

# Precipitation of platinum and base metals in a gas-liquid chloride system

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The purpose of this research was to determine the feasibility of using small amounts of sulphur from a gaseous phase to precipitate platinum ions from chloride solutions, as well as to review the mass transfer characteristics and models associated with metal sulphide precipitation in gas-liquid (G-L) system. Precipitation test work was conducted using a continuously stirred tank reactor (CSTR), with sulphur dioxide (SO<sub>2</sub>) gas as the source of sulphur. Mass transfer coefficients in the liquid phase and diffusivity of sulphur atoms at the G-L interface were described according to molecular transport models. The recovery of significant amounts of precious metals from dilute solutions by using waste SO<sub>2</sub> streams at low pressure would be attractive from both the economic and the environmental points of views. Platinum ions react readily with sulphur atoms to form stable platinum sulphide precipitates in chloride systems. The mass transfer and recovery of Pt were quantified in the G-L systems using mass balancing and a liquid film diffusion model at moderate liquid temperatures (25-50°C), and SO<sub>2</sub> gas pressures of 0.5-2.0 bar. Metal ion concentrations were varied (50-120 mg/L) in a solution with high-acid strength (1-4 M HCl). The precipitation of Pt in the presence of cations (Fe<sup>2+</sup>, Co<sup>2+</sup>, and Cr<sup>3+</sup>) was also investigated. Further test work is recommended to scale up the process to the pilot scale.

**Keywords:** CSTR, diffusivity, gas-liquid, mass transfer, platinum, recovery, precipitation, sulphur dioxide.

## Introduction

Global concerns about the impact of toxic gases and effluents on the environment have led platinum industry leaders to adopt new strategies of recycling or capturing waste streams. Carbon dioxide (CO<sub>2</sub>), for example, from coal-fired power stations and the environment is currently being captured and stored in coal seams underground (Star Energy Group, 2008; Rasul and Brown, 2007). Babcock has developed technology for converting toxic oxides of nitrogen (NO<sub>x</sub>) from well-designed boiler burners using hydrocarbon gases (Hessenmann, 2003). Researchers have also reported on the concept of capturing SO<sub>2</sub> from fluidized-bed reactors during coal gasification by using dolomite (US Department of Energy, 2005). However, there is scanty literature on the application of acidic chloride solutions containing precious metals as a means of capturing SO<sub>2</sub> from flue gases and the same time precipitating the precious metals as sulphides. Dissolved sulphur reacts readily with base and precious metal ions to form metal sulphides (Bernardis *et al.*, 2005; Danckwerts, 1970; Gomez-Diaz *et al.*, 2006). In industrial sedimentation processes, reduction of metal ions as sulphides is accomplished by contacting metal-rich solutions with commercial H<sub>2</sub>S or SO<sub>2</sub> gases. In order to utilize SO<sub>2</sub>-bearing flue gases or other sulphur-bearing gases for recovering metals from solution, it is necessary to put in place effective mechanisms for capturing and solubilizing the gases. This study investigates the capturing of SO<sub>2</sub> from industrial flue gases by means of acidic chloride solutions.

The main postulate is that dissolved sulphides can serve as precipitants for platinum group metals (PGMs) in chloride media. This implies that it is expedient to understand and control the reaction kinetics involving dissolved sulphur with transitional metal ions. The benefits of using a waste gas to remove heavy metals from industrial effluents are enormous from both an environmental and a PGM production perspective.

In conventional PGM production, the smelter matte (final product from the smelter) contains excess amounts of iron together with other metals such as copper, nickel, cobalt, zinc, chromium, and PGMs. The matte is dissolved in an appropriate solvent by non-selective acid leaching, and the base metals (Fe, Cu, Co, Ni *etc.*) are removed by precipitation with hydroxide solutions. However, significant traces of base metals remain in the leach solution, together with the PGMs. Some volatile metals such as bismuth are removed by distillation. The traces of base metals, however, are removed in fixed-bed ion exchange columns containing reactive, porous resins. The resins, such as chelating resins, used are highly selective and almost all are imported from overseas. In order to cut down on the cost of importing these resins, industries have developed their own resins that can be used in emergencies such as supply shortages, but the local resins are not comparable to imported ones.

The use of resins in fixed-bed columns or resin-in-pulp (RIP) processes for the purpose of separating PGM ions is very costly. Currently, the bulk of the base metals (Cu, Ni,

Fe, Cr, Se, and Co) is removed from matte leach solutions by varying the pH of the solution and eventually by solvent extraction to recover Cu, Ni, and Co. The residual solids from the precipitation process are mainly rich in PGMs, which are dissolved using HCl solution. However, the PGMs are still accompanied by traces of base metals such as bismuth, which must be removed (by distillation) prior to purification of the PGMs through resin columns. In this study, gas-liquid precipitation was carried out to simulate both scenarios, where initially the bulk base metals exist together with the PGMs in solution, and secondly where traces of base metals such as bismuth are present in the solution. It was hoped that PGMs would be selectively precipitated in one stage, which would provide huge economic benefits to industry when compared to costly pH-controlled precipitation, distillation, and resin column separation processes. In this study therefore, a comprehensive investigation was carried out aimed at combining waste removal and metal recovery in a synergistic manner; by capturing sulphur-bearing gases in a chloride solution containing platinum complex anions and thereby inducing PGM precipitation. In this regard, the process, which is suitable for the simultaneous absorption of waste toxic gases and metal precipitation, was designed using mass transfer models of metal sulphide crystallisation in the continuously stirred reactor. Furthermore, the selectivity of the reaction between sulphur atoms and PGM ions in a chloride system would be quantified, since the feed solution also contained base metal ions ( $Fe^{2+}$ ,  $Co^{3+}$ , and  $Cr^{3+}$  etc). The conventional process for separation and purification of PGMs in industry combines liquid-liquid precipitation in alkaline media, distillation (boiling off volatile metals), and ion exchange in resin columns. Distillation is an energy-intensive process and ion exchange processes involve high operational costs due to the cost of imported resins. The concept of selective gas-liquid precipitation of PGMs using waste sulphide gases from the smelter is therefore very attractive.

### Absorption kinetics and process modelling in G-L processes

Absorption kinetics studies in G-L processes were conducted in order to establish the parameters that affect metal (Fe, Co, and Cr) precipitation in G-L chloride systems. The study was predominantly concerned with the precipitation rates of Pt as this was the main target metal in the mixed chloride systems. Furthermore, the mass transfer coefficients ( $K_L$ ), diffusivities ( $D_L$ ), absorption rates ( $N$ ), activation energy ( $E_a$ ) and the thermodynamic properties ( $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ ) associated with platinum were quantified.

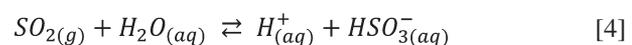
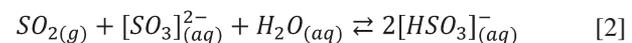
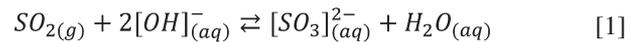
### Modelling of Pt and base metal precipitation in single- and multi-component systems

A two-film model was used to describe the process in terms of the reaction kinetics, and the reaction rates, mass transfer, and diffusion coefficients were evaluated accordingly. The focus of the gas absorption experiments is based on understanding the mass transfer processes in reactive and non-reactive solvent systems. In order to model the mass transfer of the gases, it is necessary to generate the absorption kinetics data with or without accompanying chemical reaction.

#### Absorption rate studies

In G-L process using the CSTR, chloride solutions of Pt

and base metals are used to absorb  $SO_2$ , forming solid products (precipitates). There are several reactions and physical steps that may affect the rate of  $SO_2$  absorption in acidic chloride solutions. These include (Dagaonkar *et al.*, 2001; Rodriguez-Sevilla *et al.*, 2002):



Therefore, on the basis of reactions [1] and [3],  $[SO_3]^{2-}$  ions are the main product when  $SO_2$  reacts with water  $[OH]^-$  molecules in a few stages (Dagaonkar *et al.*, 2001). It is therefore possible to correlate the absorption rate ( $N$ ) of  $SO_2$  with  $SO_3^{2-}$  in the bulk solution as shown in Equation [5]:

$$N = C_{SO_2}^* \cdot a \cdot \sqrt{D_{SO_2} \cdot k \cdot C_{SO_3^{2-}}^{bulk}} \quad [5]$$

where  $N$  is the absorption rate of  $SO_2$  ( $mol \cdot m^{-3} \cdot s^{-1}$ ),  $C_{SO_2}^*$  and  $D_{SO_2}$  the solubility and diffusivity of  $SO_2$  in the aqueous phase;  $a$  the interface area,  $k$  the rate constant for the reaction between  $SO_2$  and  $SO_3^{2-}$  ions at the interface, and  $C_{SO_3^{2-}}^{bulk}$  is the  $SO_3^{2-}$  concentration in the bulk of aqueous phase.

#### Two-film model

In the two-film model, gaseous molecules in the bulk phase diffuse through a gas-liquid film and are then transferred into the bulk solution; therefore, the total resistance to mass transfer consists of diffusion resistance at the gas-liquid interface and mass transfer resistance in the liquid phase.

The overall mass transfer of sulphur atoms from the bulk gas phase into the chloride solution ( $mol \cdot s^{-1}$ ) may be expressed by Equation [6].

$$\frac{dm}{dt} = \frac{1}{\left(\frac{1}{k_L} + \frac{1}{k_G}\right)} \cdot a \cdot (C_{A,i} - C_{A,L}) = K \cdot a \cdot (C_{A,i} - C_{A,L}) \quad [6]$$

where  $\left(\frac{1}{k_L} + \frac{1}{k_G}\right)$  is the overall mass transfer resistance,

$K$  and  $\frac{1}{k_G} \approx 0$  since the gas phase is pure, containing only sulphur atoms. The rate of mass transfer may be rewritten to take into account the constant volume of the solution ( $mol \cdot m^{-3} \cdot s^{-1}$ ) and interfacial area ( $m^2 \cdot m^3$ ) exposed to a pure gas phase as shown by Equations [7] and [8]:

$$d\left(\frac{m}{V}\right) = \frac{dC_{A,L}}{dt} = K_L \cdot a \cdot (C_{A,i} - C_{A,L}) \quad [7]$$

which reduces to

$$\frac{dC_L}{dt} = K_L \cdot a \cdot (C_i - C_L) \quad [8]$$

where  $K_L$  is the mass transfer resistance in the liquid phase. The concentration gradient can be correlated with the pressure drop of the gas during absorption (Kenig *et al.*, 1997).

## Experimental approach

### Reagents

Reagents used throughout the study were pure analytical pure standard grade solutions of platinum ( $\text{H}_2\text{PtCl}_6$ ), iron ( $\text{FeCl}_2$ ), cobalt ( $\text{CoCl}_2$ ), and chromium ( $\text{CrCl}_3$ ) assaying 1000 mg/L each; 32% analytical grade HCl. Analytical grade  $\text{SO}_2$  gas (99.9% pure) in pressurized gas cylinders was purchased from AFROX (Pty) Ltd in South Africa.

The standard solutions were prepared in equal concentrations (100 mg/L) using distilled water. The distilled water was produced in the laboratory at Tshwane University of Technology, South Africa. A buffer solution was not used.

Different concentrations of HCl solutions (1.0, 3.0, and 4.0 M) were prepared by diluting 10 M (32%) HCl with distilled water. Analytical grade  $\text{SO}_2$  gas (99.9% pure) in pressurized cylinders was used in the G-L precipitation tests at moderately high pressure (0.5, 1.0, 1.5, and 2.0 bar). The concentration (99.9%) and flow rate (177 mL/min) of  $\text{SO}_2$  gas were kept constant throughout the tests. The stirring speed (500 r/min) was also kept constant throughout the tests.

### Analytical techniques

The barren solution samples after precipitation were analysed for platinum, iron, cobalt, and chromium by inductively coupled plasma-optical emission spectrophotometry (ICP-OES) using a Shimadzu model ICPE-9000 instrument at Tshwane University of Technology.

Solid samples (precipitates) were analysed by scanning electron microscopy (SEM) at Nuclear Energy Corporation, South Africa (NECSA), and X-ray diffraction (XRD) at the University of the Witwatersrand, South Africa.

### Experimental equipment

The CSTR experiments were carried out using a 2 L capacity glass autoclave manufactured by Büchi AG, Switzerland). The following parameters were investigated:

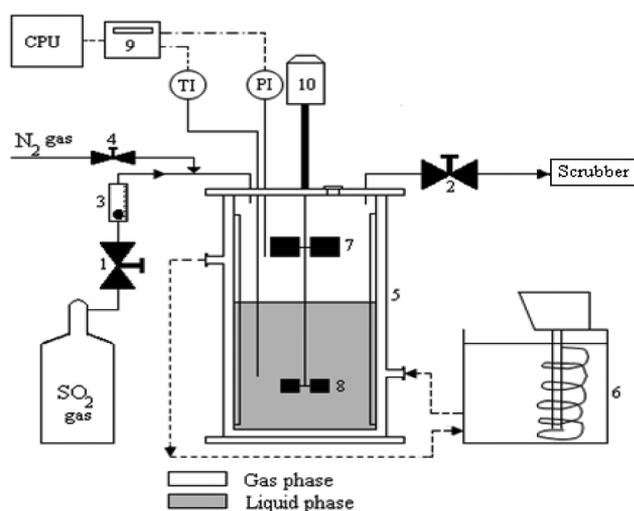


Figure 1. Stirred cell reactor:  $\text{SO}_2$  gas inlet and outlet valves (1, 2);  $\text{SO}_2$  gas flowmeter (3);  $\text{N}_2$  gas inlet valve (4); stirred cell reactor (5); thermostat water bath (6); gas stirrer (7); liquid stirrer (8); data logger (9); magnetic coupling mixer (10)

- Effect of initial metal activities in chloride media on the reactive absorption of  $\text{SO}_2$
- Effect of HCl concentration on the physical absorption of  $\text{SO}_2$
- Effect of temperature on  $\text{SO}_2$  absorption
- Effect of pressure on  $\text{SO}_2$  absorption.

### Experimental set-up

The experimental set-up is shown in Figure 1. The reactor was fitted with a thermostat and heated by a water jacket. The reactor dimensions are shown in Table I. The reactor was operated batch-wise with respect to the liquid phase, but continuously with respect to the gas phase. The liquid was stirred mildly with a six bladed Rushton turbine, diameter 50 mm, height 15 mm, located centrally in the liquid at a height above the reactor bottom equal to half the reactor diameter. The gas phase (above the liquid phase) was stirred with a three-bladed 50 mm diameter impeller. Both impellers were mounted on a single axis with a diameter of 10 mm. The speed of was kept constant at 500 r/min throughout the tests. The reactor was equipped with four symmetrically mounted glass baffles with a height of 104 mm and a width of 8 mm, which increased the effectiveness of stirring and prevented the formation of a vortex.

Isothermal conditions in the reactor were maintained by circulating hot water from a thermostatted water bath (Tamson T-1000) through the jacket of the reactor. The temperature of the reactor contents was measured by means of a K-type thermocouple. The pressure in the reactor was determined with a Druck PDCR 910 pressure transducer. The pressure and temperature transducers were connected to a Squirrel SQ 1000 series data logger and Mercer Premium computer, enabling data collection and programmed reactor operation.

The mass flow rate of pure  $\text{SO}_2$  from the cylinder to the reactor was controlled by using a mass flow meter (Brooks 5150 T). The gas leaving the reactor was passed through a caustic scrubber before discharge to the atmosphere. A pressure regulator was employed to control gas pressure in the reactor (Tescom series 1700 back-pressure regulator).

### Test protocol

For  $\text{SO}_2$  absorption experiments, the gas-liquid reactor was loaded with the specific solvent (with or without metal ions in a chloride solution). The concentration of each metal ion was kept constant at 100 mg/L. Acid strength was varied in the range 1-4 M HCl. The reactor content was initially degassed by purging with pure nitrogen gas. The starting solution was allowed to equilibrate with its own saturated vapour at room temperature. The temperature of the metal ion solution was set in the range 298 K (25°C) to 313 K (40°C), after which, at  $t = 0$ , the feed gas ( $\text{SO}_2$ ) was introduced into the reactor from a high-pressure cylinder

Reactor diameter	0.0825 m
Reactor volume	$2.0 \times 10^{-3} \text{ m}^3$
Gas-liquid contact area	$5.28 \times 10^{-3} \text{ m}^2 \text{ m}^{-3}$
Liquid impeller type	Six-bladed turbine, 0.05 m diameter
Gas impeller type	Three-bladed turbine, 0.05 m diameter

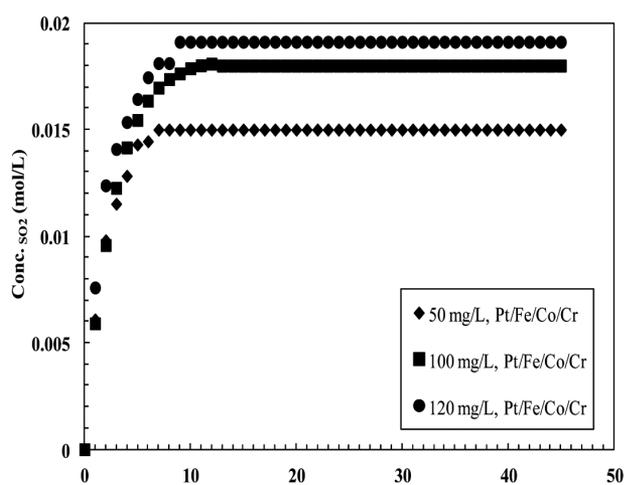
Temperature	25 - 40 °C
Initial pressure	0.5 x 10 <sup>5</sup> Pa
Liquid volume	1.5 x 10 <sup>-3</sup> m <sup>3</sup>
Gas	N <sub>2</sub> , purity >99.5%; SO <sub>2</sub> , purity >99.5%
Stirrer speed	500 r/min

fitted with a regulator at a constant flow rate of 177 Nml/min. The pressure in the reactor was varied in the range 0.5-2.0 bar (50-200 kPa). Table II summarizes the test conditions in the CSTR. After filling the reactor with SO<sub>2</sub> gas, the stirrer was started and the pressure drop in the reactor was recorded over time. At equilibrium, the pressure drop levelled off and a sample was taken from the bulk solution to determine the maximum absorption capacity of SO<sub>2</sub> and amount of precipitate formed. The amount of sulphur sequestered in metal-rich and metal-free chloride solvents (>1M HCl) was recorded. The rate of metal precipitation was not quantified due to difficulties (lack of a sampling gun) associated with solution sampling at high pressure. After 24 hours, the composite precipitate from the batch glass vessel was filtered and dried at room temperature. The composite clear filtrate was analysed for metal ions using ICP-OES. Dry precipitates were analysed for metal ions and sulphur by means of XRD) and SEM using energy-dispersive spectrometry (EDS). The flow of the gas was continuous but the liquid was stationary in the vessel. From a scale-up point of view, this can be a huge constraint. However, the objective was not to develop parameters for scaling up the process but rather to optimize SO<sub>2</sub> solubility and Pt selectivity at this stage.

## Results and discussion

### Effect of initial metal ion concentration

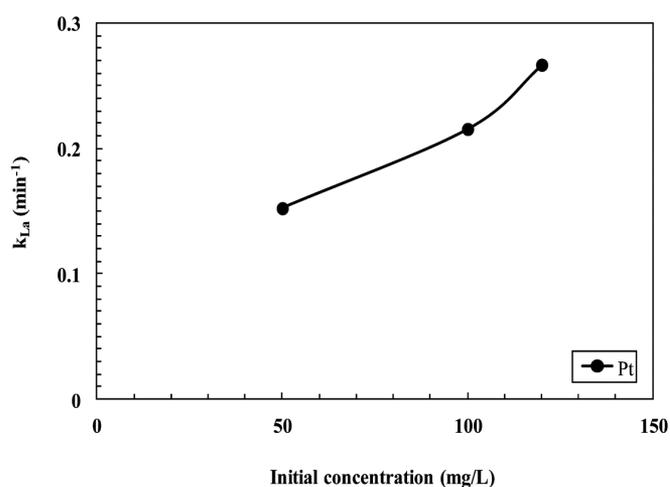
The feasibility and efficiency of a precipitation process depend not only on the properties of the precipitants, but also on the concentration of the metal ion solution. In this



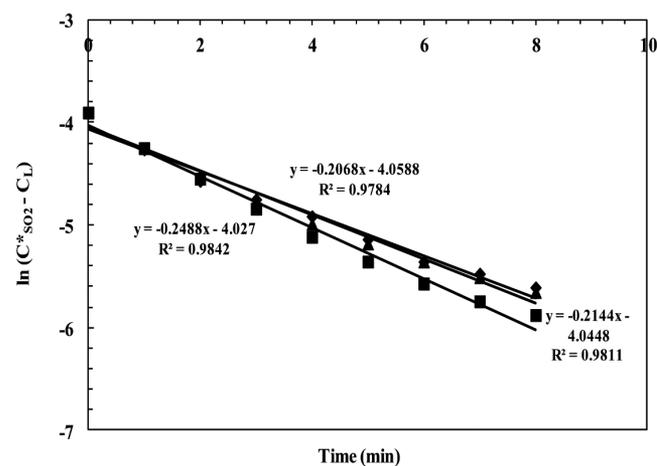
**Figure 2.** Effect of initial concentration of multi-metal system (Pt/Fe/Co/Cr) on the absorption of SO<sub>2</sub> in a CSTR. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M; [Me<sup>n+</sup>] = 100 ppm; contact time = 40 min

study, the effect of initial concentrations of metal ions (single and multi-component systems) was investigated and the results are illustrated in Figures 2-4.

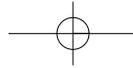
Figure 2 shows the effect of varying initial Pt and base metal (Fe, Co, and Cr) ion concentrations from 50 to 120 mg/L. The data is plotted as SO<sub>2</sub> concentration in the bulk liquid phase versus contact time. The concentration of SO<sub>2</sub> in the bulk liquid phase of chloride solution increased with an increase in initial concentration. Diffusion is a passive transport process driven by the concentration gradient at the G-L interface. At higher initial concentrations, the driving force for precipitation, which is the difference between the gas phase film concentration and the liquid phase film concentration, is higher. This leads to a higher absorption rate in a short contact time. Furthermore, Figure 2 shows that the absorption capacity increased sharply in the first 10 minutes (over 80% gas absorbed), followed by a slower absorption capacity that gradually approached an equilibrium



**Figure 3.** Mass transfer coefficient vs initial concentration of Pt ions in chloride system. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M; [Pt<sup>2+</sup>] = 100 ppm; contact time = 40 min



**Figure 4 –** Plot of  $\ln(C^*_{\text{SO}_2} - C_L)$  vs. contact time. Determination of mass transfer coefficients for absorption of SO<sub>2</sub> into 4 M HCl chloride solution containing Pt/Fe/Co/Cr ions. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M; [Me<sup>n+</sup>] = 100 ppm; contact time = 40 min



Metal ions Initial conc. (mg/L)	Pt ions		Pt/Fe/Co/Cr ions	
	$k_L a$ (min <sup>-1</sup> )	$[S^0]_{\text{equiv.}}$ (mol/L)	$k_L a$ (min <sup>-1</sup> )	$[S^0]_{\text{equiv.}}$ (mol/L)
50	0.1523	0.014	0.2068	0.015
100	0.2155	0.017	0.2144	0.018
120	0.2667	0.018	0.2488	0.019

condition. The average absorption of SO<sub>2</sub> gas after 10 minutes was 0.0165 mol/L and recovery of Pt from all chloride solutions averaged above 99% in less than 10 minutes, as shown in Figures 2. It is evident that the rate of increase of SO<sub>2</sub> in the bulk liquid phase was dependent on the initial metal ion concentration.

The absorption kinetics of SO<sub>2</sub> in chloride solution (4 M HCl) containing Pt ions and Pt/Fe/Co/Cr ions are shown in Figures 3 and 4, respectively. The rate of mass transfer ( $K_L \cdot a$ ) may be limited by resistance in the gas phase film or liquid phase film. Thus, the  $K_L \cdot a$  values were evaluated using Equation [8] (Figure 4); the results are summarized in Table III. As the initial concentrations were raised, the mass transfer coefficients increased in a nonlinear fashion as shown in Figure 3.

The experimental data in this study indicates that the rate of increase of SO<sub>2</sub> concentration in the bulk liquid phase increased by approximately 18% when the initial concentration of Pt and base metal ions concentration was doubled from 50 mg/L to 100 mg/L, and increased by approximately 27% when the initial concentration of Pt and base metal ions was increased from 50 mg/L to 120 mg/L. The highest rate of increase of SO<sub>2</sub> in the bulk liquid phase was achieved at an initial concentration of 120 mg/L in both cases (Figure 2). This indicates that metal precipitation with SO<sub>2</sub> follows the two-film theory. The mass transfer coefficients obtained for all metals increased with an increase in metal ion concentrations.

#### Determination of mass transfer coefficient

Figure 5 illustrates the absorption kinetics of SO<sub>2</sub> in 4 M HCl solution at 25°C and a gas pressure of 1 bar. The gas pressure dropped from 1.125 to 0.22 bar within approximately 20 minutes of contact time (Figure 5). The corresponding increase in sulphur concentration is a mirror image of the pressure drop. The average absorption of SO<sub>2</sub> after 20 minutes was 0.018 mol/L. This implies that physical absorption of SO<sub>2</sub> in concentrated HCl solution is possible at room temperature. The reason why we carried out absorption tests at high HCl concentration was because the final solution from the elution circuit in Pt recovery is in the range of 3.5–4.0 M, HCl. It is known that Pt can be precipitated from solutions at high HCl concentration (>3.5 M) only by using sodium thiosulphate (Kasaini *et al.*, 2001; Siame and Kasaini, 2010).

The mass transfer coefficient of SO<sub>2</sub> in HCl solution was

System	$k_L a$ , (min <sup>-1</sup> )	$[S^0]_{\text{equiv.}}$ (mol/L)
Physical absorption	0.1148	0.0161
Absorption with Pt	0.1575	0.0164
Absorption with Pt/Fe/Co/Cr	0.2495	0.0182

evaluated using Equation [8] and data points from Figure 5. Therefore,  $\ln(C_{SO_2}^* - C_{SO_2,i})$  was plotted against contact time according to Equation [8] (Figure 6). The mass transfer coefficients and corresponding concentration values of dissolved sulphur atoms are summarized in Table IV.

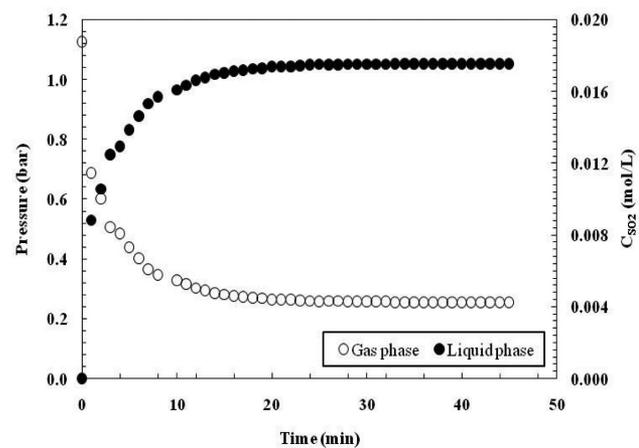


Figure 5. Plot of pressure drop of SO<sub>2</sub> vs contact time. Physical absorption of SO<sub>2</sub> into chloride solution at 25°C. [HCl] = 4 M. In gas phase the concentration of SO<sub>2</sub> gas was calculated using the ideal gas law. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M;  $[\text{Me}^{n+}] = 100$  ppm; contact time = 40 min

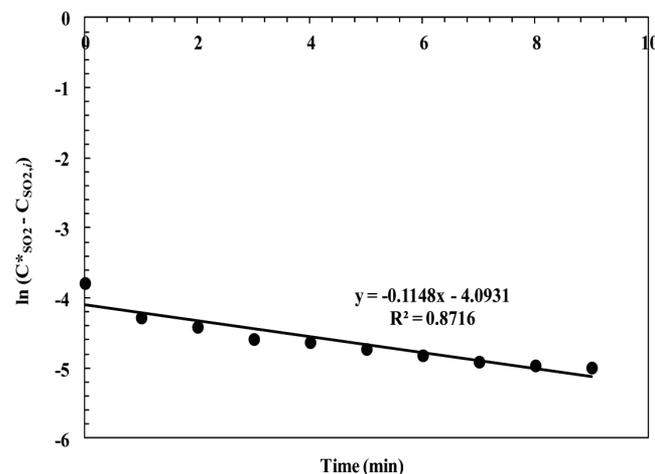
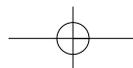


Figure 6. Plot of  $\ln(C_{SO_2}^* - C_{SO_2,i})$  vs contact time. Evaluation of mass transfer coefficient for physical absorption of SO<sub>2</sub> into 4 M (HCl) chloride solution at 25°C and a gas pressure of 1.125 bar. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M;  $[\text{Me}^{n+}] = 100$  ppm; contact time = 40 min



From the gas absorption point of view, the mass transfer characteristics of SO<sub>2</sub> from the bulk gas phase into mixed chloride solvents were established. The results showed that the presence of metal ions in the solvent accelerates the uptake of sulphur atoms from the gas phase into the liquid phase through a chemical reaction. Resistance to diffusion of a species in a pure gas phase was considered to be negligible. Therefore, the mass transfer of SO<sub>2</sub> was modelled through the absorption kinetics data with or without an accompanying chemical reaction.

#### Effect of hydrochloric acid concentration on physical absorption of SO<sub>2</sub> gas

Figure 7 show that increasing HCl concentration adversely affects the physical absorption of SO<sub>2</sub>. In this study, HCl concentration was varied in the range 1-4 M because Pt exists as anionic chloro-complexes in this range. As the concentration of HCl was increased, the mass transfer coefficient decreased in nonlinear form as shown in Figure 7. This is attributed to the salting-out effect of gaseous molecules in the acidic solution, and also probably to an increase in the interfacial tension at the liquid surface (Gomez-Diaz *et al.*, 2006). Platinum ions exist as stable chloro-complex anions in highly acidic chloride solutions (Kasaini *et al.*, 2001; Inoue *et al.*, 1990). This implies that the degree of Pt ionization is strongly dependent on the [Cl] concentration.

#### Thermodynamics of absorption

##### Effect of temperature on absorption kinetic profile

The effect of chloride solution temperature on SO<sub>2</sub> absorption was studied. The kinetic experiments were conducted at 298.15, 303.15, and 313.15 K, and all other variables were kept constant (acid strength 4 M HCl, pressure 1.125 bar, stirring speed 500r/min and metal concentration 100 mg/L). The results (Figure 8) illustrate that SO<sub>2</sub> solubility was slightly affected by temperature in the range 298.15–313.15 K. It is well known that physical absorption of gases is affected by increase in temperature due to the shift in the vapour liquid equilibrium (VLE). Thermodynamically, molecules prefer to exist in the gas

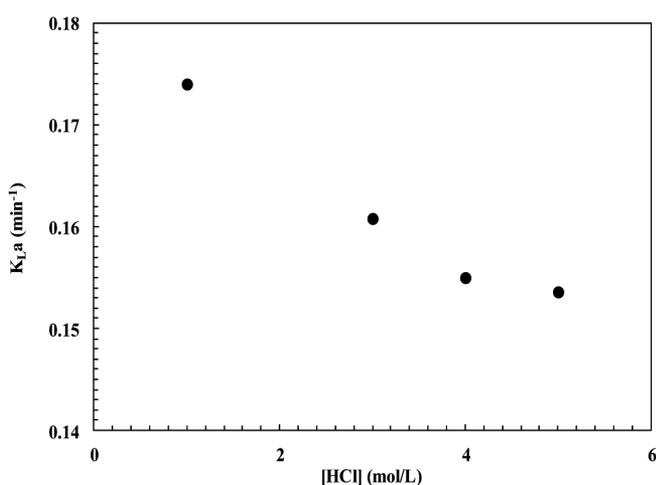


Figure 7. Plot of mass transfer coefficients in liquid phase vs [HCl]. Conditions:  $P = 1.125$  bar;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 1-4 M; [Me<sup>n+</sup>] = 100 ppm; contact time = 40 min

phase at high temperatures.

Table VI illustrates the calculated values of the diffusion coefficient,  $D_L$ , from Equation [5] and rate constant,  $k_R$  at different temperatures. The diffusion coefficient ( $D_{SO_2}$ ) values for SO<sub>2</sub> into the metal chloride system increased with temperature, as expected. The relationship between the diffusion coefficients of SO<sub>2</sub> in metal solution and temperature is linear, as shown in Figure 9, (Koliadima *et al.*, 2009; Least, 1984).

The decrease in  $k_R$  value with temperature is due to the fact that  $k_R$  is a 'phenomenal' constant that corresponds not only to the reaction between SO<sub>2</sub> and metal ions in the solution, but to the total phenomenon whereby the uptake of SO<sub>2</sub> by metal ions in the solution takes place first (Boniface *et al.*, 2000).

The thermodynamic behaviour of SO<sub>2</sub> absorption was further investigated by considering the dependence of the

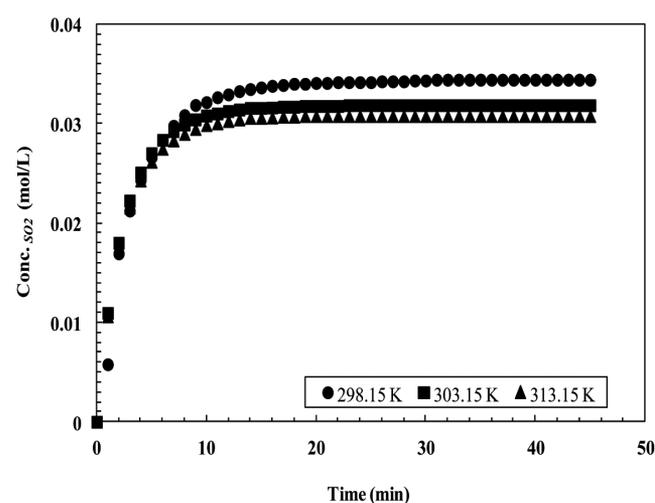


Figure 8. Dependence of concentration of SO<sub>2</sub> on contact time at different temperatures. The effect of temperature on physical absorption of SO<sub>2</sub> in chloride solution at 298.15, 303.15, and 313.15 K.  $P = 1.125$  bar; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 1-4 M; [Me<sup>n+</sup>] = 100 ppm; contact time = 40 min

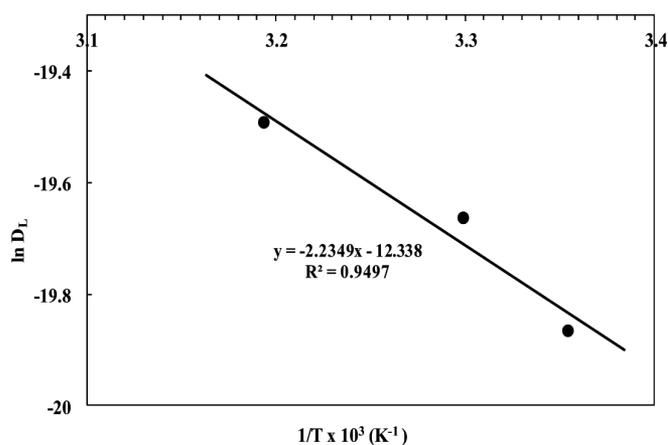


Figure 9. Dependence of effective diffusion coefficient on temperature: Arrhenius plot. Conditions:  $P = 1.125$  bar;  $T = 298$ –313 K; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M; [Me<sup>n+</sup>] = 100 ppm; contact time = 40 min

**Table V**  
Summary of thermodynamic properties of SO<sub>2</sub> absorption in G-L chloride system as a function of temperature

Temperature (K)	$D_{SO_2}(10^{-9} \text{ m}^2/\text{s})$	$\Delta H$ (kJ/mol)	$\Delta G$ (kJ/mol)	$\Delta S$ [J/(mol·K)]
298.15	2.36	16.12	-3.14	64.59
303.15	2.89	16.08	-3.16	63.47
313.15	3.43	15.99	-3.24	61.41

diffusion coefficient on solution temperature (Figure 9). A change in  $D_{SO_2}$  for activation diffusion can be correlated with temperature by use of the Arrhenius-type equation given by:

$$D_{SO_2} = Ae^{-\frac{E_a}{RT}} \quad [9]$$

where  $A$  is the pre-exponential factor,  $R$  the universal gas constant,  $T$  the absolute temperature, and  $E_a$  the activation energy, representing the minimum energy that the reacting system must attain for absorption to proceed. The value of  $E_a$  depends on the controlling regime in the absorption process. According to Juang and Chen (1997), an absorption process is said to be film-diffusion-controlled when  $E_a < 16$  kJ/mol, and chemical-reaction-controlled when  $E_a > 50$  kJ/mol. Linearization of equation [9] gives

$$\ln D_{SO_2} = \ln A - \frac{E_a}{RT} \quad [10]$$

The logarithmic diffusional time constant,  $\ln D_{SO_2}$  was plotted against the reciprocal of absolute temperature,  $1/T$  as shown in Figure 9. The experimental activation energy was determined from the slope of the plot. An activation energy value of 18.6 kJ/mol was obtained, confirming that film diffusion might be the essential rate-limiting step in the absorption process.

The enthalpy, free energy, and entropy changes were also determined. The enthalpy change,  $\Delta H$ , is given by

$$\Delta H = E_a - RT \quad [11]$$

The enthalpy change determined according to Equation [11] was 16.12, 16.08, and 15.99 kJ/mol for chloride solution temperatures of 298.15, 303.15, and 313.15 K, respectively. The positive values of  $\Delta H$  confirm the endothermic nature of the absorption/precipitation process. When absorption is endothermic, the precipitation or recovery of the target ions increases with an increase in solution temperature.

The values for the free energy change ( $\Delta G$ ) were calculated at different solution temperature using the following expression:

$$\Delta G = -RT \ln \left( \frac{C_{SO_3^{2-}}}{C_{SO_2}^*} \right) \quad [12]$$

where  $C_{SO_3^{2-}}$  is the gas concentration of SO<sub>2</sub> with SO<sub>3</sub><sup>2-</sup> in the bulk liquid phase of chloride solution at equilibrium (mol/L), and  $C_{SO_2}^*$  the interfacial concentration of SO<sub>2</sub> (mol/L) at equilibrium. The  $\Delta G$  values were -3.14, -3.16, and -3.24 kJ/mol for chloride solution temperatures of 298.15, 303.15, and 313.15 K, respectively. The  $\Delta G$  values indicate the spontaneous nature of the absorption of SO<sub>2</sub> into chloride solution.

The entropy change ( $\Delta S$ ) was determined according to the expression:

$$\Delta G = \Delta H - T\Delta S \quad [13]$$

**Table VI**  
Effect of temperature on the absorption rate ( $N$ ), diffusivity ( $D_{SO_2}$ ) and rate constant ( $k_R$ )

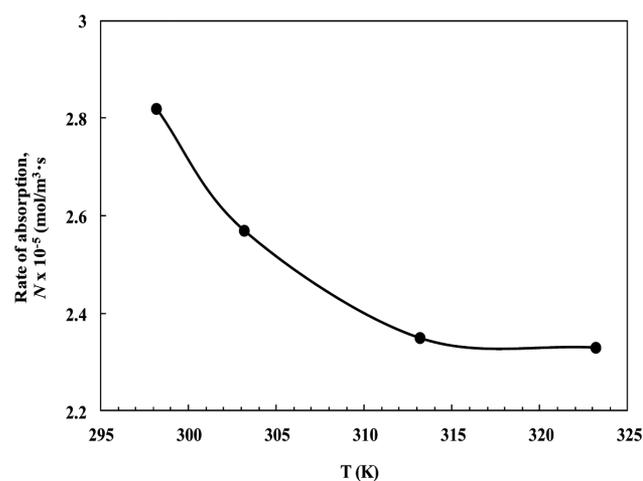
$T$ (K)	$N$ ( $10^{-5} \text{ mol/m}^3\cdot\text{s}$ )	$D_{SO_2}(10^{-9} \text{ m}^2/\text{s})$	$k_R(\text{m}^3/\text{mol}\cdot\text{s})$
298.15	2.82	2.36	8.81
303.15	2.57	2.89	7.46
313.15	2.35	3.43	6.10

$\Delta S$  values of 64.59, 63.47, and 61.41 J/(mol·K) were obtained for chloride solution temperature of 298.15, 303.15 and 313.15 K, respectively. The positive values of the entropy change show the increased mobility or randomness at the gas-liquid interface and an affinity of the absorbent (chloride solution) towards SO<sub>2</sub>. The thermodynamic parameters of SO<sub>2</sub> absorption in gas-liquid chloride systems as function of temperature are summarized in Table V.

#### Evaluation of absorption rate and diffusivity

The absorption rate ( $N$ ) and diffusivity ( $D$ ) values of SO<sub>2</sub> in the chloride system of the continuous stirred tank reactor were evaluated by using Equation [5], considering the gas-liquid interfacial area as 0.00528 m<sup>2</sup>/m<sup>3</sup> liquid. The absorption rate and diffusivity of SO<sub>2</sub> were in the order of 10<sup>-5</sup> mol/m<sup>3</sup>·s and 10<sup>-9</sup> m<sup>2</sup>/s respectively.

The absorption rate and diffusivity values of SO<sub>2</sub> were evaluated at different temperatures of the solution (298–313 K). By combining information from Equation [5] and Figures 8 and 10, values for the absorption rate, diffusivity, and rate constant of SO<sub>2</sub> were evaluated. The results are



**Figure 10.** Effect of temperature on average specific absorption rate. The effect of temperature on physical absorption of SO<sub>2</sub> in chloride media at 298, 303, and 313 K.  $P = 1.125$  bar; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 1-4 M; [Me<sup>II+</sup>] = 100 ppm; contact time = 40 min

Metal ions initial conc. (mg/L)	Pt ions		Pt/Fe/Co/Cr ions	
	$k_L a$ ( $\text{min}^{-1}$ )	$[S^0]_{\text{equiv}}$ (mol/L)	$k_L a$ ( $\text{min}^{-1}$ )	$[S^0]_{\text{equiv}}$ (mol/L)
50	0.15	0.014	0.21	0.015
100	0.22	0.017	0.21	0.018
120	0.27	0.018	0.25	0.019

summarized in Table VI.

As shown in Figure 10, the absorption rate is found to decrease considerably with increasing temperature, leading to an equilibrium state. In the case of gas absorption with an accompanying chemical reaction, the influence of temperature on absorption rate is determined primarily by two opposing factors: decrease in gas solubility and increase in reaction rate (for irreversible reactions) as the temperature is increased. The results from this study indicate that the rate of absorption decreases by about 17% for an increase of temperature from 298 to 313 K. For the same change in temperature, the physical solubility and reaction equilibrium constant decrease by 27% and 10% respectively. The decrease in physical absorption rate is also around 27%. The experimental data further shows that the decrease in absorption rate in the multi-component system (Pt/Fe/Co/Cr) is more sensitive to temperature increases from 303 K to 313 K than from 298 K to 303 K, compared to the physical absorption rate. This indicates that the reverse reaction rate is more temperature-sensitive than the forward reaction rate. The temperature variation across the liquid film was, however, neglected in the interpretation of the data in consideration of the low heat of reaction.

#### Reactive absorption of SO<sub>2</sub> gas in the presence of metal ion species

In the presence of Pt ions, the solubility of SO<sub>2</sub> was enhanced slightly (Figure 11) due to the chemical reaction with Pt to form Pt-S bonds. The increase was not significant because the stoichiometric amount of sulphur atoms

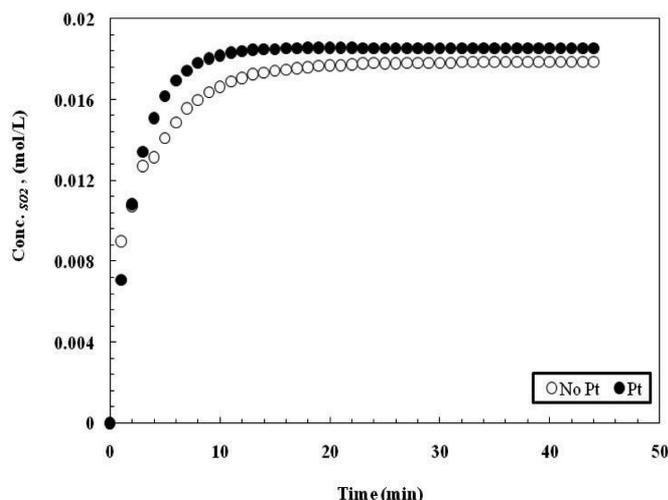


Figure 11. Plot of SO<sub>2</sub> concentration vs contact time. Reactive absorption of SO<sub>2</sub> in solution with or without Pt ions. [HCl] = 4 M;  $P = 1.125$  bar;  $T = 25$  °C; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%;  $[Me^{n+}] = 100$  ppm; contact time = 40 min

required to react with the traces of Pt ( $5.0 \times 10^{-4}$  mol/L) in solution was small. Initial concentration of Pt was the limiting factor in the reactive solubility of SO<sub>2</sub>.

As it can be seen from Tables IV and VII, the presence of metal ions in the solution has an effect on the mass transfer coefficient. The resistance to mass transfer increases slightly as more metal ions are added to the solution. This could be attributed to the fact that the interfacial area decreases due to the presence of solid particles in the liquid phase. The formation of solid particles could also influence the effective interfacial area.

#### Effect of pressure

According to Levenspiel (1999), the initial pressures ( $P_A$ ) are converted to concentrations ( $C_A$ ) because the rate equations developed in terms of pressures and the calculated values of activation energy are incorrect when these units are used. Therefore, in this study, the initial pressure values of SO<sub>2</sub> were converted into concentration values using the idea gas law:

$$P_A V = n_A R T \quad [14]$$

$$P_A = n_A / V R T; P_A = C_A R T$$

Therefore,

$$C_A = P_A / R T \quad [15]$$

where  $C_A = n_A / V$  is the concentration of component A (mol/L);  $P_A$  is partial pressure of component A (bar);  $V$  is volume (L);  $n_A$  is moles of the component A;  $R$  is the ideal

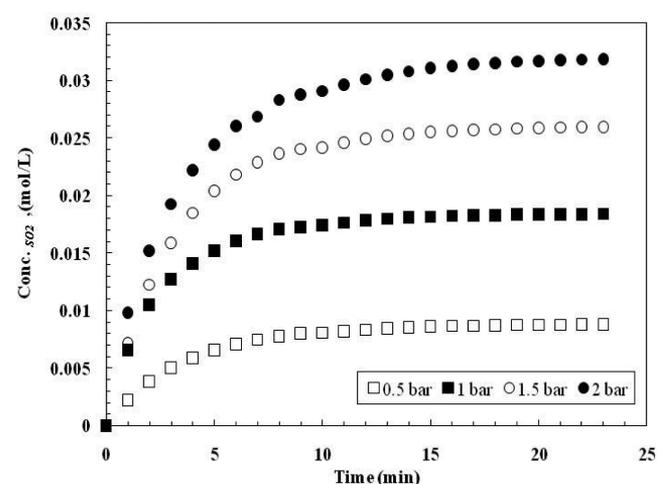
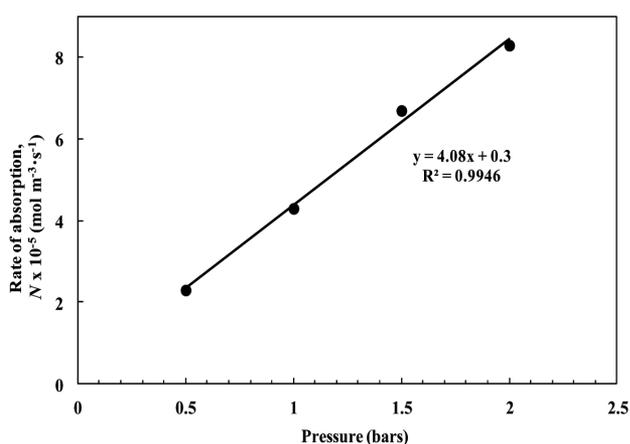


Figure 12. Plot of SO<sub>2</sub> concentration v. time. The effect of initial pressure of SO<sub>2</sub> at ambient conditions. Conditions:  $P = (0.5-2$  bar);  $T = 25$  °C; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%; [HCl] = 4 M;  $[Me^{n+}] = 100$  ppm; contact time = 40 min

Pressure (bar)	$D_L$ ( $10^{-9}$ m <sup>2</sup> /s)	$k_R$ (m <sup>3</sup> /mol · s)
0.5	1.36	16.60
1.0	1.62	9.82
1.5	1.99	8.52
2.0	2.22	5.20



**Figure 13.** Effect of SO<sub>2</sub> pressure on SO<sub>2</sub> absorption rate at ambient conditions. Conditions:  $P = (0.5-2 \text{ bar})$ ;  $T = 25^\circ\text{C}$ ; stirring speed = 500 r/min; inlet SO<sub>2</sub> gas conc. = 99.9 vol%;  $[\text{HCl}] = 4 \text{ M}$ ;  $[\text{Me}^{n+}] = 100 \text{ ppm}$ ; contact time = 40 min

gas law constant (L·bar/mol·K); and  $T$  is the absolute temperature (K).

Figures 12 and 13 show the plot of SO<sub>2</sub> concentration vs time and the effect of initial pressure of SO<sub>2</sub> gas on its absorption at ambient conditions, respectively. It is evident that the initial pressure has an effect on gas solubility. The SO<sub>2</sub> absorption rate increases as the SO<sub>2</sub> initial pressure increases from 0.5 to 2.0 bar. For instance, the SO<sub>2</sub> absorption rate increases 72.3% ( $2.3 \times 10^{-5}$  mol/m<sup>3</sup>·s to  $8.3 \times 10^{-5}$  mol/m<sup>3</sup>·s) at 25°C as SO<sub>2</sub> initial pressure increases from 0.5 to 2.0 bar. This is due to the fact that, under the experimental conditions, the SO<sub>2</sub> absorption process is a gas-phase mass transfer controlled process. As a result, the initial SO<sub>2</sub> pressure has a great impact on its absorption rate.

The results in Table VIII shows that as the initial gas pressure value of SO<sub>2</sub> was increased, the diffusion coefficient value of SO<sub>2</sub> into solution increased. Furthermore, it was observed that increasing SO<sub>2</sub> gas concentration (initial gas pressure) increased the rate of metal depletion in solution.

### Conclusions

Based on the SO<sub>2</sub> solubility data in the G-L system for both physical and reactive absorption conditions, it is possible to introduce significant amounts of sulphur into HCl solutions. In the presence of Pt ions in solution, the sulphur will induce a precipitation reaction between sulphur and Pt ions. The maximum physical absorption of SO<sub>2</sub> was achieved at a temperature of 298.15 K and initial pressure of 2 bar. The optimum absorption capacity was 0.015 mol/L SO<sub>2</sub>. In reactive absorption, the absorption of SO<sub>2</sub> was achieved at a

temperature of 289.15 K and initial pressure of 2 bar. The maximum capacity of SO<sub>2</sub> absorbed was 0.018 mol/L SO<sub>2</sub>. The presence of metal ions thus led to a 17% increase in absorption. The model that best describes the diffusion of SO<sub>2</sub> in a chloride system is the two-film model. The rate constants were evaluated, and could be used to predict the correct size of industrial contactors. Sulphur atoms exhibited a higher affinity for Pt.

The changes in enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ) and Gibbs' free energy ( $\Delta G$ ) of Pt precipitation were 15.99 kJ/mol, -3.24 kJ/mol, and 61.41 J/(mol·K) respectively at optimum temperature of 313.15 K (40°C). The positive ( $\Delta S$ ) values and low ( $\Delta G$ ) suggested that some energy is required, albeit a small amount, for the reactive absorption reaction to proceed.

SO<sub>2</sub> gas absorption in the chloride system was achieved in short contact time (10 minutes). Precipitates appeared after 24 hours, due to the low metal ion concentration (50-120 mg/L). Higher metal ions concentrations (>120 mg/L) were not investigated due to high cost of the reagents. Therefore, it is recommended that in future, solutions with higher metal ion concentrations should be prepared in order to achieve a minimum residence time for precipitate formation.

The results from this study confirmed the concept that it is possible to replace liquid precipitants such as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> with SO<sub>2</sub> gas as a cost-effective precipitant for Pt.

### NOMENCLATURE

$a$	gas – liquid interfacial area (m <sup>2</sup> m <sup>-3</sup> liquid)
$C_A$	concentration of species A (mol m <sup>-3</sup> )
$C_{SO_2}^*$	interfacial concentration of SO <sub>2</sub> (mol m <sup>-3</sup> )
$C_{A,i}$	gas concentration in liquid at the interface (mol m <sup>-3</sup> )
$C_{A,L}$	gas concentration in liquid bulk phase (mol m <sup>-3</sup> )
$D_{L,SO_2}$	diffusivity of SO <sub>2</sub> in the liquid phase (m <sup>2</sup> s <sup>-1</sup> )
$dm/dt$	rate of mass transfer (mol s <sup>-1</sup> )
$K$	overall mass transfer resistance
$K_L$	mass transfer resistance in liquid phase
$k_L$	mass transfer coefficient in liquid phase (m <sup>3</sup> m <sup>-2</sup> s <sup>-1</sup> )
$k_G$	mass transfer coefficient in gas phase (m <sup>3</sup> m <sup>-2</sup> s <sup>-1</sup> )
$N$	absorption rate (mol s <sup>-1</sup> )
$t$	time (s)
$T$	temperature (K)

### SUBSCRIPT AND SUPERScript

$A$	species A
$i$	interface
$n$	order of reaction
$G$	referring to the gas phase
$L$	referring to the liquid phase

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I completed my high school education in 1988 at Mpelembe Secondary School in Kitwe, Zambia and later enrolled at Voronezh State Technological Academy, Voronezh, Russian Federation for a master's degree in Chemical Engineering. I received my master's degree in 1997 following a taught programme and project research dissertation titled "Design and Production of Injection-moulded Products from Polyolefin with a Production Capacity of 360 ton/year".

In 1998, I joined the University of Zambia as a part-time Lecturer/Tutor and two years later I was appointed as a Lecturer at the Copperbelt University, Kitwe, Zambia within the Department of Chemical Engineering, School of Technology then, now it is School of Mines and Mineral Sciences where I am currently based. I have been with the Copperbelt University for 14 years now.

In 2006, I was awarded a scholarship by the Copperbelt University to enrolled as M. Tech.-Chemical Engineering student at Tshwane University of Technology (TUT) and was awarded a master's degree in September 2008 following a research dissertation entitled "Physical Beneficiation of PGM Tailings by Gravity Separation and Elutriation Techniques".

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