

A new development in the oxidative precipitation of Fe and Mn by SO₂/air

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The use of dilute sulphur dioxide (SO₂) gas mixtures with air or oxygen has been explored extensively for the oxidative precipitation of iron (Fe) and manganese (Mn) base metal sulphate solutions. The strong oxidizing properties displayed by SO₂/air have raised a lot of interest in this technology, especially for plants running a sulphide mineral roaster or sulphur burner. However, the conventional SO₂/air technology where SO₂ and air are introduced as gas mixtures resulted in variations in the performance of the system.

In an attempt to address some of the challenges inherent to the conventional SO₂/air technology, a new method is proposed that involves introduction of SO₂ as an aqueous stream containing dissolved SO₂, as opposed to direct sparging in a gas mixture with air. The new method is beneficial as it allows: (i) better control of SO₂ addition, (ii) improved oxygen mass transfer, and hence (iii) a more efficient, controllable and consistent system. The work described in this paper also includes scoping experiments conducted to demonstrate the proof-of-principle of using dilute SO₂ solution and air to carry out the oxidative precipitation of Fe and Mn from a dilute cobalt solution. Aspects associated with the implementation of the technology on an industrial scale are also discussed.

Introduction

The processing of nickel/cobalt/zinc ores often leads to the presence of unwanted cations such as manganese and iron in solution. Many technologies exist for the removal of these impurities from solution, each having its own advantages and disadvantages. One of these technologies that has received much attention during the past years is oxidative precipitation using a gas mixture of sulphur dioxide (SO₂) and air (or O₂) (Zhang *et al.*, 2000a, 2002; Van Rooyen *et al.*, 2007; Mouton *et al.*, 2007; Mulaudzi *et al.*, 2009; S. Bello-Teodoro *et al.*, 2011). The SO₂/air technology offers many advantages, especially for plants running a sulphur burner or a sulphide roasting facility on site. The SO₂ could be sourced from the off-gas and used in a mixture with air for oxidation purposes. Furthermore, the SO₂/air mixture is a relatively cheap and strong oxidant that allows the oxidative precipitation of Fe and Mn at relatively low pH values.

Mintek has conducted numerous studies investigating the oxidizing properties displayed by SO₂/air, particularly for the removal of iron and manganese from dilute cobalt sulphate solutions. The effects of parameters such as SO₂/O₂ molar ratio and pH on the removal of iron and manganese (Mouton *et al.*, 2007; Mulaudzi *et al.*, 2009) were studied. From a commercial-scale point of view, however, the use of SO₂ gas in a mixture with air presents a number of drawbacks, including:

- The possibility of poor gas-liquid mass transfer due to changes in partial pressures of the individual gases,
- The possible liquefaction of SO₂ prior to entering the reactor as the gas mixture would be introduced against a slurry head
- Excessive air flows required to dilute SO₂ to < 3% (v/v) in air.

These difficulties resulted in poor and inconsistent performance of the SO₂/air oxidative precipitation system. Furthermore, safety precautions would be needed due to the environmental and health risks associated with systems using SO₂ gas.

Recognizing the challenges associated with the conventional SO₂/air technology, Mintek developed an improved system that would allow a significantly more controllable and consistent performance. This improved system is primarily based on introduction of SO₂ as sulphurous acid (H₂SO₃), significantly reduced air flows, and efficient oxygen mass transfer. This paper presents the new method, and addresses practical considerations for the implementation of the technology on an industrial scale.

Background

Applications of SO₂/air in hydrometallurgy

SO₂ is a toxic, colourless gas, released naturally into the atmosphere from volcanoes. It is commonly produced by burning sulphur, by the combustion of sulphurous fossil fuels, and as a by-product in various industrial processes, such as the roasting of sulphide ores. SO₂ has found various applications in industry. Common uses include as a catalyst in the petroleum industry, or in acid plants for the production of sulphur trioxide as a precursor of sulphuric acid. In hydrometallurgical processes, SO₂ is used widely as an effective reducing agent, for processes such as the reductive dissolution of cobalt and reductive leaching of cobalt from heterogenite ores. Oxygen is widely used as a weak oxidant in oxidative precipitation of iron. However, when combined with SO₂ gas, the mixture displays significantly stronger oxidizing properties compared to O₂ alone. This practice is not novel and has been used on industrial plants.

The available literature on the use of SO₂/O₂ or SO₂/air as an oxidant for metal ions in acidic media is quite broad. Many authors have researched various applications for this technology, including but not limited to the oxidative precipitation of manganese and iron from cobalt, nickel, and zinc streams in base metal circuits, leaching of uranium ores (Ho and Quan, 2007), oxidative precipitation of arsenic from arsenical fume leachates, and leaching of sulphide minerals such as chalcocite (Cu₂S) using regenerated Fe(III) (Zhang *et.al*, 2000b).

In particular, the SO₂/air technology has found great interest in copper-cobalt operations for the oxidative precipitation of iron and manganese from plant liquors. The Central African Copperbelt region, stretching from the Democratic Republic of Congo (DRC) to Zambia, has vast deposits of copper and cobalt, which have attracted major investment interests for many years. The processing of these orebodies, via H₂SO₄ leaching, leads to the presence of manganese and iron in solution, which need to be removed prior to any metal recovery. The typical treatment of Copperbelt ores involves agitated leaching followed by copper solvent extraction (SX) and electrowinning (EW) to produce a high-grade copper metal. A bleed stream of the copper SX raffinate is used for the recovery of cobalt as an intermediate precipitate or as high-grade metal. The effective removal of iron and often manganese from the bleed stream is essential in order to produce high-quality cobalt products. These impurities can be removed using the SO₂/air technology, which has recently been commercialized in a number of copper-cobalt plants such as Ruashi and Tenke Fungurume in the DRC.

Fe (II) and Mn (II) oxidation by SO₂/air

Thermodynamic considerations

Iron and manganese speciation in sulphate solutions is controlled primarily by the pH and oxidation-reduction potential conditions prevailing in a particular system. Thermodynamic stability diagrams, such as Pourbaix diagrams, can be used as a tool to predict thermodynamic reactions under specific conditions of concentration, temperature, and medium.

Figure 1 shows the possible species that can form during Mn oxidation and precipitation with SO₂/air at 25°C. For iron oxidation, the regions where the different species may form are illustrated in Figure 2. The thermodynamic equilibrium information was generated using the HSC Chemistry software. Based on the conditions applied, the diagrams were used as a tool to predict regions where Fe and Mn solid oxidative products are predominant, while Co(II) would remain in solution. The formation of Mn₂O₃ during oxidative precipitation of Mn(II) is thermodynamically feasible if the redox potential of the system increases above that of the Mn₂O₃/Mn(II) line. At pH 3.0, precipitation of Mn(II) as Mn₂O₃ becomes thermodynamically feasible at redox potentials > 800 mV (SHE). Similarly, the Fe-Co-S diagram predicts the precipitation of Fe(II) as Fe(OH)₃ at redox potential > 550 mV (SHE).

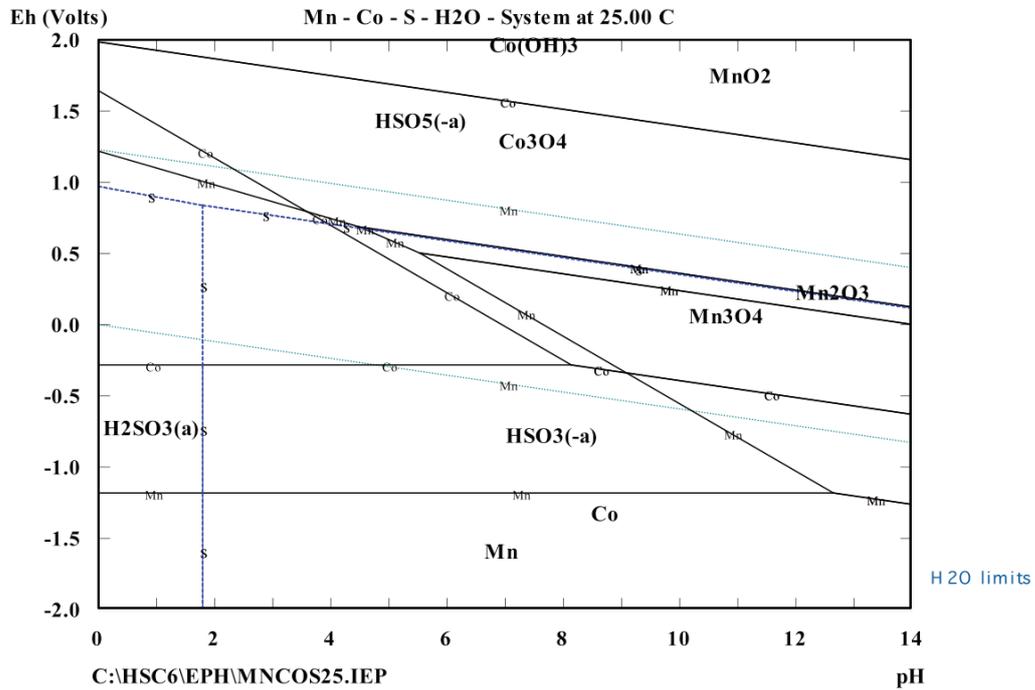


Figure 1. Thermodynamic equilibrium for Mn-Co-S-H₂O (6 g/L cobalt, 2 g/L manganese, and 6 g/L sulphur) system at 25°C and 1 atm.

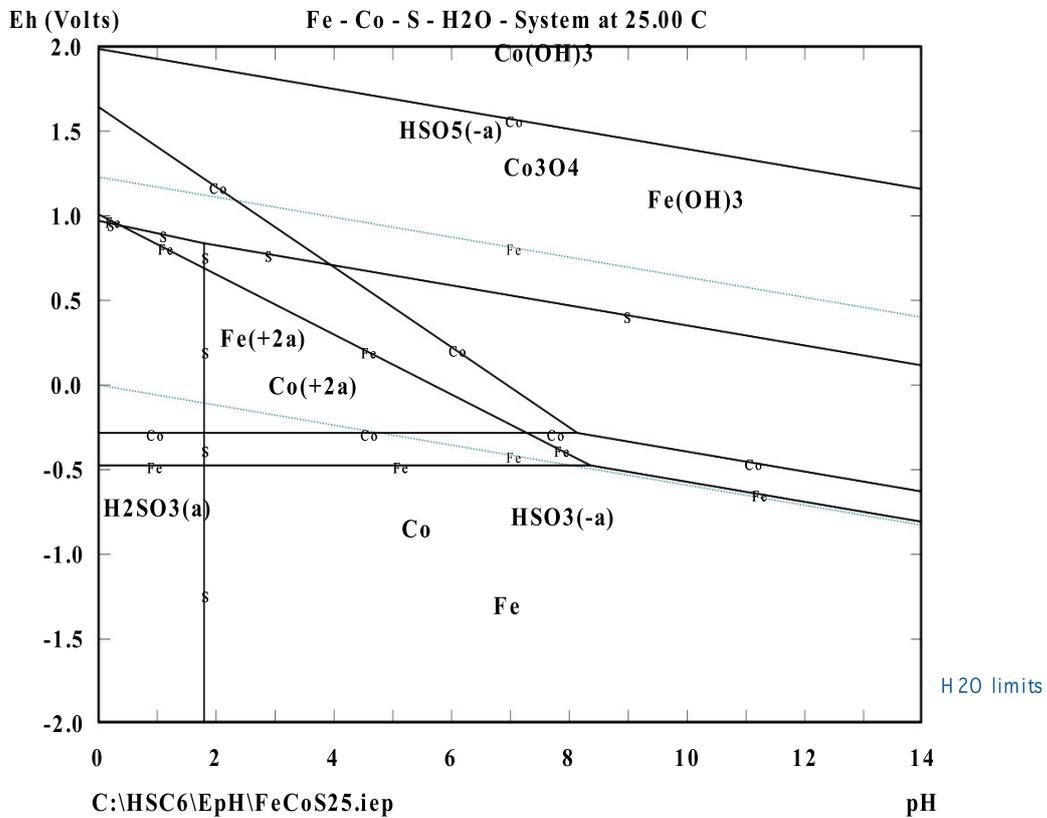


Figure 2. Thermodynamic equilibrium for Fe-Co-S-H₂O (6 g/L cobalt, 2 g/L iron, and 6 g/L sulphur) system at 25°C and 1 atm.

Reaction mechanisms

Earlier studies on the use of SO₂/O₂ as an oxidant date back to 1915, by Australian metallurgist Du Faur (1915), who patented a process that utilizes a gas mixture of SO₂ and air for the oxidation of ferrous to ferric in sulphate solutions. Later studies were conducted by Ralston (1927), who investigated the preparation of solutions of ferric sulphate or sulphuric acid with a mixture of air and sulphur dioxide. Ralston also studied the effects of bubble size of the gas mixture on ferrous oxidation. The experiments were conducted using ferrous solutions of different concentrations in the range of approximately 1-5 g/L. The SO₂/air gas mixtures contained 0.1-13% (v/v) of SO₂. The author reported that less oxidation of iron was obtained with bigger gas bubbles. Under the conditions tested, faster oxidation kinetics was obtained with gas mixture containing up to 7% (v/v) of SO₂.

In recent years, Zhang *et al.* (2000b) studied the kinetics of iron oxidation by SO₂/O₂ to generate Fe(III) or form H₂SO₄ for subsequent leaching processes, such as the leaching of chalcocite and oxidation and precipitation of manganese from nickel/cobalt solutions. The authors found that the rate of oxidation of Fe(II) is enhanced in the presence of SO₂/O₂ gas mixtures (as opposed to O₂ alone), and is influenced by the ratio of dissolved SO₂ to dissolved O₂. The authors studied the effect of the SO₂/O₂ ratio at different temperatures and pH, and concluded that there is an optimal ratio above which the oxidation of Fe(II) is inhibited due to reduction of Fe(III) by excess SO₂. The optimal SO₂/O₂ ratio was found to be dependent on temperature, pH, and reactor design. At 80°C, the optimum gas concentration of SO₂ in the gas mixture was approximately 2% (v/v) with a solution containing 0.1 M Fe(II) as sulphate (approx. 5.6 g/L Fe²⁺).

Zhang *et al.* (2000b) proposed a radical chain reaction mechanism for the auto-oxidation of S(IV) by O₂ in the presence of Fe, as shown in Equations [1-8]. Initially, there is a slow formation of a ferric sulphite complex (Equations [1-3]) and decomposition to produce the sulphite radical SO₃^{•-} (Equation [4])



In the presence of O₂, the SO₃^{•-} radical reacts rapidly with oxygen to form a peroxy-monosulphate species, SO₅^{•-} (Equation [5]).



The SO₅^{•-} radical is responsible for the oxidation of Fe (II) as shown in Equations [6-8]:



A few years later, Zhang *et al.* (2002) also studied the mechanism of oxidation of Mn(II) with SO₂/O₂ and reported that it is similar to Fe(II) oxidation. The study demonstrated that, for the removal of manganese impurities from cobalt and nickel leach solutions, the oxidative precipitation of Mn(II) as MnO₂ or Mn₂O₃/Mn₃O₄ should be carried out at pH 3-4 in order to minimize co-precipitation of nickel and cobalt. The authors also emphasized the influence of the O₂ gas transfer rate on the oxidation of Fe(II) and Mn(II) in SO₂/air systems. Due to the lower solubility of O₂ compared to SO₂, the rate of transfer of oxygen from the gas phase to the liquid medium limits the rate of reaction. This observation was also noted by Menard *et al.* (2007) in their study of the removal of Mn(II) from zinc neutral leach liquors. They found that the manganese removal process was controlled by gas transfer kinetics, which was highly influenced by the reactor design and agitation system used.

The use of SO₂/air as an oxidant for oxidative precipitation of Mn(II) was also investigated by Mulaudzi (2009), whose results validated those found by Zhang *et al.* (2002). The results showed that low concentrations of Mn(II) can be selectively oxidized and precipitated from Co(II) solutions at around pH 3, with less than 1% co-precipitation of cobalt.

Practical considerations in implementing the conventional SO₂/air technology

In SO₂/air systems, it is common practice to source the SO₂ from a sulphur burner or sulphide mineral roaster, if available on site. The SO₂ gas is combined with air at a specific molar ratio of SO₂:O₂ prior to introduction into the reactor. This method presents a number of challenges:

- The roaster off-gas usually contains a large volume of inert gas, which would give rise to large gas flow rates. Larger pipes and multistage blowers would have to be used to handle the large volumes. Furthermore, the oxygen content in the total gas mixture is diluted by the inert gas, which would reduce the partial pressure of oxygen and hence reduce the mass transfer coefficient of oxygen
- This type of system has a high energy requirement for mixing, which would result in higher capital and operating costs
- Fluctuations in SO₂ concentrations in the roaster off-gas may influence the oxidation reaction kinetics. Hence, it would be necessary to control effectively the SO₂/O₂ ratio in the gas mixture
- If the system is not carefully designed, back pressure or temperature variations might result in the liquefaction of SO₂, which would then enter the tank as a liquid and cause 'hot 'spots' that would be reductive. This would result in inefficient oxidation
- Health and safety precautions should be put in place when handling SO₂ gas.

As a consequence of these factors, an alternative method is proposed for the introduction of SO₂ in SO₂ /air systems for oxidative precipitation of Fe and Mn.

New development in SO₂/air technology

Mintek patented a new method for the introduction of SO₂ in a system where SO₂ was previously introduced in the gas phase. The SO₂ is introduced into the reactor in aqueous, dissolved form as sulphurous acid (H₂SO₃), separately from the oxygen gas or air. An appropriate gas absorption unit could be used to scrub the SO₂ gas into an aqueous stream to produce H₂SO₃. It is known that SO₂ gas is fairly soluble in water. Sulphurous acid, H₂SO₃, which is also known as the aqueous form of SO₂, has never been isolated in aqueous solution; hence its presence in water has not been detected. The hydrogen sulphite ion, HSO₃⁻, on the other hand, is the reducing agent that has been detected in such solutions (Equations [1] and [2]).

The new method of adding SO₂ holds more advantages over conventional reagent introduction, particularly for operations that have a sulphide mineral roaster, as the off-gas, which typically contains low concentrations of SO₂, could be contacted with a process stream or water to absorb the SO₂. The resulting dilute acid solution will then be pumped to the reactor to carry out the oxidative precipitation of iron and manganese. Amongst the benefits is an increase in O₂ mass transfer and more controllable SO₂ introduction. Due to the oxygen source being introduced separately from the SO₂, hence being free from additional inert gas (which would normally be present in the SO₂ off-gas), smaller ducts for gas streams and fewer blowers would be needed to supply the gas to the reactor, hence the equipment cost will be lower. Lastly, the SO₂ gas absorption technology is well known and there are readily available systems for SO₂ scrubbing, which can be easily integrated into the precipitation system.

Experimental

Scoping laboratory tests were conducted using H₂SO₃ and air for oxidative precipitation of iron and manganese from cobalt-bearing solutions. The aim was to prove the principle of using SO₂ in aqueous dissolved form, as opposed to direct sparging.

Materials and apparatus

Synthetic solutions used as feed in the experiments were prepared using sulphate salts of Analytical Research (AR) grade. The feed solutions resembled the liquor obtained from cobalt leach operations in acid media containing approximately 6-7 g/L Co(II), 2 g/L Mn(II), and 2g/L Fe(II). Sulphurous acid (5-6% w/w SO₂ content) solution was used as a source of SO₂. Hydrated lime slurry (20% w/w) was used for pH control.

The experiments were conducted in a 17 L cylindrical tank, equipped with controllers for temperature and agitation speed, and fitted with four equally spaced baffles (Figure 3). Mechanical agitation was provided by means of a Rushton turbine impeller. The impeller was selected to provide efficient mixing and mass transfer of the gas into the liquid phase.

Air was fed into the system through an L-shaped gas sparger with three orifices (diameter: 2 mm) equally spaced at 20 mm. The tube (sparger) was located below the impeller.

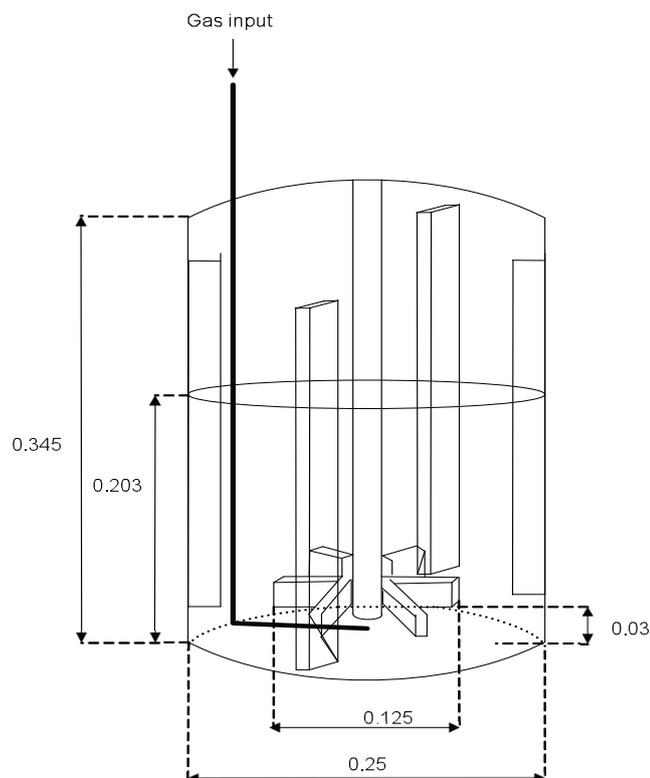


Figure 3. Schematic diagram of the reactor (dimensions in metres)

Experimental methodology

The effects of temperature, air flow rate, and flow rate of SO_2 (as sulphurous acid) were studied. All tests were performed at atmospheric pressure, at an agitation speed of 350 r/min and at a pH of 3.0. The test matrix is shown in Table I. Each experiment was conducted for 6.5 hours using 10 L of feed solution. The experiments were conducted at room temperature, except for one test done at 40°C . H_2SO_3 solution was added continuously over a period of 6.5 hours to achieve the targeted addition rate of SO_2 . The latter was based on the stoichiometric addition of SO_2 necessary to achieve complete removal of iron and manganese species (where applicable) present in the feed liquor over 6 hours. Solid samples were assayed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Liquors were analysed by atomic absorption spectrometry (AAS) and ICP-OES.

Table I. Experimental matrix

Parameter	Range
Species present in feed sample	Fe, Mn, and Co
Temperature, $^\circ\text{C}$	Ambient (no temperature control) - 40
Sulphurous acid (5-6% SO_2) flow rate, mL/min	1.5; 3; 6
Targeted SO_2 addition (\times stoichiometric amount required for complete removal of Fe and Mn)	1; 1.7; 3.4
Air flow rate, mL/min	200; 1000
Agitation speed, r/min	350
pH	3.0

Results and discussion

Effect of temperature

The effect of temperature was investigated by varying the solution temperature from ambient (approx. 20°C) to 40°C at pH 3.0 and an air flow rate of 1000 mL/min. The acid flow rate was maintained at 3 mL/min, which was equivalent to a supply of 1.7 times the stoichiometric requirement of SO₂ with respect to iron and manganese present in the feed solution, for the precipitation of ferric and MnO₂.

The precipitation efficiencies of manganese and iron are plotted in Figure 4 for both experiments. It is evident that > 99.5% of the initial ferrous ion has been oxidized and precipitated within 1.5 hours of reaction time in both experiments. The figure also shows that the kinetics of manganese removal was enhanced after complete removal of iron (as expected). The kinetics of manganese removal was, however, slower for the test conducted at a higher temperature; only approximately 30% (w/w) of Mn was removed within 3 hours at 40°C, as opposed to approximately 50% (w/w) for the experiment conducted under ambient conditions. This could possibly be attributed to a decrease in the solubility of oxygen at higher temperature.

Similar overall manganese precipitation efficiencies were noted in both experiments, and cobalt losses were less than 3%.

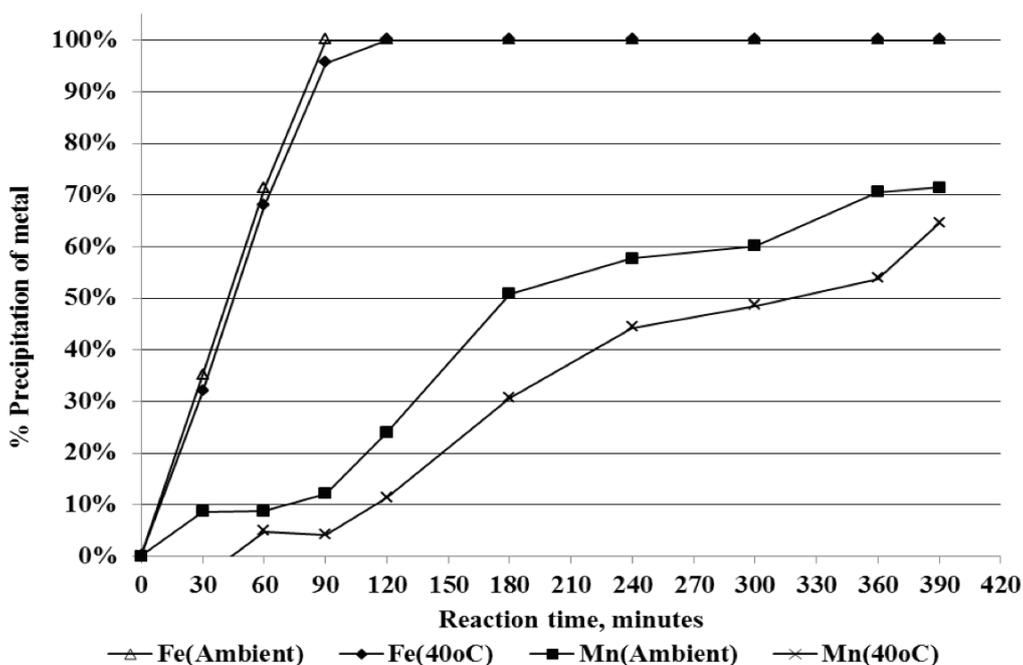


Figure 4. Mn and Fe precipitation efficiencies at different temperatures. pH = 3.0; agitation speed: 350 r/min; air flow rate = 1000 mL/min; temperatures: room temperature and 40°C; H₂SO₃ flow rate: 3 mL/min

An average dissolved oxygen (DO) concentration of 7 mg/L was measured for the test conducted at ambient conditions. At 40°C, the initial DO concentration was 4 mg/L, which remained constant throughout the experiment. This indicated that temperature had an effect on the availability of dissolved oxygen in solution. It is common knowledge that the solubility of oxygen decreases with an increase in temperature, as a result of an increase in kinetic energy which leads to the breaking of the intermolecular bonds, and the escape of the gas molecules. In both tests, the oxygen supply was found to be sufficient to sustain the chemical oxidation reactions, and ensure the removal of > 99.5% of iron and approximately 70% of manganese within 6 hours.

From a scale-up point of view, the knowledge of the volumetric gas mass transfer coefficient ($K_L a$) and oxygen uptake rate for this particular system would be needed to determine the optimal flow rate of air (or oxygen) that would ensure the minimal allowable supply of oxygen needed for the precipitation reactions. This would avoid oxygen becoming a limiting factor inside the system, but also prevent an oversupply of oxygen, which would have cost implications. Ideally, the rate of oxygen utilization in the oxidation reactions should be lower than the rate of gas transfer across the gas-liquid interface per unit liquid volume. The latter is described by the equilibrium concentration

of oxygen in the liquid as well as the volumetric mass transfer coefficient (K_1a). This coefficient is an important parameter for reactor design and scale-up applications.

Effect of acid and air flow rates

A number of experiments were conducted at various H_2SO_3 flow rates (1.5, 3, and 6 mL/min) and air flow rates (200 and 1000 mL/min) in order to investigate the effects of variations of H_2SO_3 and air flow rates on the precipitation efficiency.

The first set of tests was performed at an air flow rate of 1000 mL/min, and acid flow rates of 3 and 6 mL/min. This is equivalent to a stoichiometric addition of 1.7 and 3.4 times respectively for forming MnO_2 . Figure 5 shows the effects of variations in the flow rates of H_2SO_3 on the precipitation kinetics. The kinetics of removal of iron and manganese increased with an increase in the flow rate of aqueous SO_2 , as expected. Complete removal of iron was achieved within 60 minutes at a higher acid flow rate, while it took longer when the acid flow rate was halved. The increase in reaction kinetics as a result of an increase in acid addition was expected, as more SO_2 was made available more rapidly for the oxidation reactions. In addition, an adequate supply of oxygen was maintained in both experiments.

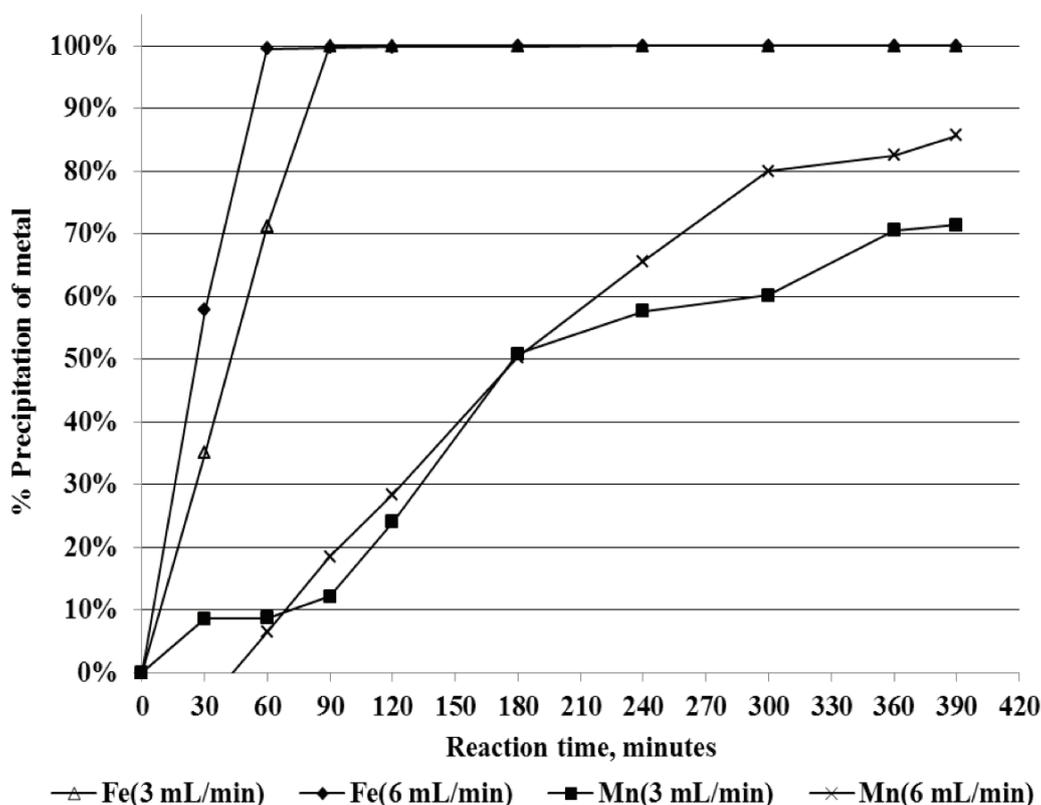


Figure 5. Mn and Fe precipitation efficiencies at different flow rates of H_2SO_3 , pH = 3.0; agitation speed: 350 r/min; air flow rate = 1000 mL/min; H_2SO_3 flow rates: 3 and 6 mL/min

Two additional tests were conducted at an air flow rate of 200 mL/min, and acid flow rates of 3 and 1.5 mL/min. The same observation was made when comparing the results from the tests done at acid flow rates of 3 mL/min and 1.5 mL/min, and a lower gas flow rate of 200 mL/min. Complete iron removal was achieved within 1.5 hours with an acid flow rate of 3 mL/min, while it took close to 3 hours for complete iron removal when the acid flow rate was halved due to the slow flow rate of H_2SO_3 . Slower kinetics was also observed for manganese precipitation, which resulted in longer residence times. Cobalt losses were less than 3% (w/w) in all tests. In all experiments, it was observed that the lime consumption increased with an increase in acid addition.

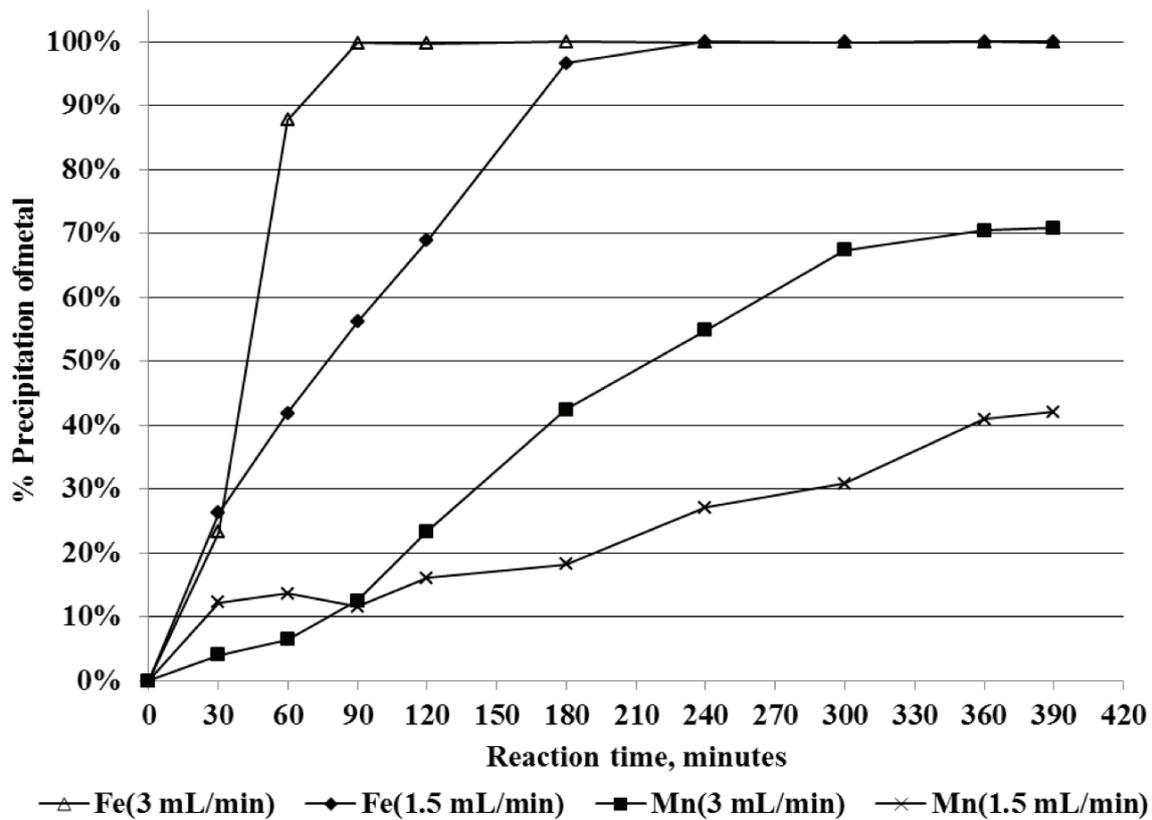


Figure 6. Mn and Fe precipitation efficiencies at different flow rates of H₂SO₃, pH = 3.0; agitation speed: 350 r/min; air flow rate = 200 mL/min; H₂SO₃ flow rates: 1.5 and 3 mL/min

When comparing the results of the tests performed to investigate the effect of gas flow rates on precipitation kinetics, i.e. an acid flow rate of 3 mL/min, and gas flow rates of 200 and 1000 mL/min (Figure 7), the kinetics of Fe removal was more or less similar. However, the Mn kinetics was about 10% faster at the higher air flow rate, as more dissolved oxygen was made available for the oxidation reaction. However, the economics of this increase versus doubling the air flow rate would have to be considered during the final optimization of the system.

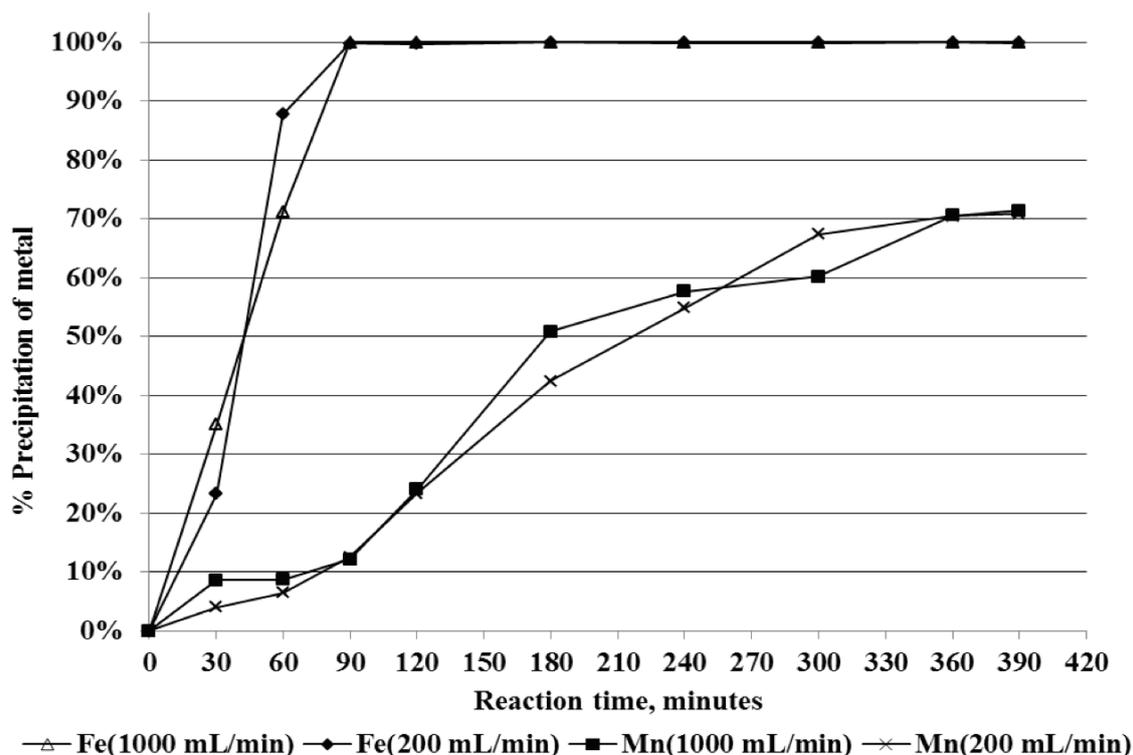


Figure 7. Mn and Fe precipitation efficiencies at different gas flow rates. pH = 3.0; agitation speed: 350 r/min; H₂SO₃ flow rate = 3 mL/min; gas flow rates: 200 and 1000 mL/min

Zhang *et al.* (2000b) reported the influence of the oxygen gas transfer rate on the oxidation of Fe(II) and Mn(II) in SO₂/O₂ systems. The authors indicated that the rate of transfer of oxygen to the liquid phase limits the rate of oxidation. In the tests conducted, the results obtained indicated that there was sufficient dissolved oxygen available for the oxidation reactions, even at the lower air flow rate of 200 mL/min. This statement can be backed up by the DO concentrations monitored during each test. At a gas flow rate of 1000 mL/min, the initial DO concentration decreased from approximately 9 mg/L to 7 mg/L. A more pronounced decrease was observed in the experiment where the air supply was maintained at 200 mL/min. The DO concentration dropped from approximately 7 mg/L to 3 mg/L under the operating conditions tested. Even though the rate of Mn(II) oxidation was slightly slower at the lower gas flow rate, the mass transfer dynamics of oxygen under the operating conditions tested provided sufficient amount of oxygen for the oxidation reactions.

Practical considerations

The new approach of introducing a dilute SO₂ solution to carry out the oxidative precipitation of manganese and iron in the presence of oxygen has been demonstrated satisfactorily at the laboratory scale. Under the operating conditions tested, it was observed that the kinetics of iron and manganese oxidation depended on the mass transfer of oxygen gas, although an adequate supply of oxygen was maintained in the experiments.

There are a few practical aspects to take into account with regard to the technology. The rate of transfer of oxygen from the gas to the liquid phase is influenced by the reactor design, and agitation and sparging systems in place. Proper care should be taken when dealing with gas-liquid systems to ensure efficiency in oxygen transfer and improved process performance. However, the design for optimum oxygen mass transfer is established technology.

The SO₂ aqueous stream could be produced using an adequate gas absorption system to scrub the SO₂ gas into a liquid stream, prior to introduction in the precipitation reactor. In this way, the control of SO₂ addition is simplified in the system as the SO₂ is introduced as a solution of known concentration, originating from a gas absorption unit. The absorption of SO₂ into water is also established technology, and hence the risk around this would be minimal.

Conclusions

The introduction of SO₂ as an aqueous stream has the potential to alleviate some of the issues related to the conventional SO₂/air technology. The advantages of the new approach include:

- Significantly lower capital and operating expenditure for the required oxygen mass transfer ;
- Efficient and more controllable SO₂ addition, and
- Improved process control.

Technologies for oxygen mass transfer from air and absorption of SO₂ are provided by various vendors as technology packages, which often include process performance guarantees. Hence, the risk around the introduction of the SO₂/air oxidation technology has been minimized.

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