

## **OXIDATIVE PRECIPITATION OF Fe AND Mn BY AIR/SO<sub>2</sub>**

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Mintek has been involved in numerous projects to remove Fe and Mn from dilute Co sulphate solutions by means of oxidative precipitation using air/SO<sub>2</sub>. Test work was done using a gas induction system, designed and supplied by Outotec. Various aspects, such as SO<sub>2</sub> concentration, SO<sub>2</sub> flowrate, impeller rotation speed and pH were investigated on a 2 m<sup>3</sup> scale. Batch tests were performed using a residence time of 5 hours.

Complete Fe removal and ~ 70% Mn removal was obtained when SO<sub>2</sub> concentrations in the feed gas of up to 10% (v/v) were used, with corresponding average removal rates of ~2g/L/h and ~0.3g/L/h of Fe and Mn respectively.

Impeller rotation speeds of 0-220 rpm were tested, and it seemed that speeds of between 80 and 220 rpm gave similar Fe and Mn removal rates.

Co and Cu losses were generally below 1% and 5% respectively at pH 3.

### **1. INTRODUCTION**

Mintek has been involved in numerous projects to remove Fe and Mn from dilute Co sulphate solutions by means of oxidative precipitation using air/SO<sub>2</sub>. This technology is attractive for Fe and Mn removal as it can be done at ambient temperature, relatively low pH, and Fe (present as ferrous in the feed solution) is quantitatively removed within 1-2 hours.

The basic Cu/Co purification flowsheet is depicted in Figure 1. In order to produce the desired quality Co cathode, Fe, Mn, Cu, Zn, and Al are generally required to be removed from the Co bleed stream. The primary reason for Mn removal is to limit the size of the bleed stream from the Co electrowinning circuit. The requirements to produce an intermediate Co salt are generally less stringent, but Fe, Al and Mn are usually still required to be removed.

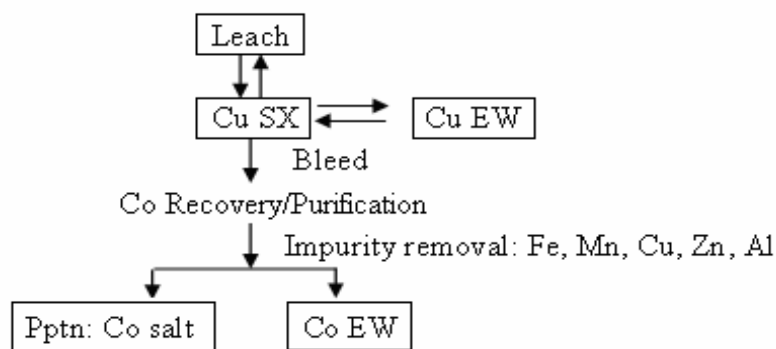


Figure 1: Flowsheet: Cu/Co purification.

Test work at Mintek is generally done on a 5-40 L scale, as the mass of ore available, and thus volume of process liquor, is often limited. However, the keen interest shown in this technology more recently has encouraged Mintek to do some work on a 2 m<sup>3</sup> scale to identify potential scale-up issues. Various agitators and gas induction systems have previously been investigated at this scale, and finally a high-shear impeller designed and supplied by Outotec, was selected for further test work.

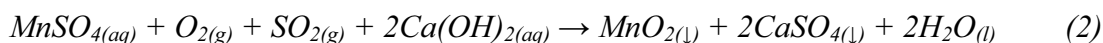
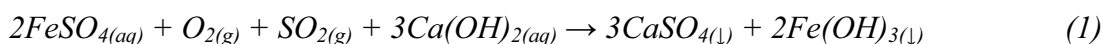
Various tests were performed using the gas dispersion system from Outotec. Test work was planned in order to investigate the major issues around the air/SO<sub>2</sub> technology, namely SO<sub>2</sub> concentration, SO<sub>2</sub> flowrate, pH, impeller rotation speed and temperature. Optimisation tests remain to be done on power consumption and various aspects around gas induction.

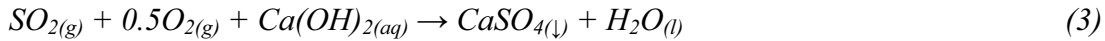
## 2. BACKGROUND THEORY

The oxidation of Mn(II) and precipitation as MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> occurs spontaneously using SO<sub>2</sub>/O<sub>2</sub> gas mixtures in the pH range ~2-6 and temperature range 25-80°C. The rate of oxidation of Mn(II) is slow at pH < 3 and increases rapidly at pH > 4. Any Fe(II) is oxidised and precipitated before Mn(II). Low concentrations of manganese (0.01 M) can be selectively oxidised and precipitated from cobalt and nickel solutions (up to 0.2 M) at pH 3-4 with less than 1% co-precipitation of cobalt and nickel in the laboratory batch tests. The parameters identified as influencing the rate at which manganese is removed from solution are: SO<sub>2</sub>/O<sub>2</sub> gas composition; dissolved SO<sub>2</sub> and O<sub>2</sub>; and the temperature and pH of the solution (Zhang *et al.*, 2002).

## 3. CHEMICAL REACTIONS

The chemical reactions involved in the oxidation of Fe and Mn by air/SO<sub>2</sub> and the subsequent precipitation as Fe(OH) and MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub> respectively are outlined in Equations 1-3. The Ca(OH)<sub>2</sub> used in the equations can be replaced by CaCO<sub>3</sub> if limestone is to be used as neutralising agent instead of hydrated lime.





Based on the overall reactions around  $Fe^{2+}$  and  $Mn^{2+}$  (including the oxidative reaction with  $SO_2$ ), 1.5 and 2 mole of gypsum are respectively formed for each mole of  $Fe^{2+}$  and  $Mn^{2+}$  removed from the feed liquor. A further 1 mole of gypsum is formed for every mole of  $SO_2$  that did not participate in the oxidation reactions, but which formed sulphurous acid which was oxidised by air to sulphuric acid that was neutralised (Equation 4).

$$Ca(OH)_2 \text{ consumption} = Ca(OH)_2 \text{ for } (Mn_{ppt} + Fe_{ppt} + pH_{adjustment} + SO_{2 \text{ unreacted}}) \quad (4)$$

Hence, the lime consumption was calculated as the sum of the moles of  $Ca(OH)_2$  used to achieve the actual Mn precipitation during each test (1.5 times moles Mn precipitated), the moles of  $Ca(OH)_2$  used to achieve the actual Fe precipitation during each test (2 times moles Fe precipitated), the moles of  $Ca(OH)_2$  used to obtain the targeted solution pH, and the moles of  $Ca(OH)_2$  required to neutralise every mole of  $SO_2$  that did not participate in the oxidation reactions. This lime consumption was then stated relative to the total mass of Mn and Fe that precipitated during each test ( $kg \text{ Ca(OH)}_2 / kg \text{ (Fe+Mn)}_{ppt}$ ).

The oxidation of 1 mole  $Fe^{2+}$  uses 0.5 mole  $SO_2$ , while the oxidation of 1 mole  $Mn^{2+}$  uses 1 mole  $SO_2$ . Equation 5 indicates the expression that was used for  $SO_2$  consumption relative to the Fe and Mn precipitation that was achieved during each test.

$$SO_2 \text{ consumption} \equiv \frac{\text{mol } SO_2}{\text{mol } \frac{Fe^{2+}}{2} + \text{mol } Mn} \quad (5)$$

#### 4. EXPERIMENTAL SET-UP

The experimental set-up is illustrated in Figure 2.

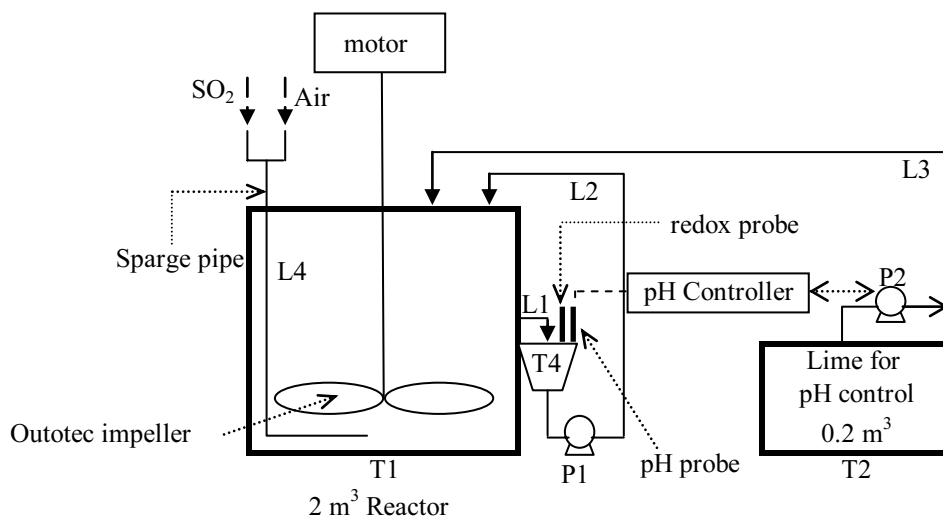


Figure 2: Experimental set-up of batch tests.

Batch tests were performed using a 2 m<sup>3</sup> reactor (T1) and 1.3 m<sup>3</sup> of feed solution. A 20% m/m Ca(OH)<sub>2</sub> slurry was prepared in a lime make-up tank and batch volumes were transferred to the lime tank that was used for pH control (T2). Air and SO<sub>2</sub> were introduced into the reactor by means of a venturi-type gas induction system. The gas mixture was sparged into the reactor, below the impeller, by means of a sparge pipe (L4). The air and SO<sub>2</sub> flow rates were measured by means of rotameters, while the SO<sub>2</sub> was also measured by difference in the gas bottle weight prior to, and upon completion of, each test.

The reactor tank (T1) was equipped with the Gas Liquid Solid (GLS) impeller from Outotec, and is illustrated in Figure 3. The GLS impeller was developed for efficient gas dispersion in a slurry medium. Gas is injected below the impeller via a single gas pipe. Inner radial blades break the initial bubbles to a fine dispersion and outer axial blades distribute the bubbles uniformly to the tank. Unlike a Ruston turbine, the GLS impeller generates comprehensive axial mixing to the bottom region of the tank. This feature ensures good slurry suspension properties and prevents sanding.

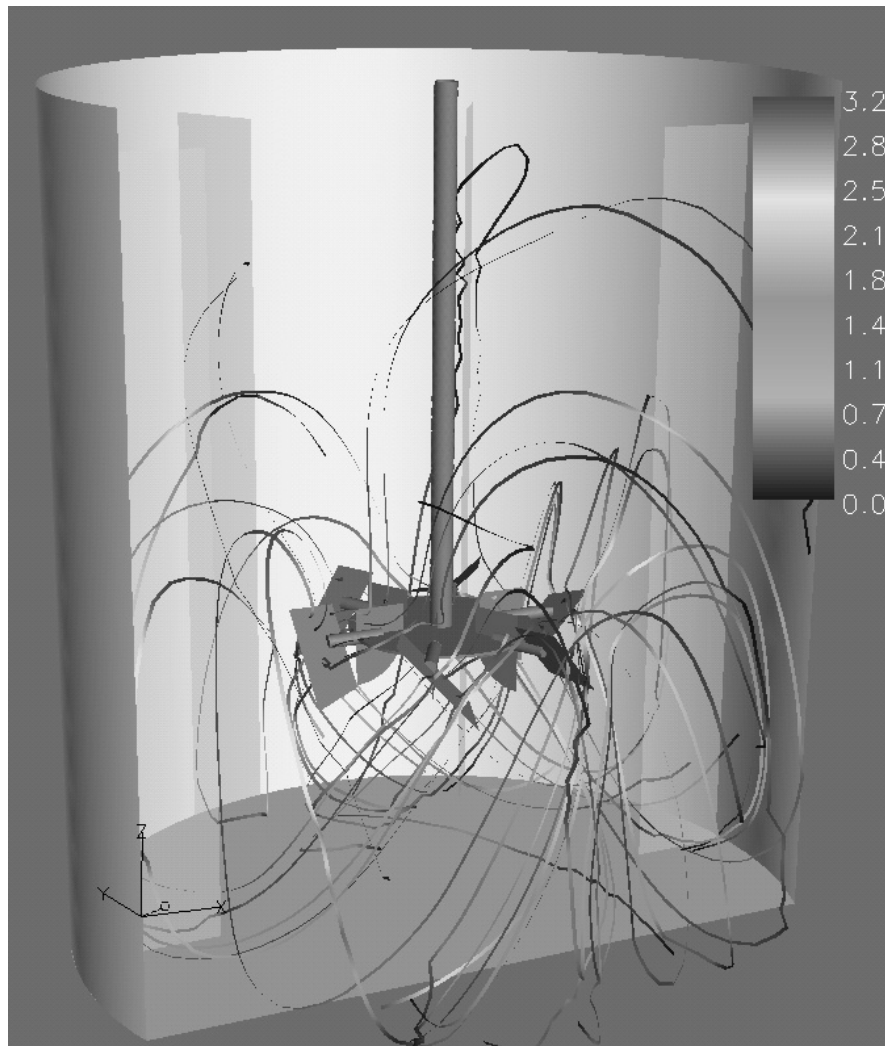


Figure 3: Construction of GLS impeller and computed flow patterns in the test reactor

pH and Eh measurements were done in an outside loop, in order to protect the probes. Slurry was allowed to overflow into a small reactor (T4) outside the main reactor (T1). Foxboro pH- and Eh probes were positioned in the small reactor. The solution residence time in the small reactor was manually controlled to be limited to ensure that the overflow slurry was reasonably representative of the slurry in the reactor. The slurry in the small reactor (T4) was recycled to the main reactor (T1). The pH probe in L2 was connected to a controller, which pumped the lime slurry directly into the reactor (P2 and L3 from T2) for pH control.

After completion of the test, the slurry was pumped onto pan filters and filtered. The filtrate was pumped to a feed make-up tank (not shown) where Mn and Fe were spiked to the desired concentrations of 1.5 g/L and 2 g/L respectively. Due to the large volume of solution used per test and hence the relatively high costs for the salts to make up fresh solution, the filtrate solution was re-used (and spiked to original Fe and Mn concentrations) for each test.

The ranges for the operating parameters that were investigated are listed in Table 1.

Table 1: Operation parameters

Parameter tested	Unit	Range
SO <sub>2</sub> concentration	%	1.5 – 10
pH	-	3
Impeller rotation speed	rpm	0 – 220
Intermediate filtration		At t <sub>3hr</sub>
pH increase during test		pH 2.5 (t <sub>0</sub> –t <sub>1.5hr</sub> ), pH 3.5 (t <sub>1.5hr</sub> –t <sub>5hr</sub> )

## 5. RESULTS AND DISCUSSION

It was generally found that during the test programme the Eh followed a specific trend and this trend persisted throughout all the tests. The bulk of Fe precipitated from solution within the first hour of operation and, during this time the Eh remained at around 380 mV. After Fe removal (at t<sub>1hr</sub>), the Eh increased rapidly to >600 mV after which Mn removal started. Figure 4 illustrates this behaviour of incremental Eh increases during the test programme, using data from Test 5.

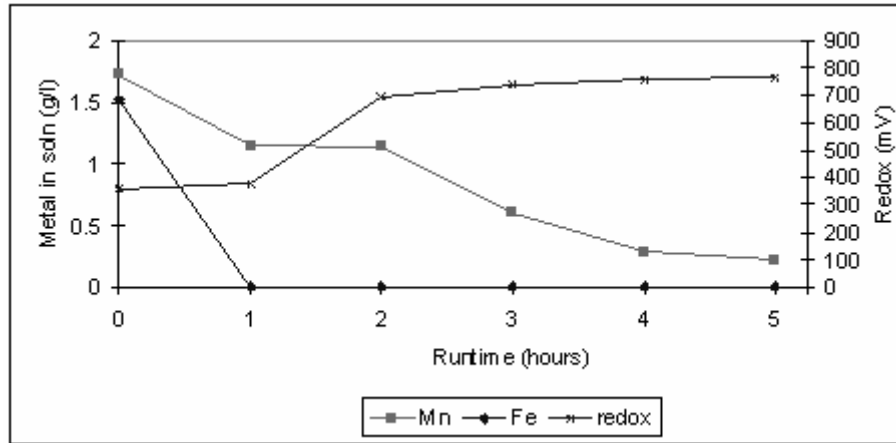


Figure 4: Redox potential increases during test work.

During test work, the energy input of the high-shear impellers caused an increase in solution temperature. For example, during Test 11, the impeller speed was 220 rpm and no external heating source was used. The solution temperature increased from 27°C to 52°C within 5 hours. This temperature increase caused difficulties when control needed to be applied to investigate the effect of different temperatures on the extent of Fe and Mn removal. This effect will be investigated during future test work.

Tables 2 (Fe removal) and 3 (Mn removal) give a summary of the results that were obtained from the tests that were performed.

Table 2: Results: Fe removal

Test	SO <sub>2</sub> conc.		pH	SO <sub>2</sub>		SO <sub>2</sub> $\frac{SO_2}{(Mn + Fe/2)}$ mol/mol	SO <sub>2</sub> $\frac{SO_2}{Fe_{ppt}(t_0 - t_{1hr})}$ mol/mol	$\frac{Ca(OH)_2}{(Fe + Mn)_{ppt}}$ kg/kg	Duration hr	Initial Fe g/L	Fe at t <sub>1hr</sub> g/L	Fe removal %	Fe removal rate g/L/h	Temperature, °C		Comments
	%			Initial	Final											
<b>SO<sub>2</sub> concentration</b>																
1A	1.5	3	2.7	0.3	3.9	5	1.65	0.01	99.96%	1.64	31	40	Tests performed at 220 rpm			
2	3	3	3.9	0.4	4.9	5	1.83	0.01	99.97%	1.82	35	45				
10	5	3	4.2	0.5	5.2	5	1.79	0.01	99.97%	1.78	25	49				
11	10	3	5.3	0.6	6.2	5	1.51	0.01	99.95%	1.50	27	52				
<b>Impeller rotation speed</b>																
3	3	3	6.0	0.6	6.7	5	1.99	0.01	99.96%	1.98	34	53	RPM=220			
4	3	3	3.9	0.4	4.8	5	2.05	0.02	99.92%	2.03	36	47	RPM=180			
5R	3	3	3.2	0.3	4.2	5	1.97	0.01	99.98%	1.96	34	42	RPM=150			
6	3	3	3.6	0.4	4.6	5	1.82	0.02	99.95%	1.81	26	37	RPM=120			
7	3	3	4.7	0.5	5.5	5	1.75	0.01	99.97%	1.74	36	40	RPM=80			
16	3	3	3.5	0.2	4.8	5	2.07	1.01	87.09%	1.06	46	45	RPM=50			
15	3	3	2.9	0.2	4.3	3	2.41	1.30	73.68%	1.11	41	44	RPM=0			
<b>Variable pH, 2.5 for t<sub>0</sub> to t<sub>1hr</sub>, 3.5 for t<sub>1.5hr</sub> to t<sub>5hr</sub></b>																
8	3	2.5, 3.5	3.5	0.4	4.6	5	1.64	0.03	99.97%	1.61	32	47	RPM=180			
<b>Intermediate filtration at t<sub>5hr</sub></b>																
9	3	3	2.5	0.4	3.5	3	1.87	0.02	99.95%	1.85	26.4	37	RPM=180			
9F	3	3	7.0	-	10.7	3	0.01	0.0	99.98%*	0.01	32.4	41				

\* This value indicates the total Fe removal that was obtained during Tests 9 and 9F.



### 5.1      SO<sub>2</sub> concentration in feed gas

High Fe and Mn removal rates (~2 g/L/h and ~0.3 g/L/h respectively) were obtained during Tests 10 and 11 (5% and 10% SO<sub>2</sub> respectively). These favourable results would ensure that pipe sizes on industrial plants could be around 50% smaller if 10% SO<sub>2</sub> could be used instead of 2% SO<sub>2</sub>, the air compressor would be smaller and cheaper, and the reactors would be smaller. Increase of SO<sub>2</sub> concentration decreases the gas flux and required mixing intensity as shown in Figure 6. That has a positive impact on investment and operation cost. Due to previous successful results that were achieved using 3% SO<sub>2</sub>, it was decided to continue with this concentration during the remaining tests. It was decided to perform optimisation tests using the higher SO<sub>2</sub> concentrations upon completion of the pre-determined test matrix.

### 5.2      Impeller rotation speed

Rotation speeds of 0, 50, 80, 120, 150, 180, 220 rpm were tested. A power consumption of 2.3 kW/m<sup>3</sup> solution was measured at an impeller speed of 220 rpm. Speeds of 0 and 50 rpm produced poor Mn removal results, as was expected; however, the Fe removal rate was around 1 g/L/hr. Without mechanical agitation, the incoming gas bubbles remained large, causing a small surface area for mass transfer, resulting in inefficient utilisation of the incoming gas. A high Mn removal rate of 0.3 g/L/h (87% Mn removal) was achieved during Test 5, which was performed using an impeller speed of 150 rpm. However, due to the insignificant difference between the results of Tests 3-7 (220-80 rpm), the additional energy requirement at higher impeller speeds would probably render a speed of 80 rpm more feasible with regard to power consumption.

### 5.3      pH variations

During Test 8, the pH was maintained at 2.5 for the first 1.5 hours of operations, after which the pH was increased to 3.5. This resulted in Fe being removed in the low pH range while Mn removal was targeted at the higher pH. Fe was completely removed in 1 hour and a total Mn removal of 85% was achieved (Figure 5).

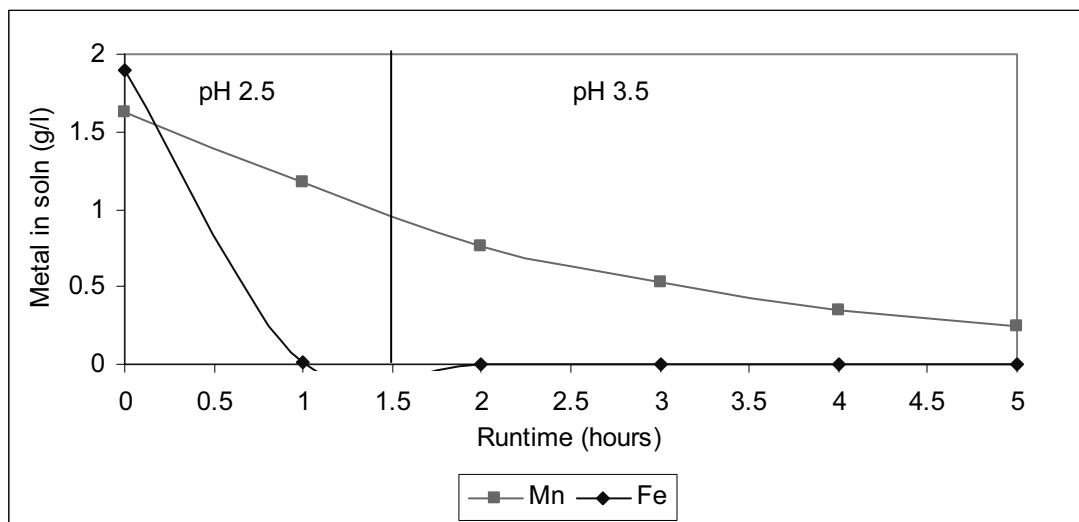


Figure 5: Test 8: Fe and Mn removal during pH variations.

#### 5.4 Intermediate filtration

It was hypothesised that the presence of  $MnO_2$  solids in the slurry may slow down precipitation as equilibrium is reached between Mn in solution and Mn in the solids. This was investigated during Tests 9 and 9F. A filtration step was incorporated after 3 hours of operations of Test 9. The filtrate from Test 9 was used as feed to Test 9F, which also had a residence time of 3 hours.

Complete Fe removal, and 61% Mn removal, were obtained during Test 9. Subsequently, 90% of Mn (relative to feed concentration of Test 9F) was removed during Test 9F, thus achieving a total Mn removal of 95% during the 6 hours combined runtime of Tests 9 and 9F. This was the highest Mn removal that was achieved during the test work programme.

#### 5.5 Cu and Co losses

Cu and Co losses were generally low, i.e. <1% Co loss and ~5% Cu loss. The Co and Cu concentrations decreased slightly during the test work and, as the Co and Cu losses could only be stated when fixed initial concentrations were used, it was decided not to explicitly state the Co and Cu losses that were obtained during each test.

#### 5.6 $SO_2$ consumption

The  $SO_2$  consumption was, on average, around 2.8 (varied between 2.7 and 6) mol  $SO_2$ /mol ( $Mn+(Fe/2)$ ). The bulk of Fe in solution precipitated within the first hour of operation, after which Mn precipitation occurred. The  $SO_2$  that was added during the first hour of operation was therefore used predominantly for Fe precipitation, which resulted in an average  $SO_2$  consumption of 0.4 mol  $SO_2$ /mol  $Fe_{pptd}$  (from  $t_{0hr}$  to  $t_{1hr}$ ). Subsequently, the  $SO_2$  that was added from  $t_{1hr}$  to  $t_{5hr}$  was mainly used for Mn precipitation; hence, an average  $SO_2$  consumption of 6 mol  $SO_2$ /mol  $Mn_{pptd}$  (from  $t_{1hr}$  to  $t_{5hr}$ ) was obtained. The  $SO_2$  flowrate was based on the Fe and Mn concentrations of the

feed solution and at an addition of 2 mol SO<sub>2</sub>/mol Mn and 1 mol SO<sub>2</sub>/mol Fe, distributed over 4 hours. The tests were run for an additional hour, i.e. 5 hours in total. The SO<sub>2</sub> that was added to the reactor was therefore 250% of the stoichiometric required amount for Fe and Mn precipitation (0.5 mol SO<sub>2</sub>/mol Fe and 1 mol SO<sub>2</sub>/mol Mn). Optimisation tests regarding SO<sub>2</sub> flowrate and excess addition remain to be done.

### 5.7 Lime consumption

During the test work, the average lime consumption was 5 (varied between 3 and 7) kg Ca(OH)<sub>2</sub>/kg(Fe+Mn)<sub>ppt</sub>.

### 5.8 Gas-liquid-solid (GLS) impeller

The dispersion capacity of an impeller, in terms of gas flux, is dependent on rotation speed and mixing intensity. In Figure 6, an empirically defined operation range of the GLS impeller is compared to a standard pitch blade impeller (four 45° blades), based on a 2 m<sup>3</sup> scale.

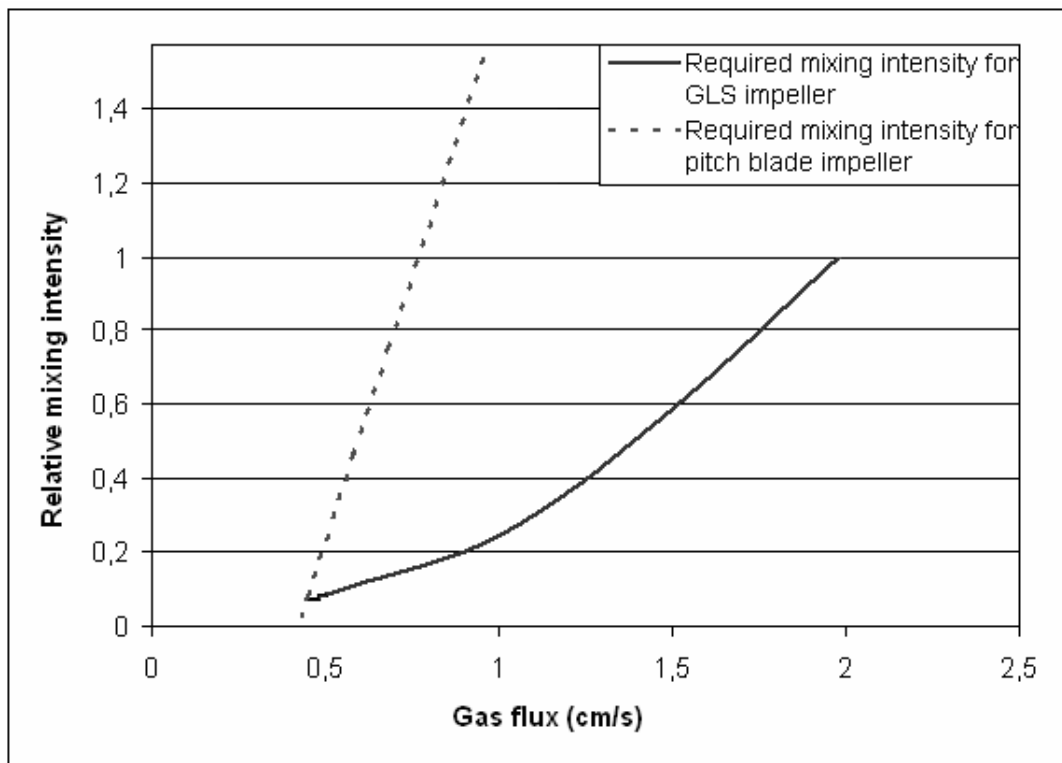


Figure 6: Predicted mixing intensity for dispersion generation for different impeller types on 2 m<sup>3</sup> scale

It is shown in Figure 6 that, in order to disperse the gas flux applied in the test campaign, the pitch blade impeller requires a mixing intensity that is two magnitudes higher than the mixing intensity required when using the GLS impeller.

According to the results obtained during the test programme the effect of the various impeller speeds that were used is rather small, but it is emphasised during scale-up. The gas flux applied in the test programme can be scaled up to industrial process

requirements according to Figure 7. It is shown in Figures 6 and 7 that the gas flux increased rapidly relative to the size of a reactor, and the required mixing intensity for dispersion generation increased relative to gas flux faster for pitch blade impellers than for the GLS impellers.

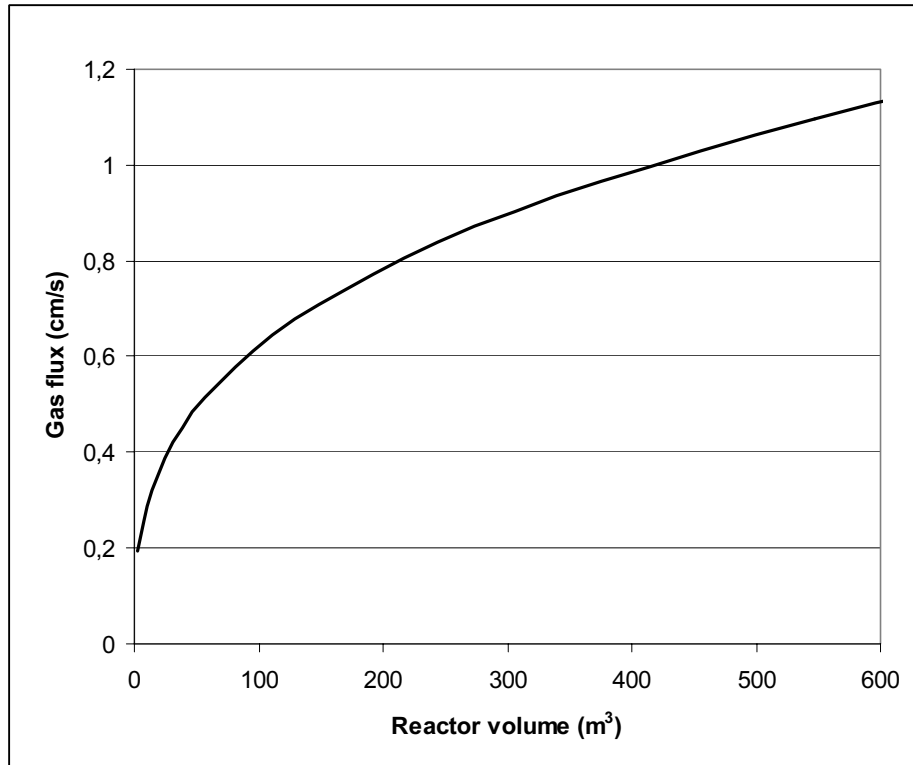


Figure 7: Batch test gas flux scale-up curve for series of three industrial size reactors.

## 6. CONCLUSION

- Effective Fe and Mn removal was achieved when SO<sub>2</sub> concentrations of up to 10% were used.
- The highest Mn removal rate of 0.3 g/L/h (87% Mn removal) was achieved during Test 5, which was performed using an impeller speed of 150 rpm however, the insignificant difference between the results of Tests 3-7 (220-80 rpm) indicates that gas mass transfer rate is not limiting the reaction rate once dispersion is established. Therefore, the effect of power consumption would probably render an impeller speed of 80 rpm more effective for scale-up.
- The average SO<sub>2</sub> consumption was 2.8 mol SO<sub>2</sub>/mol (Mn+(Fe/2)) over the total runtime of 5 hours. This translated to an average SO<sub>2</sub> consumption of 0.4 mol SO<sub>2</sub>/mol Fe<sub>ppt</sub> (during t<sub>0</sub> and t<sub>1hr</sub>), and 6 mol SO<sub>2</sub>/mol Mn<sub>ppt</sub> (during t<sub>1hr</sub> and t<sub>5hr</sub>). The SO<sub>2</sub> flowrate was calculated as 2 mol SO<sub>2</sub>/mol Mn and 1 mol SO<sub>2</sub>/mol Fe in the feed solution and was calculated for 4 hours of runtime, however, each test was run for an additional hour (hence, 5 hours in total).
- The average lime consumption was 5 kg Ca(OH)<sub>2</sub>/kg(Fe+Mn)<sub>pptd</sub>.
- During all the tests excluding Tests 16 and 15 (poor process results), the mixing intensity was above the threshold of dispersion generation. Therefore, operation in the range of well established bubble dispersion should be secured when process is

scaled-up to an industrial application. Due to the high gas flux specific to this process any industrial application will require a high dispersion duty agitator in order to reach the threshold of dispersion generation.

## **7.        RECOMMENDATIONS AND FURTHER TEST WORK**

Further test will be performed to optimise the use of higher SO<sub>2</sub> concentrations, as well as optimisation of power consumptions versus impeller speeds. The effect of temperature on Mn and Fe removal will be investigated, however, the effect of temperature increase caused by the high-shear impellers will need to be addressed foremost.

## **8.        REFERENCES**

- Zhang, W., Pritam, S. and Muir, D. (2002) *Oxidative precipitation of manganese with SO<sub>2</sub>/O<sub>2</sub> and separation from cobalt and nickel*, Elsevier, Hydrometallurgy 63 (2002) 127-135.

