.00090	12.0	2.74E-02	4.0	305	0.00020	0.00021	0.0164	0.0164
50	0.00090	12.0	3.36E-02	4.0	305	0.00019	0.00019	0.0145	0.0146
60	0.00091	12.0	4.14E-02	4.0	305	0.00015	0.00016	0.0129	0.0129

Table 8-13: Continuous Test Changing the Gas Mixture

Temperature	30 °C
pH	4.0 -
Mn Solution Conc.	1.5 g/l
NaOH Solution Conc.	3 M
Starting Volume	3015 ml
Working Volume at 1000rpm	2840 ml
Impeller Speed	800 rpm

Gas Range:	SO ₂ Flow:	O ₂ Flow:	
actual flow rate	30	470	ml/min 6 % SO ₂
actual flow rate	60	440	ml/min 12 % SO ₂
meter reading	22.7	346	ml/min 6 % SO ₂
meter reading	44.6	323	ml/min 12 % SO ₂

Test Number:
SO₂ in Gas Mixture:
O₂ Flow Rate:
SO₂ Flow Rate:
MnSO₄ Flow Rate:
Retention Time:

G1	(continuous)
variable	%
variable	ml/min
variable	ml/min
50	ml/min
60	min

	Time (hours : min)	Time (min)	Temperature (°C)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/l/re)	[S from gas] (moles/l/re)	Mn Conc (moles/l)	Actual Incremental Mn Removal Rate (dX/dt)
6% SO ₂	00:00	0	35.5	405	5.9	0	0	0	1467	0.00	868	0.00E+00	0.00E+00	0.00E+00	2.87E-02	0.00E+00
	00:15	15	34.0	565	26.4	470	30	13.3	1375	0.06	1012	2.64E-05	4.49E-03	4.50E-03	2.50E-02	9.90E-04
	00:30	30	33.7	569	27.2	470	30	26.8	1316	0.10	1130	4.34E-05	8.18E-03	8.19E-03	2.40E-02	1.62E-03
	00:45	45	33.4	576	27.8	470	30	40.4	1271	0.13	1240	5.63E-05	1.16E-02	1.16E-02	2.31E-02	2.11E-03
	01:00	60	33.5	578	27.6	470	30	53.7	1218	0.17	1301	7.15E-05	1.35E-02	1.35E-02	2.22E-02	2.68E-03
	01:30	90	33.5	585	28.1	470	30	80.4	1170	0.20	1406	8.53E-05	1.68E-02	1.68E-02	2.13E-02	3.20E-03
	02:00	120	33.5	594	28.1	470	30	106.8	1151	0.22	1458	9.08E-05	1.84E-02	1.84E-02	2.10E-02	3.40E-03
	02:30	150	33.6	603	27.2	470	30	133.2	1145	0.22	1466	9.25E-05	1.87E-02	1.87E-02	2.08E-02	3.47E-03
	03:00	180	33.4	608	28.1	470	30	159.7	1144	0.22	1504	9.28E-05	1.98E-02	1.99E-02	2.08E-02	3.48E-03
	03:30	210	33.5	614	28.0	470	30	186.0	1143	0.22	1523	9.31E-05	2.04E-02	2.05E-02	2.08E-02	3.49E-03
12% SO ₂	04:00	240	33.8	618	28.0	470	30	212.4	1109	0.24	1535	1.03E-04	2.08E-02	2.08E-02	2.02E-02	3.85E-03
	04:30	270	33.6	627	28.0	470	30	238.7	1069	0.26	1549	1.09E-04	2.13E-02	2.13E-02	1.98E-02	4.07E-03
	05:00	300	33.6	633	28.0	470	30	265.0	1057	0.28	1551	1.18E-04	2.13E-02	2.13E-02	1.92E-02	4.41E-03
	05:15	315	34.1	622	24.8	440	60	291.3	1018	0.31	1788	1.39E-04	2.81E-02	2.81E-02	1.85E-02	5.19E-03
	05:30	330	33.9	660	27.5	440	60	316.0	981	0.33	1888	1.50E-04	3.18E-02	3.18E-02	1.79E-02	5.62E-03
	05:45	345	33.8	654	27.2	440	60	340.0	953	0.35	1943	1.59E-04	3.35E-02	3.36E-02	1.73E-02	5.94E-03
	06:00	360	33.9	656	27.6	440	60	361.8	945	0.36	2012	1.61E-04	3.57E-02	3.58E-02	1.72E-02	6.03E-03
	06:30	390	33.8	662	27.8	440	60	410.7	941	0.36	2082	1.62E-04	3.79E-02	3.79E-02	1.71E-02	6.08E-03
	07:00	420	33.9	669	27.8	440	60	457.7	937	0.36	2122	1.64E-04	3.91E-02	3.92E-02	1.71E-02	6.13E-03
	07:30	450	33.9	677	27.8	440	60	504.7	936	0.36	2154	1.64E-04	4.01E-02	4.02E-02	1.70E-02	6.14E-03
08:00	480	33.9	683	27.8	440	60	551.7	935	0.36	2155	1.64E-04	4.02E-02	4.02E-02	1.70E-02	6.15E-03	
08:30	510	33.9	688	27.8	440	60	599.0	932	0.36	2181	1.65E-04	4.10E-02	4.10E-02	1.70E-02	6.19E-03	
09:00	540	34.0	692	27.7	440	60	645.9	927	0.37	2194	1.67E-04	4.14E-02	4.14E-02	1.69E-02	6.24E-03	
09:30	570	33.9	693	27.8	440	60	693.1	927	0.37	2235	1.67E-04	4.27E-02	4.27E-02	1.69E-02	6.24E-03	
10:00	600	34.0	695	27.7	440	60	747.8	923	0.37	2256	1.68E-04	4.33E-02	4.34E-02	1.68E-02	6.29E-03	

Table 8-13: Continuous Test Changing the Gas Mixture (Continued)

	Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 30min	not measured	not measured	not measured
30 to 60min	1380	45	63
60 to 90min	1370	46	62
90 to 120min	1410	47	60
120 to 180min	2830	47	60
180 to 240min	2795	47	61
240 to 300min	2690	45	63
Retention Time over Last Hour:			63 min
[O ₂] over Last Hour:			0.00088 M
PSO ₂ /Ptot over Last Hour:			0.06 fraction
[S from gas] over Last Hour:			2.13E-02 M
Average pH over the Last Hour:			4.0 -
Average Temperature over the Last Hour:			307 Kelvin
Average [Mn] over the Last Hour:			0.0195 moles
Model d[Mn]/dt over the Last Hour:			0.000118 moles/min
Calculated Mn Concentration Out of Reactor:			0.0193 M
Calculated Mn Concentration Out of Reactor:			1063 mg/l
Actual Mn Concentration Out of the Reactor:			1057 mg/l
Accuracy of Model:			99 %

	Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 30min	not measured	not measured	not measured
30 to 60min	1290	43	66
60 to 120min	2870	48	59
120 to 180min	2890	48	59
180 to 240min	2870	48	59
240 to 300min	2890	48	59
Retention Time over Last Hour:			59 min
[O ₂] over Last Hour:			0.00087 M
PSO ₂ /Ptot over Last Hour:			0.12 fraction
[S from gas] over Last Hour:			4.30E-02 M
Average pH over the Last Hour:			4.0 -
Average Temperature over the Last Hour:			307 Kelvin
Average [Mn] over the Last Hour:			0.0168 moles
Model d[Mn]/dt over the Last Hour:			0.000160 moles/min
Calculated Mn Concentration Out of Reactor:			0.0172 M
Calculated Mn Concentration Out of Reactor:			945 mg/l
Actual Mn Concentration Out of the Reactor:			923 mg/l
Accuracy of Model:			98 %

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Table 8-14: Continuous Test Changing the Solution Temperature

Temperature varies	4.0 -	First 5 hours	20C
pH	1.5 g/l	Last 4 hours	50C
Mn Solution Conc.	3 M		
NaOH Solution Conc.	3015 ml		
Starting Volume	2840 ml		
Working Volume at 1000rpm	800 rpm		
Impeller Speed			

Test Number:	G3	(continuous)
SO ₂ in Gas Mixture:	12.0	%
O ₂ Flow Rate:	440	ml/min
SO ₂ Flow Rate:	60	ml/min
MnSO ₄ Flow Rate:	50	ml/min
Retention Time:	60	min

Time (hours : min)	Time (min)	Temperature (°C)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/lire)	[S from gas] (moles/lire)	Mn Conc (moles/l)	Actual
															Incremental Mn Removal Rate (dX/dt)
20C	00:00	0	22.8	468	7.4	0	0	1413	0.00	899	0.00E+00	0.00E+00	0.00E+00	2.57E-02	0.00E+00
	00:15	15	23.5	609	31.0	440	60	23.0	1274	1183	4.47E-05	8.86E-03	8.86E-03	2.32E-02	1.74E-03
	00:30	30	23.8	629	32.6	440	60	47.3	1217	1442	6.30E-05	1.69E-02	1.69E-02	2.22E-02	2.45E-03
	00:45	45	24.0	635	32.8	440	60	71.3	1151	1649	8.42E-05	2.34E-02	2.34E-02	2.10E-02	3.28E-03
	01:00	60	24.3	9.9	32.8	440	60	95.0	1116	1754	9.55E-05	2.67E-02	2.67E-02	2.03E-02	3.71E-03
	01:30	90	24.6	647	32.6	440	60	141.5	1093	1925	1.03E-04	3.20E-02	3.20E-02	1.99E-02	4.00E-03
	02:00	120	25.0	654	32.3	440	60	187.8	1080	2050	1.07E-04	3.59E-02	3.59E-02	1.97E-02	4.16E-03
	03:00	180	25.4	668	32.0	440	60	280.4	1071	2150	1.10E-04	3.90E-02	3.90E-02	1.95E-02	4.28E-03
	04:00	240	25.6	677	31.9	440	60	372.9	1039	2194	1.20E-04	4.04E-02	4.04E-02	1.89E-02	4.68E-03
	05:00	300	25.7	690	31.9	440	60	465.3	1037	2223	1.21E-04	4.13E-02	4.13E-02	1.89E-02	4.70E-03
50C	05:15	315	49.4	675	22.0	440	60	492.9	950	2202	1.49E-04	4.07E-02	4.07E-02	1.73E-02	5.79E-03
	05:30	330	50.7	675	21.6	440	60	518.6	929	2203	1.56E-04	4.07E-02	4.07E-02	1.69E-02	6.05E-03
	06:00	360	49.4	678	22.0	440	60	569.2	898	2166	1.66E-04	3.95E-02	3.95E-02	1.63E-02	6.44E-03
	06:30	390	50.0	678	21.8	440	60	619.5	870	2203	1.75E-04	4.07E-02	4.07E-02	1.58E-02	6.79E-03
	07:00	420	50.0	679	21.8	440	60	669.8	805	2203	1.95E-04	4.07E-02	4.07E-02	1.47E-02	7.60E-03
	08:00	480	50.1	682	21.8	440	60	769.5	829	2172	1.88E-04	3.97E-02	3.97E-02	1.51E-02	7.30E-03
	09:00	540	50.0	681	21.8	440	60	868.9	827	2209	1.88E-04	4.09E-02	4.09E-02	1.51E-02	7.33E-03

20C Solution Flow:

Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 32min	not measured	not measured
32 to 60min	1160	41
60 to 120min	2800	47
120 to 180min	3050	51
180 to 240min	2970	50
240 to 300min	3010	50

Retention Time over Last Hour:	57	min
[O ₂] over Last Hour:	0.00100	M
PSO ₂ /Ptot over Last Hour:	0.12	fraction
[S from gas] over Last Hour:	4.13E-02	M
Average pH over the Last Hour:	4.0	-
Average Temperature over the Last Hour:	299	Kelvin
Average [Mn] over the Last Hour:	0.0189	moles
Model d[Mn]/dt over the Last Hour:	0.000148	moles/min
Calculated Mn Concentration Out of Reactor:	0.0173	M
Calculated Mn Concentration Out of Reactor:	951	mg/l
Actual Mn Concentration Out of the Reactor:	1037	mg/l
Accuracy of Model:	123	%

50C SO₂ Solution Flow:

Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 30min	not measured	not measured
30 to 60min	1440	48
60 to 120min	2870	48
120 to 180min	2950	49
180 to 240min	3010	50

Retention Time over Last Hour:	57	min
[O ₂] over Last Hour:	0.00068	M
PSO ₂ /Ptot over Last Hour:	0.12	fraction
[S from gas] over Last Hour:	4.09E-02	M
Average pH over the Last Hour:	4.0	-
Average Temperature over the Last Hour:	323	Kelvin
Average [Mn] over the Last Hour:	0.0151	moles
Model d[Mn]/dt over the Last Hour:	0.000207	moles/min
Calculated Mn Concentration Out of Reactor:	0.0139	M
Calculated Mn Concentration Out of Reactor:	761	mg/l
Actual Mn Concentration Out of the Reactor:	827	mg/l
Accuracy of Model:	111	%

Table 8-15: Continuous Test Changing the pH

Temperature	30 C	first 4 hours last 4 hours	pH 4.0 pH 5.0
pH	varies -		
Mn Solution Conc.	1.5 g/l		
NaOH Solution Conc.	3 M		
Starting Volume	3015 ml		
Working Volume at 1000rpm	2840 ml		
Impeller Speed	800 rpm		

Test Number:	G4	(continuous)
SO2 in Gas Mixture:	12.0	%
O2 Flow Rate:	440	ml/min
SO2 Flow Rate:	60	ml/min
MnSO4 Flow Rate:	50	ml/min
Retention Time:	60	min

	Time (hours : min)	Time (min)	Temperature (°C)	vs. Ag/AgCl EMF (mV)	Dissolved O ₂ (ppm)	O ₂ Flow (ml/min)	SO ₂ Flow (ml/min)	Cumulative NaOH Used (ml)	Mn (mg/l)	X (fraction)	S total (mg/l)	Incremental Mn Removal Rate (moles/l/min)	Non Acidic Sulfur (moles/litre)	[S from gas] (moles/litre)	Mn Conc (moles/l)	Actual Incremental Mn Removal Rate (dX/dt)
pH 4.0	00:00	0	32.2	445	6.0	0	0	0	1398	0.00	901	0.00E+00	0.00E+00	0.00E+00	2.54E-02	0.00E+00
	00:15	15	32.2	662	27.1	440	60	24.0	1275	0.09	1198	4.05E-05	9.21E-03	9.20E-03	2.32E-02	1.59E-03
	00:30	30	32.5	676	28.5	440	60	48.3	1131	0.19	1464	8.38E-05	1.76E-02	1.76E-02	2.08E-02	3.49E-03
	00:45	45	32.3	684	28.5	440	60	74.2	1073	0.23	1674	1.08E-04	2.41E-02	2.41E-02	1.95E-02	4.25E-03
	01:00	60	32.0	687	28.6	440	60	98.1	1030	0.26	1816	1.22E-04	2.86E-02	2.85E-02	1.87E-02	4.82E-03
	01:30	90	32.6	697	28.4	440	60	146.4	986	0.29	1953	1.34E-04	3.28E-02	3.28E-02	1.81E-02	5.26E-03
	02:00	120	32.1	700	28.8	440	60	194.5	973	0.30	2049	1.41E-04	3.58E-02	3.58E-02	1.77E-02	5.57E-03
	03:00	180	32.2	700	28.7	440	60	290.2	972	0.30	2112	1.42E-04	3.78E-02	3.78E-02	1.77E-02	5.58E-03
04:00	240	32.3	702	28.7	440	60	385.1	964	0.31	2147	1.44E-04	3.89E-02	3.89E-02	1.75E-02	5.68E-03	
pH 5.0	04:15	255	32.3	576	27.8	440	60	420.8	749	0.46	2186	2.16E-04	4.01E-02	4.01E-02	1.36E-02	8.51E-03
	04:30	270	32.2	576	28.5	440	60	452.1	640	0.54	2188	2.53E-04	4.02E-02	4.01E-02	1.16E-02	9.95E-03
	04:45	285	32.0	579	28.5	440	60	482.3	578	0.59	2195	2.73E-04	4.04E-02	4.04E-02	1.05E-02	1.08E-02
	05:00	300	32.2	581	28.5	440	60	512.0	524	0.62	2198	2.92E-04	4.04E-02	4.04E-02	9.54E-03	1.15E-02
	05:30	330	32.2	584	28.4	440	60	570.8	485	0.65	2208	3.05E-04	4.08E-02	4.08E-02	8.83E-03	1.20E-02
	06:00	360	32.2	585	28.5	440	60	629.0	476	0.66	2213	3.08E-04	4.09E-02	4.09E-02	8.66E-03	1.21E-02
	07:00	420	31.9	585	28.5	440	60	744.6	462	0.67	2230	3.12E-04	4.15E-02	4.14E-02	8.41E-03	1.23E-02
	08:00	480	32.0	585	28.4	440	60	858.5	454	0.67	2231	3.15E-04	4.15E-02	4.15E-02	8.26E-03	1.24E-02

pH 4.0 Solution Flow:

	Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 33min	not measured	not measured	not measured
33 to 60min	1230	46	62
60 to 120min	2640	44	65
120 to 180min	3100	52	55
180 to 240min	3130	52	54

Retention Time over Last Hour:	54	min
[O ₂] over Last Hour:	0.00090	M
PSO ₂ /Ptot over Last Hour:	0.12	fraction
[S from gas] over Last Hour:	3.89E-02	M
Average pH over the Last Hour:	4.0	-
Average Temperature over the Last Hour:	305	Kelvin
Average [Mn] over the Last Hour:	0.0175	moles
Model d[Mn]/dt over the Last Hour:	0.000170	moles/min
Calculated Mn Concentration Out of Reactor:	0.0161	M
Calculated Mn Concentration Out of Reactor:	884	mg/l
Actual Mn Concentration Out of the Reactor:	964	mg/l
Accuracy of Model:	118	%

pH 5.0 SO₂ Solution Flow:

	Volume Out of Reactor (ml)	Flowrate Out of Reactor (ml/min)	Retention Time in Reactor (min)
0 to 30min	not measured	not measured	not measured
30 to 60min	1480	49	58
60 to 120min	3030	51	56
120 to 180min	3140	52	54
180 to 240min	3130	52	54

Retention Time over Last Hour:	54	min
[O ₂] over Last Hour:	0.00089	M
PSO ₂ /Ptot over Last Hour:	0.12	fraction
[S from gas] over Last Hour:	4.15E-02	M
Average pH over the Last Hour:	5.0	-
Average Temperature over the Last Hour:	305	Kelvin
Average [Mn] over the Last Hour:	0.0083	moles
Model d[Mn]/dt over the Last Hour:	0.000319	moles/min
Calculated Mn Concentration Out of Reactor:	0.0081	M
Calculated Mn Concentration Out of Reactor:	445	mg/l
Actual Mn Concentration Out of the Reactor:	454	mg/l
Accuracy of Model:	101	%