

MANGANESE REMOVAL FROM COBALT SOLUTIONS WITH DILUTE SULPHUR DIOXIDE GAS MIXTURES

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Abstract

The use of dilute sulphur dioxide (SO₂) gas mixtures for the oxidation/precipitation of manganese has been explored widely in recent years. The technical merit of the concept is well proven and implementation of the technology on commercial scale is imminent.

This paper reviews the technology of manganese removal by means of dilute SO₂ gas mixtures and highlights some of the challenges associated with its implementation on industrial scale.

A brief review of the technology is presented; the review considers both the mechanism and chemistry of manganese oxidation/precipitation with dilute SO₂ gas mixtures. The impact of variables such as temperature, pH and SO₂ concentrations on the manganese removal process is assessed.

Challenges associated with implementation of the technology on industrial scale are discussed. Gas dispersion is highlighted as a critical design consideration.

1. Introduction

Sulphur dioxide (SO₂) is typically used as a strong reducing agent in hydrometallurgical applications. It is, however, well known that dilute SO₂/O₂ gas mixtures exhibit strong oxidising properties.

The use of dilute SO₂ gas mixtures to remove manganese from cobalt containing solutions has received considerable attention in recent years. The technology is of particular interest to cobalt producers in central Africa where cobalt is often associated with appreciable quantities of manganese; removal of this impurity is required to prevent contamination of cobalt salt products and/or problematic accumulation in the electrolyte inventory of cobalt electrowinning facilities.

Commonly used cobalt/manganese separation techniques include sulphide precipitation and solvent extraction (using D2EHPA as extractant). Although these technologies are well established, they are not without operational difficulties. Sulphide precipitation requires the use of hazardous hydrogen sulphide, while solvent extraction introduces the risk of fire and the potential of organic cross contamination when other solvent extraction circuits are used in the process flowsheet.

Manganese oxidation/precipitation with dilute SO₂ gas mixtures is a relatively simple alternative to more established cobalt/manganese separation techniques. It is typically proposed to oxidise manganese with dilute SO₂/air mixtures in agitated tanks whilst promoting precipitation with the addition of limestone/lime. The use of SO₂/air is generally preferred over SO₂/O₂ in order to avoid the use of costly oxygen.

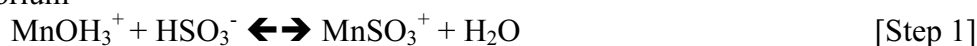
This paper reviews the technology of manganese removal with dilute SO₂/air mixtures and the implementation of the technology in agitated vessels at the industrial scale.

2. Theory of oxidative precipitation of manganese

2.1. Mechanistic Considerations

Zhang¹ concluded that manganese oxidation with dilute SO₂ gas mixtures proceeds via a radical chain mechanism that includes the formation of highly oxidative peroxy-monosulphate species. The proposed mechanism involves the slow initial formation of a sulphite complex and decomposition to produce the sulphite radical SO₃^{•-}. This is followed by a fast reaction with O₂ to form a peroxy-monosulphate species SO₅^{•-}, and subsequent HSO₅⁻ which are believed to be responsible for the oxidation of Mn(II) and sulphite species. The major steps are believed to be:

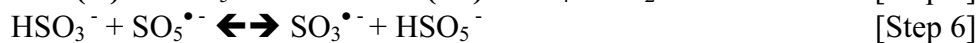
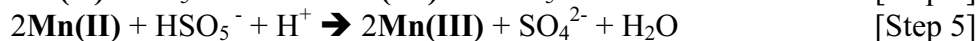
Equilibrium



Initiation



Oxidation



Termination



2.2. Chemical Considerations

Zhang¹ investigated the oxidation of iron and manganese with dilute SO₂ gas mixtures and observed that the metals are removed via a similar chemical mechanism. Typically observed batch oxidation of Fe(II) is characterised by a curved induction period, followed by linear concentration increase in Fe(III) (according to Forward Reaction [R1]), and a curved completion period when an apparent equilibrium is reached. Oxidation is nearly complete when gas mixtures of low SO₂ content are used, but incomplete for richer gas mixtures. Incomplete oxidation of iron was attributed to the reverse reduction of Fe(III) by SO₂ (according to Reaction [R2]).

Oxidation of Fe(II)



Reduction of Fe(III)



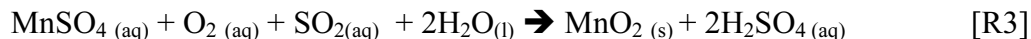
Krause² investigated the oxidation of Fe(II) with SO₂/O₂ gas mixtures and concluded that the oxidation process is influenced by factors such as pH, temperature, gas mixture, SO₂ concentration, and gas-liquid mass transfer efficiency (amongst others). Most notably, Krause² concluded that the efficiency of iron removal with dilute SO₂ mixtures is

dependent on the dissolved O₂: dissolved SO₂ ratio. Krause² identified an ‘oxygen excess’ regime (dissolved O₂: dissolved SO₂ > 60) which is associated with efficient oxidation and an ‘oxygen starvation’ regime (dissolved O₂: dissolved SO₂ < 60) where SO₂ also exhibits reducing properties. Under the latter condition, manganese is first oxidised (by the ‘forward reaction’) and then partially reduced (by the ‘reverse reaction’) in an apparent inefficient net reaction. Krause’s work showed that unwanted ‘reverse reactions’ are minimized when <5% v/v SO₂/O₂ mixtures (equivalent to <1% v/v SO₂/air) are used.

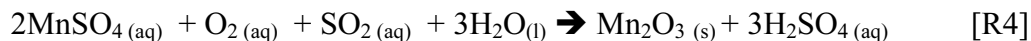
In line with the observations by Zang¹ and Krause², Van Rooyen³ argued that SO₂ can follow several reaction routes in the Mn-SO₂-O₂-H₂O system, most notably the oxidation/precipitation of Mn(II) (refer to Reaction [R3], by the ‘forward reaction’), the reduction of MnO₂ (refer to Reaction [R5], by the ‘reverse reaction’), and the formation of acid. The extent to which SO₂ reports to a specific reaction route is determined by the relative rate of that route. The oxidation/precipitation of manganese is most efficient under conditions that promote the rate of MnO₂ formation at the expense of MnO₂ reduction and direct acid formation.

The oxidation/precipitation of Mn (by the ‘forward reaction’) in the presence of O₂/SO₂ proceeds according to⁽¹⁾:

At pH <4



At pH 5-7



The reduction of manganese precipitation products (by the ‘reverse reaction’) to sulphate proceeds as follows:

Reduction of MnO₂



Reduction of Mn₂O₃



An illustration of the interaction of the ‘forward reaction’ and ‘reverse reaction’ of the SO₂/air-manganese system is available from Figure 1. Note that the air/SO₂-manganese system at pH 6 is heavily dominated by the formation of Mn₂O₃ (refer to Reaction [R4]) when gas mixtures of less than 7.5% v/v SO₂/O₂ (equivalent to ~1.5% v/v SO₂/air) is used; the measured oxidation rate compares well with stoichiometric requirements thus suggesting minimal competing reactions for SO₂. Above a gas mixture concentration of 7.5% v/v SO₂/O₂ it can be seen that competing reactions become prominent; the apparent net rate of manganese oxidation decreases and near stoichiometric SO₂ consumption is no longer achieved.

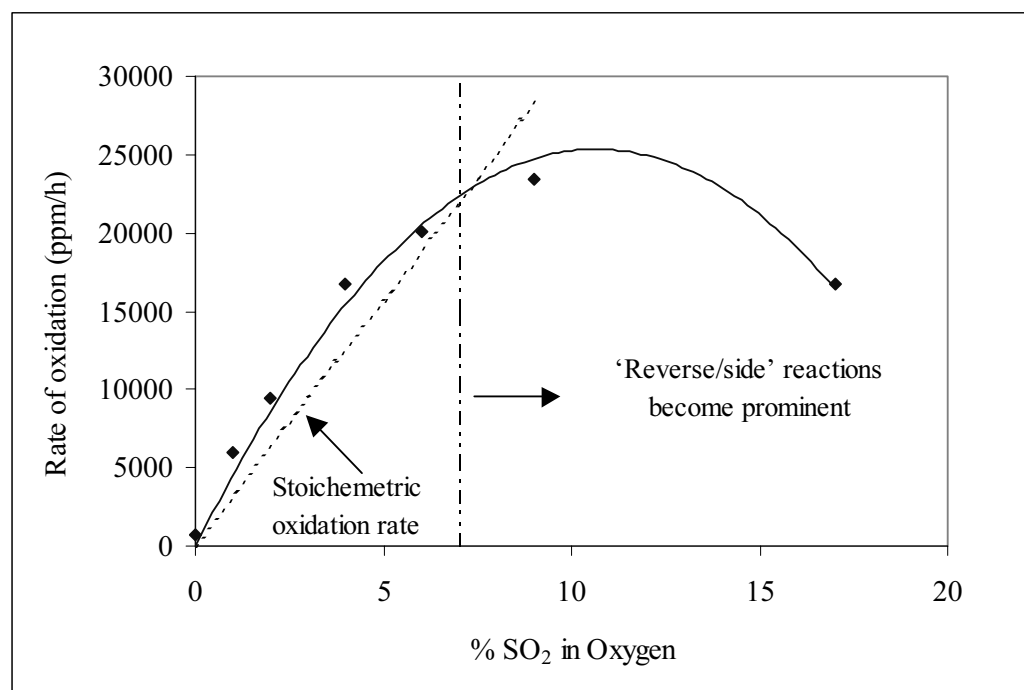


Figure 1: Effect of gas composition on Mn oxidation rate (ref: Zhang¹) (at 0.1M MnSO₄, pH6 and 80°C)

A further illustration of the interaction of the ‘forward reaction’ and ‘reverse reaction’ of the SO₂/air-manganese system is provided by Zhang¹. Batch oxidation/precipitation of manganese was performed up to a point where the net removal rate has slowed noticeably. The precipitated manganese was physically removed from the batch system and removal was again attempted. Improved net manganese removal rates were achieved in the absence of precipitate that can drive the ‘reverse reaction’.

2.3. Kinetic Considerations

The rate of manganese oxidation with dilute SO₂ gas mixtures shows a first order dependence on sulphite species up to about 5.7% v/v SO₂ (refer to Figure 1) and a 0.5 order dependence on pH in a range of 1.5-6 (refer to Figure 2)¹.

Note from Figure 2 that a manganese oxidation rate of ~600 ppm/h can be expected at a pH of 3.0 and a temperature of 80°C when a 2% v/v SO₂/O₂ mixture is used. This is consistent with measurements at 50°C by a well-established South African research facility.

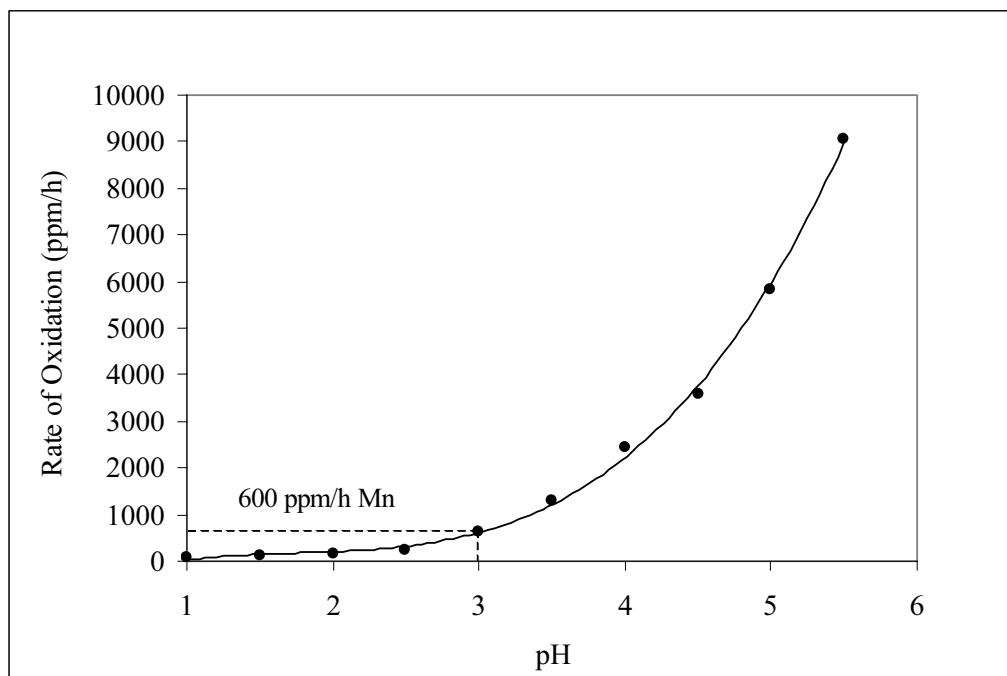


Figure 2: Effect of pH on Mn oxidation rate (ref: Zhang¹) (at 0.1M FeSO₄, MnSO₄, 2% v/v SO₂/O₂ and 80°C)

Zhang¹ illustrated the effect of pH and SO₂ concentration on manganese removal rate; a manganese removal rate of 2500 ppm/h was recorded at a temperature of 50°C and a pH of 3.5 with a 1% v/v SO₂/air mixture (equivalent to ~5% v/v SO₂/O₂).

2.4. Co-precipitated cobalt loss

A key consideration when using SO₂ gas mixtures for manganese removal from cobalt containing solutions is the extent of co-precipitated cobalt loss. Zhang¹ investigated the co-precipitation loss of cobalt at 50°C and after near complete removal of manganese had been achieved (refer to Figure 3). Figure 3 shows that co-precipitated cobalt loss is strongly dependent on pH; at pH levels below 3.5, losses of lower than 1% is achieved. Cobalt loss increases significantly above a pH of 3.5. It was concluded that cobalt precipitation can be minimized by controlling the pH and also optimizing the residence time required for manganese removal.

2.5. Gas-Liquid Mass Transfer Considerations

Krause² identified gas-liquid mass transfer as an important consideration when using dilute SO₂ gas mixtures as an oxidant.

This paper considers the removal of manganese with SO₂/air in agitated vessels. Important considerations in the design of these vessels include the ability of the agitation system to provide solids suspension and to satisfy the mass transfer and gas dispersion requirements of the Mn-SO₂/air system. The latter is the more probable design constraint when a dilute mixture of SO₂/air is used to support a significant Mn removal duty.

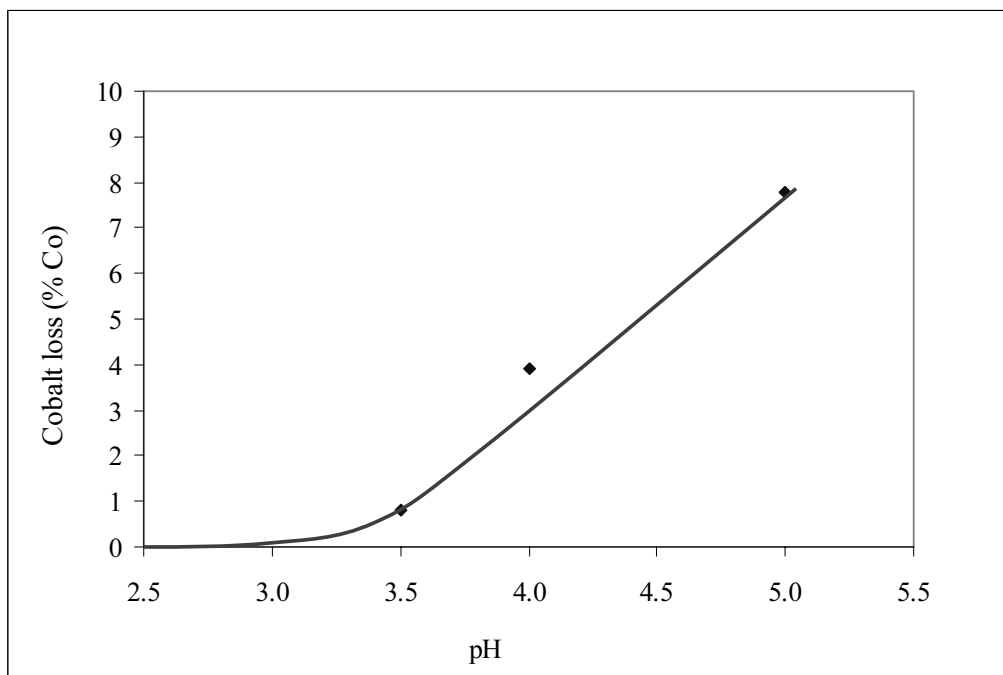


Figure 3: Effect of pH on co-precipitated cobalt loss at 50°C (ref: Zhang¹)

Agitators are characterised by a unique relationship between power consumption and its ability to generate flow. Flow conditions at the impeller and within the vessel are defined by the dimensionless Impeller Reynolds Number⁵ (refer to Equation [Eq1]). Turbulent conditions at the impeller and laminar flow in other regions of the vessel exist at Impeller Reynolds Numbers between 10 and 10000; turbulent conditions exist throughout the vessel for Reynolds Numbers greater than 10000.

$$N_{Re} = (D_a^2 N \rho) / \mu \quad [Eq1]$$

where

- N = rotational speed (s⁻¹)
- D_a = impeller diameter (m)
- ρ = fluid density (kg/m³)
- μ = fluid viscosity (Pa.s)

The agitator shaft power is defined by Equation [Eq2].

$$P_{Ag} = N_p \rho N^3 D_a^5 \quad [Eq2]$$

where N_p = dimensionless power number (unique to agitator type)
 D_a = impeller diameter (m)
 N = rotational speed (s^{-1})
 ρ = fluid density (kg/m^3)

The dimensionless agitator power number is dependent on numerous factors such as the type of agitator, its arrangement within the vessel as well as the dimensions of both the impeller and tank. The impeller discharge/pumping rate is defined by Equation [Eq3].

$$Q = N_Q N D_a^3 \quad [Eq3]$$

where N_Q = dimensionless pumping number (unique to agitator type)
 D_a = impeller diameter (m)
 N = rotational speed (s^{-1})

The dimensionless agitator discharge/pumping number is dependent on the impeller's geometric variables such as the number of blades, blade pitch, impeller-to-diameter ratio and the impeller height above the base of the vessel.

The effect of aeration in an agitated vessel is defined by the dimensionless Aeration Number given in Equation [Eq4] that is calculated using the actual gas flowrate and the impeller pumping rate determined in Equation [Eq3]. The aeration number is a measure of gas-to-liquid flow rate in the agitated vessel. The maximum aeration number that can be supported by an agitation system is known as the 'flood point' of the agitator and represents the maximum allowable gas dispersion rate for the system.

$$N_{AE} = Q_A / Q \quad [Eq4]$$

where Q_A = actual gas flowrate (m^3/s)
 Q = impeller discharge/pumping rate (m^3/s)

3. Discussion

The use of dilute sulphur dioxide (SO_2) gas mixtures allows the removal of manganese from cobalt solution with low cobalt losses. The use of air with $<1\%$ v/v SO_2 is typically proposed as this results in high efficiency of SO_2 utilisation for manganese removal (refer to Reactions [R3] and [R4]). Although the oxidation/precipitation rate of Mn increases with increasing pH values (as shown in Figure 2), the technology is normally utilised at pH levels between 3 to 4 in order to limit co-precipitation of Co (refer to Figure 3). Operation in this pH range and with 0.5% v/v SO_2 -in-air gas mixtures results in Mn removal rates at laboratory scale of ~ 600 ppm/hr with losses of less than 1% of the contained cobalt.

Figure 4 considers the removal of Mn at a temperature of $50^\circ C$ and a pH range of 3.0 when 0.5% v/v SO_2 /air mixtures are utilised. The expected manganese removal kinetics (~ 600 ppm Mn/hour) are compared with the maximum removal rate that can be supported by a

high solidity agitator (producing an axial flow with a top-to-bottom circulation pattern) at various scales of operation.

Note that Figure 4 was developed with reference to the following:

- the chemistry of Reaction [R3]
- an assumed SO₂ utilisation for the ‘net forward reaction’ of 80%
- vessel height-to-diameter ratio of 1,
- impeller-to-tank diameter of 0.4,
- impeller tip speeds of 5 m/s,
- pumping number supplied by a well known vendor,
- an aeration number approaching ‘flooded’ conditions

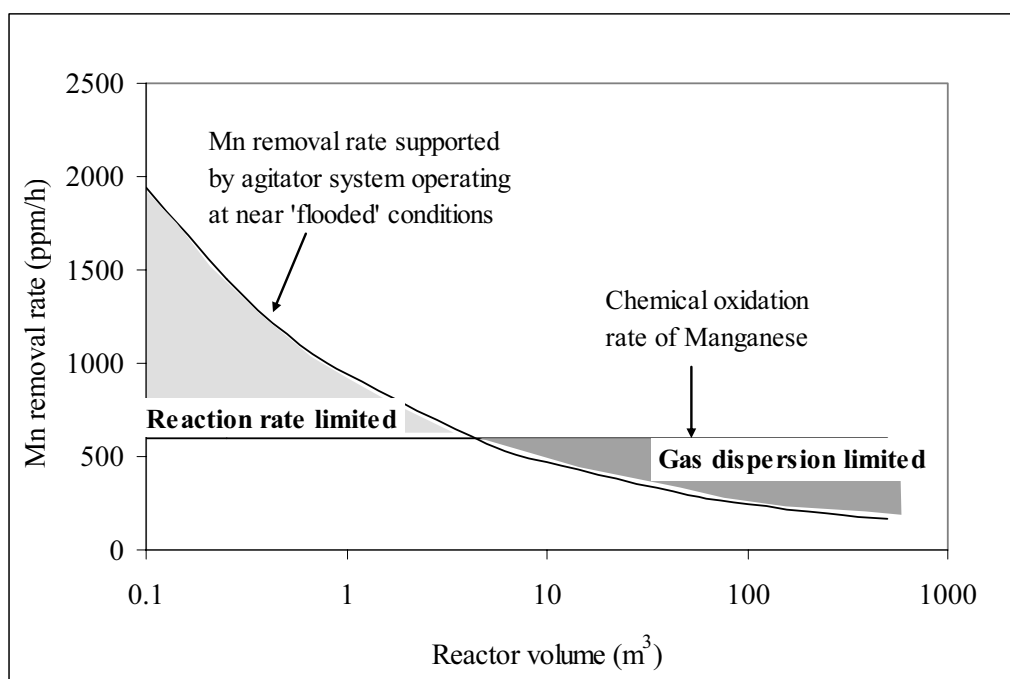


Figure 4. Comparison of expected chemical oxidation rate and gas dispersion limited rate in agitated vessels (0.5% v/v SO₂ and pH of 3.0, near ‘flooded’ conditions)

Figure 4 shows that Mn removal is ‘reaction rate limited’ at smaller scales of operation, and ‘gas dispersion limited’ at larger scales of operation; equipment - imposed limitations on gas dispersion rate prohibits the chemical reaction rate from being achieved at the industrial scale.

Figure 5 is an interpretation of Figure 4 and shows the rate of Mn removal that can be achieved in agitated vessels operating under ‘gas dispersion limited’ conditions.

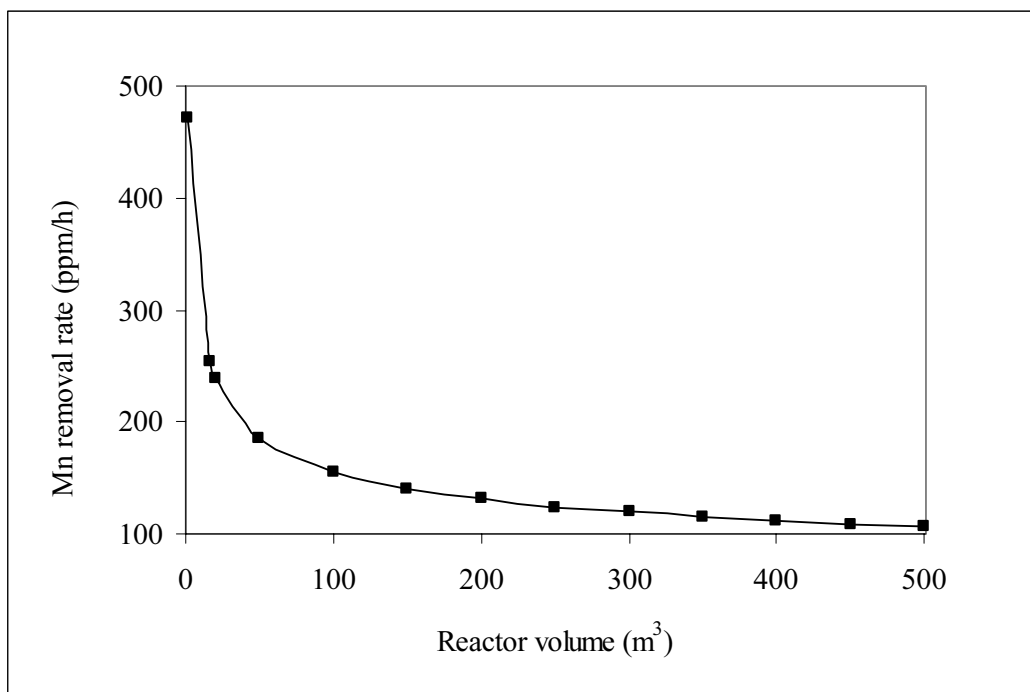


Figure 5. Mn removal rate under ‘gas dispersion limited’ conditions (0.5% v/v SO₂/air and pH of 3, at near ‘flooded’ conditions)

Table 1 provides an example of an industrial system operating under ‘gas dispersion limited’ conditions. The information shows that significant tankage and high agitation power is required to satisfy the stated manganese removal duty. Note further that an overall removal rate of only ~130 ppm/h Mn is achieved; this compares poorly with an expected chemical removal rate of ~600 ppm/h Mn.

The information of Table 1 identifies ‘gas dispersion’ as an important consideration in the design of Mn-SO₂/air systems. The removal of appreciable amounts of Mn with dilute mixtures results in significant gassing requirements that impose limitations on dispersion equipment. These limitations impact the design requirements, and therefore capital cost, of Mn-SO₂/air systems, and implies that the use of SO₂/air is most appropriate for the removal of moderate amounts of manganese.

4. Conclusions

The oxidation of manganese with dilute SO₂ mixtures is an emerging technology that allows the removal of manganese from cobalt containing solutions with relatively low co-precipitated cobalt losses.

It is typically proposed to remove manganese from cobalt containing solutions with SO₂/air gas mixtures containing <1 v/v % SO₂ (equivalent to <5% v/v SO₂/O₂) and in a pH range of 3-4; these conditions ensure high utilisation of SO₂ for manganese oxidation, acceptable reaction rates and relatively low co-precipitated cobalt loss.

Table 1. Manganese removal from bleed steam of a proposed central African copper/cobalt plant (performed in agitated vessels) (0.5% v/v SO₂/air, pH 3, at near ‘flooded’ conditions)

Mn Removal Duty		
Flowrate	200	m ³ /hr
[Mn] in feed	2	g/L
[Mn] in effluent	<0.1	g/l
Mass flowrate of Mn	400	kg/hr
Mn removal rate (Figure 5)	130	ppm/hr
System Requirements		
Reactor volume	250	m ³
Number of reactors	13	
Total reactor volume	3250	m ³
Total SO ₂ -in-air flowrate	33000	Nm ³ /h
Total agitator shaft power	340	kW
Gas Flow Rate	10	Nm ³ /h/m ³
Agitator shaft power	100	W/m ³

An important consideration when implementing this technology is potential manganese removal rate constraints imposed by gas dispersion equipment; such gas dispersion constraints are rarely encountered at laboratory scale, but become prominent when appreciable quantities of manganese are removed with dilute SO₂/air. As a result, significant tankage and agitation power is required to remove large quantities of manganese with dilute SO₂/air. The use of SO₂/air is therefore considered to be most appropriate for the removal of moderate amounts of manganese only.

The removal of substantial quantities of manganese with dilute SO₂/air results in significant gas dispersion requirements. These requirements can clearly be reduced by the use of more concentrated SO₂/air or even SO₂/O₂; these mixtures support higher oxidation rates thus reducing capital investment in tankage and agitation equipment. These options are, however, associated with additional process and cost implications; concentrated SO₂/air results in lower SO₂ utilisation (‘reverse and side reactions’ become prominent), while the use of SO₂/O₂ introduces costly oxygen as a reagent.

The gas dispersion requirement of the Fe-SO₂/air system is markedly lower than that of the Mn-SO₂/air system. The stoichiometric SO₂ requirement for iron removal is only half of that required to remove manganese as MnO₂, while efficient iron removal can also be achieved at elevated SO₂ concentrations. As a result, the use of SO₂/air is particularly attractive for the oxidation/precipitation of iron.

5. References

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