PHYSICAL MODELLING OF MASS TRANSFER IN A
PEIRCE-SMITH CONVERTER

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ABSTRACT

A 1/4 scale Plexiglas model of a copper converter has been used to measure the fraction of gas absorbed during horizontal gas injection. In this work, sulphur dioxide gas was injected into hydrogen peroxide solution under conditions where mass transfer in the gas phase was rate limited. The $SO_2$ absorption rate was measured as a function of the gas flow rate, tuyere submergence, number of tuyeres, and percent filling.

The fraction of gas absorbed correlated well with the total trajectory length which included the spout height. It increased with tuyere submergence but decreased with the air flow rate and remained almost constant after a certain flow rate.

The mass transfer parameter, $k_{SO_2}$, was computed from the results. It compared favourably with the work of previous investigators but could not be used to explain some of the results, especially, the effect of gas flow rate on the fraction of sulphur dioxide absorbed.

Further analysis of the experimental results was based on bubble formation period and rise time. The fraction of gas absorbed increased with total residence time. About 74% of the injected gas was absorbed during the formation period. A mechanism to explain the overall absorption was proposed. An equation relating the absorption efficiency and the residence time was obtained for the physical model. This method was extended to the analysis of industrial data for the comparison of measured and predicted oxygen utilization efficiency.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$A_k$</td>
<td>Volumetric mass transfer coefficient, cm$^3$s$^{-1}$.</td>
</tr>
<tr>
<td>$A$</td>
<td>Interfacial area of gas bubble, cm$^2$.</td>
</tr>
<tr>
<td>$A_o$</td>
<td>Cross-sectional area of tuyere, cm$^2$.</td>
</tr>
<tr>
<td>$C$</td>
<td>Gas fraction in the jet.</td>
</tr>
<tr>
<td>$[C_{SO_2}]_0$</td>
<td>Concentration of sulphur dioxide gas entering the bath, mol cm$^{-3}$.</td>
</tr>
<tr>
<td>$[C_{SO_2}]$</td>
<td>Concentration of sulphur dioxide gas in the bulk of gas phase or gas bubble, mol cm$^{-3}$.</td>
</tr>
<tr>
<td>$[C_{SO_2}]_e$</td>
<td>Equilibrium concentration of sulphur dioxide gas at the reaction interface, mol cm$^{-3}$.</td>
</tr>
<tr>
<td>$[C_{SO_2}]_f$</td>
<td>Concentration of sulphur dioxide gas leaving the bath, mol cm$^{-3}$.</td>
</tr>
<tr>
<td>$D_{A-B}$</td>
<td>Diffusion coefficient of substance $A$ in $B$, cm$^2$s$^{-1}$.</td>
</tr>
<tr>
<td>$d_o$</td>
<td>Diameter of tuyere, cm.</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of jet at a horizontal distance $x$, from the tuyere exit, cm.</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency of gas bubble, s$^{-1}$.</td>
</tr>
<tr>
<td>$f_g$</td>
<td>Gas phase mass transfer coefficient for forming bubbles, cm$^3$s$^{-1}$.</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration due to gravity, cm s$^2$.</td>
</tr>
<tr>
<td>$h$</td>
<td>Height of spout, cm.</td>
</tr>
<tr>
<td>$K$</td>
<td>&quot;Enhancement factor&quot; during bubble formation.</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Liquid phase mass transfer coefficient, cm s$^{-1}$.</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Liquid phase mass transfer parameter per unit length, cm$^2$s$^{-1}$.</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Gas phase mass transfer coefficient, cm s$^{-1}$.</td>
</tr>
<tr>
<td>$k_a$</td>
<td>Gas phase mass transfer parameter per unit length, cm$^2$s$^{-1}$.</td>
</tr>
<tr>
<td>$k_{SO_2}$</td>
<td>Mass transfer parameter per unit length for sulphur dioxide, cm$^2$s$^{-1}$.</td>
</tr>
<tr>
<td>$m$</td>
<td>Slope of the $H_2SO_4$ concentration-time plots, mol cm$^{-3}$ s$^{-1}$.</td>
</tr>
<tr>
<td>$N_{Re}$</td>
<td>Reynolds number at the tuyere orifice.</td>
</tr>
</tbody>
</table>
\( N'_{Fr} \) Modified Froude number.

\( N_{Ma} \) Mach number.

\( n_{SO_2} \) molar flow rate of sulphur dioxide to the bubble interface, mol s\(^{-1}\).

\( P_8 \) Partial pressure of a soluble gas in the bulk of gas phase, atm.

\( P_{SO_2}^o \) Partial pressure of sulphur dioxide gas at the tuyere exit, atm.

\( P_{SO_2}^\circ \) Partial pressure of sulphur dioxide gas at the bath surface, atm.

\( Q \) Gas flow rate, cm\(^3\) s\(^{-1}\).

\( q_{SO_2} \) Molar flow rate of sulphur dioxide gas, mol cm\(^{-3}\).

\( R \) Radius of rising bubbles, cm.

\( R_0 \) Radius of bubble during formation, cm.

\( s \) Distance along jet trajectory from tuyere orifice, cm.

\( S_o \) Distance along jet trajectory from tuyere orifice to the quiescent level of the bath, cm.

\( S_t \) Dimensionless distance along jet trajectory from tuyere orifice.

\( t \) Time, s.

\( t_f \) Residence time of bubble, s.

\( u_o \) Nominal gas velocity at the tuyere, cm s\(^{-1}\).

\( u_r \) Bubble rise velocity, cm s\(^{-1}\).

\( u_s \) Superficial gas velocity, cm s\(^{-1}\).

\( V_B \) Volume of bath, cm\(^3\).

\( W \) Mass of gas bubble, g.

\( V_b \) Volume of gas bubble, cm\(^3\).

\( X \) Total fraction of gas absorbed.

\( X_f \) Fraction of gas absorbed during bubble formation.

\( x \) Horizontal distance of gas jet, cm.

\( x_t \) Dimensionless horizontal distance of a gas jet.

\( y \) Vertical distance of gas jet or tuyere submergence, cm.

\( y_t \) Dimensionless vertical distance of gas jet.
\( \varepsilon_p \)  Specific power density, watts kg\(^{-1}\).

\( \lambda_r \)  A term in Equation 6.8.

\( \lambda_f \)  A term in Equation 6.12.

\( \theta_c \)  Jet cone angle, degrees.

\( \theta_o \)  Angle the tuyere makes with the horizontal, degrees.

\( \mu \)  Dynamic viscosity, g cm\(^{-1}\)s\(^{-1}\).

\( \rho_g \)  Density of gas, g cm\(^3\).

\( \rho_l \)  Density of liquid, g cm\(^3\).

\( \sigma \)  Surface tension, dynes cm\(^{-1}\).
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CHAPTER 1

INTRODUCTION

1.1 Metallurgical uses of submerged gas injection.

Submerged injection of gas into liquid metals for refining purposes has been in use since the days of the Bessemer. Several metallurgical processes including nickel and copper converting, zinc slag fuming, steelmaking and gaseous deoxidation of liquid copper depend on the mass transfer between the injected gas and the melt [1, 2, 3, 4].

Gas injection may be achieved by the use of tuyeres, porous plugs, or a lance, and the gas may be blown from the top, side or bottom of the furnace. The behaviour of the resulting gas bubbles is a subject of considerable interest in the fields of both Chemical and Metallurgical Engineering. In general, high production rates are achieved during gas injection due to the generation of large gas-liquid interfacial areas which result in high mass transfer rates. Gas injection has therefore become the most commonly used technique in metal smelting and refining.

1.2 The copper converting process

The most important application of submerged gas injection in the non-ferrous industry is the converting of copper and nickel mattes. Mattes are molten sulphides of heavy metals, often containing oxides. Copper matte, which essentially consists of FeS and Cu$_2$S is an intermediate product in the extraction of copper from sulphide ores. These sulphide ores may be chalcopyrite (CuFeS$_2$), bornite (Cu$_2$FeS$_4$) or chalcocite (Cu$_2$S). Low
concentrations of these minerals occur in an orebody ranging from 1/2 to 2% Cu. Processes involved in extraction are crushing, flotation, roasting, matte smelting and converting. In some cases, hydrometallurgical techniques are used whereby the crushed ore is leached with a suitable solvent followed by precipitation or electrowinning of the copper from solution [5].

The conversion of copper matte to metallic copper is carried out in a Peirce-Smith Converter (Figure 1.1). During converting air is blown through a number of horizontal, side-mounted tuyeres into the molten matte to oxidize iron and sulphur. The process, which takes place in two stages, is exothermic with bath temperatures ranging from 1100 to 1300°C.

1.2.1 The slag forming stage

During this stage, iron sulphide is oxidized to ferrous oxide, magnetite and sulphur dioxide according to the following reactions:

\[ FeS + \frac{3\nu}{2}O_2 = FeO + SO_2 \]  \hfill (1.1)

\[ 3FeS + 5O_2 = Fe_3O_4 + 3SO_2 \]  \hfill (1.2)

The oxides of iron then combine with the silica flux to form slag. As the slag builds up, it is periodically skimmed off and more matte and silica are added. The cyclic operation continues until the charge consists of essentially white metal \((Cu_2S)\).
Figure 1.1 Schematic of Peirce-Smith copper converter.
1.2.2 Blister copper forming stage

This is the second stage of blowing and involves the oxidation of the white metal to blister copper according to the reaction below:

\[ Cu_2S + O_2 = 2Cu + SO_2 \]  (1.3)

The product (approximately 99% Cu) is further treated in an anode furnace to remove dissolved oxygen, i.e.

\[ 3[O]_{Cu} + CH_4 = CO + 2H_2O \]  (1.4)

The copper is then refined electrolytically. In recent years, considerable work has been done in developing processes where the smelting of the concentrate, the slagging of the iron and the production of blister copper are carried out in a single furnace. Examples include the Worcra, Noranda and Mitsubishi processes [6].

1.3 Problems that occur during copper converting

Several of the problems associated with this process are directly linked to the gas injection process. Examples are accretion growth, tuyere blockage, refractory wear, tuyere erosion, splashing and slopping.

In converting operations the tuyeres become plugged periodically with accretions which must be removed by forcing a punching bar through individual tuyeres. The gradual blockage of a given tuyere causes a reduction in the air flow which in turn reduces converter productivity. The exothermic reactions that occur in the furnace, coupled with the high temperatures of operation and the heat and mass flow patterns that exist in the bath, provide harsh conditions in the furnace which lead to tuyere and refractory erosion. The rate of refractory erosion may depend on tuyere punching practice, temperature variation in the converter, matte grade, blowing rate and refractory
type. Part of the energy of the injected air results in splashing, a situation where particles of liquid are carried out with the gas above the surface of the bath. Accretions are therefore built at the mouth of the converter which must be removed occasionally.

Extensive research work has been pursued at the Department of Metals and Materials Engineering in UBC to investigate the following aspects of converter operations: gas injection into the bath, accretion growth at the tuyere tip, slopping of the bath, kinetics of bath oxidation and heat losses from the interior of the converter during out-of-stack periods. The study of these subjects has involved several types of lab experiments, plant measurements, physical and mathematical modelling [7, 8, 9, 10].

Brimacombe et al. [11] conducted high pressure experiments at Tacoma Smelter of ASARCO to address the problem of accretion growth at the tuyeres and tuyere blockage. At higher pressures, tuyere punching was not necessary but at lower pressures punching was required because of tuyere blockage. The accretion growth was also reduced or eliminated altogether with oxygen enrichment (28% $O_2$). There was a reduction in the build up when air was injected into low-grade mattes because of the increase in the rate of heat evolution.

The principal factors which determine the production rates of copper converters are the matte grade and the air blowing rate. In general, high oxygen efficiencies are expected during converting, however, the Johnson survey [12] indicates there are a significant number of operations with relatively low efficiencies. Much attention has not been paid to factors affecting oxygen utilization and its impact on converter productivity. Very few studies have been conducted in this area [12]. For example, it is not clear whether all the reaction between injected gas and the bath takes place below the bath surface or whether other gas-liquid contact areas are important during converting.
The processes that occur at the tuyeres including bubble formation and the subsequent reaction may depend on the gas flow rate, the pressure of injection and the heat transfer from the liquid to the bubble. The bubbles formed at the tuyeres tend to expand due to the heat transfer that takes place. Bustos et al. [8] undertook a study on injection phenomena in an industrial converter and measured the pressure pulses at the tuyeres during injection. Periods of constant, low pressure between pressure pulses were observed due to the interaction among adjacent tuyeres. The interaction of adjacent tuyeres led to the coalescence of bubbles which created a horizontal, unstable gas envelope at the tuyere line. Therefore, for part of the time, a given tuyere would feed the envelope with little resistance from surrounding liquid, and the tuyere pressure will remain low until the envelope collapsed.

Since there are different regions in the gas-liquid zone of the converter, the extent of reaction in each region is likely to differ. That is, the fraction of gas that reacts during bubble formation may be different from that during bubble rise. If the gas reacted in each region can be estimated quantitatively, then effective control of the various parameters that influence the gas utilization efficiency in the bath can be exercised. Therefore it is necessary to understand the rate controlling process of the reaction during gas injection. A physical model of the converter was used in this work to measure mass transfer rates in injection regimes similar to the industrial converter. Variables such as gas flow rates, tuyere submergence, modified Froude number and gas residence time were employed in this study.
CHAPTER 2

LITERATURE REVIEW

Since this work involves mass transfer studies in a converter during gas injection, it was necessary to review available literature that provides understanding of the various aspects of the topic. The areas which have been discussed are gas injection studies and mass transfer models in non-ferrous metallurgy.

2.1 Gas injection studies

Studies have been conducted by various investigators on injection phenomena in non-ferrous reactors to predict what occurs in the melt. Depending on the type of experiments conducted and the nature of results obtained, various researchers have come out with different models that presumably depict the actual injection process in a converter. Some have observed a jetting behaviour in the bath [13] whilst others have observed that the injected air enters the converter in the form of bubbles [9].

2.1.1 Jetting and bubbling behaviour.

Oryall [7] has reviewed bubble formation in liquids. His findings indicated that three distinct regimes of bubble formation occur during injection.

2.1.1.1 Static regime  $N_{Re} < 500$

At very low flow rates the frequency of bubble formation is proportional to the gas flow rate while the bubble size is almost constant and depends only on the orifice diameter.
2.1.1.2 Dynamic regime $500 < N_{Re} < 2100$

In this range the bubble volume increases with gas flow rate while the frequency remains almost constant (usually higher than 80 bubbles per second).

2.1.1.3 Non-homogeneous jets $N_{Re} > 2100$

At higher flow rates ($N_{Re} > 2100$), a bubble stream is produced where larger bubbles of irregular shapes issuing from the orifice explode into smaller bubbles very close to the tip of the nozzle. McNallan and King [14] reported that at very high flow rates ($N_{Re} > 10000$, $N'_{Fr} > 1000$) the bubbling behaviour ceases altogether, and the gas enters the liquid as turbulent jet.

In the paper by Hoefele and Brimacombe [9], the conditions which give rise to bubbling and steady jetting were delineated in terms of the modified Froude number, $N'_{Fr}$ and $\rho_g/\rho_l$ as shown in Figure 2.1. $N'_{Fr}$ is defined by the equation:

$$ N'_{Fr} = \frac{\rho_g u_0^2}{(\rho_l - \rho_g)gd_o} \tag{2.1} $$

$\rho_g$ is the gas density, $\rho_l$ is the liquid density, $u_0$ is the nominal gas velocity at the tuyere, $g$ is the acceleration due to gravity and $d_o$ is the tuyere diameter.

Motion pictures that were taken indicated that at low values of $N'_{Fr}$, corresponding to blowing conditions in the copper converter ($N'_{Fr} = 10 - 14$, Pressure = 60 kPa), the gas discharges in the form of bubbles at a frequency of about $10 \, s^{-1}$. At higher flow rates steady jetting predominated in which gas flowed from the tuyeres continuously. The flow regimes and the forward penetration of the gas depended on both the modified Froude number and the gas-liquid density ratio.
Figure 2.1  Bubbling and jetting behaviour as predicted by Hoefeke and Brimacombe [9].
Ozawa and Mori [15] in their study on the behaviour of gas jets injected into liquid metal bath (nitrogen in mercury) observed that the injected gas does not form a continuous gas channel even at sonic velocities but breaks up at some distance from the orifice exit. Sano and Mori [16] studied the bubbling and jetting behaviour of gas liquid systems by injecting nitrogen gas (90-7800 cm$^3$s$^{-1}$) through an orifice ($d_o = 0.2-0.4$ cm) into water. In this work, the transition from bubbling to jetting occurred at a $N_{Ma}$ (the ratio of gas velocity to the velocity of sound in air) greater than 1.3 - 1.4. They observed that the transition occurred more abruptly with increasing ratio of gas to liquid densities.

2.1.1.4 Bubble frequency

Irons and Guthrie [17] injected gas ($Q = 0.15 - 100$ cm$^3$s$^{-1}$, nozzle diameter = 0.16 - 0.64 cm) into molten pig iron and observed a constant bubble frequency of 10 s$^{-1}$. Andreini et al.[18] reported a bubble frequency of 20 s$^{-1}$ when liquid copper was deoxidized with a jet of CO ($Q = 1 - 8$ cm$^3$s$^{-1}$ and $d_o = 0.05 - 0.1$ cm). When argon was injected into molten copper and silver at gas flow rates up to 19 cm$^3$s$^{-1}$, Fruehan [19] observed a bubble frequency of about 22 s$^{-1}$. Patankar and Spalding [20] observed that at flow rates between $10^3$ and $10^4$ cm$^3$s$^{-1}$, a constant frequency regime occurs in which the frequency of bubble formation remains constant at about 10 s$^{-1}$, and the volume of bubbles formed and released become larger and larger. At very high flow rates ($10^3$ to $3\times10^5$ cm$^3$s$^{-1}$), Hoefele and Brimacombe [9] observed tuyere pressure pulsations of 10 Hz in liquid metals which indicate the formation of large bubbles. These large bubbles or gas envelopes tend to exhibit hydrodynamic instability [21].

Bustos [22] in his experiments in a physical model of the copper converter, observed a dependency of bubble frequency on tuyere diameter, gas flow rate and the modified Froude number. Using five tuyeres with diameters of 1.6 cm and 1.2 cm, bubble
frequencies of 13 to 14 s\(^{-1}\) were obtained at low flow rates (5000 to 9000 cm\(^3\)s\(^{-1}\) and modified Froude numbers between 0.4 and 2.5). An increase in gas flow rate resulted in an almost linear increase in the pulse frequency. Industrial measurements showed that bubbling frequencies also depended on the state of the refractory. The pulse frequency was about 14 s\(^{-1}\) for the first campaign in a newly relined converter but dropped to about 7 s\(^{-1}\) at the end of the 12\(^{th}\) charge [22].

It can be summarized that at lower flow rates bubble frequency is a function of flow rate. At higher flow rates, however, most systems enter a constant frequency regime with a corresponding increase in bubble volume. This relationship can also be expressed as a constant bubble volume regime for very low gas flow rates and a constant frequency regime for higher flow rates. The bubble frequencies reported in the literature show that the formation of bubbles may differ from system to system. In industrial practice, furnace conditions such as the state of the refractory, heat transfer to the bubble and the bath circulation may have a major effect on bubble formation process. The work by Hoefele and Brimacombe [9] has shown that in matte converting and other industrial gas injection systems, the transition from bubbling to jetting regime can be delineated more appropriately by using the modified Froude number (which takes into account the inertia and bouyancy forces that predominates in industrial practice) and the gas-to-liquid density ratio.

### 2.1.2 Trajectory equation

Themelis et al. [13] used momentum and mass balances to derive a dimensionless equation that described the trajectory of a gas injected horizontally into liquid. The jet equation was found to be a function of the modified Froude number. The equation is shown below:
\[
\frac{d^2 y_r}{dx_r^2} = 4N_r \left[ \frac{\tan^2(\theta_e/2)}{\cos \theta_e} \right] \left[ 1 + \left( \frac{dy_r}{dx_r} \right)^2 \right] x_r^2 C
\] 

(2.2)

\( y_r \) is the dimensionless vertical distance, \( x_r \) the dimensionless horizontal distance, \( \theta_e \) the jet cone angle, \( \theta_\circ \) the angle the tuyere makes with the horizontal and \( C \) is the gas fraction in the jet.

The trajectories of air jets injected into water, as predicted by the above equation were found to correlate well with averaged jet boundaries measured experimentally by a photographic technique. It was concluded that the cone angle is a function of the jet fluid properties and that the jet diameter was a function of the horizontal distance from the orifice.

Engh and Bertheussen [23] modified the above model to calculate the trajectories of two-phase submerged jets. In their model, the jet diameter, \( d \), was a function of the distance along the jet axis. The predictions made by this model were in agreement with that predicted by Themelis et al. [13]. The equations used by the two models for the jet diameter are shown below:

\begin{align*}
\text{Themelis et al. [13]:} & \quad d = 2x \tan(\theta_e/2) \\
\text{Engh and Bertheussen [23]:} & \quad d = 2s \tan(\theta_e/2)
\end{align*}

(2.3)

(2.4)

where \( s \) is the distance along the jet trajectory from the tuyere orifice.

In computing the trajectory of the air jet, Themelis et al. [13] used a cone angle of 20°. Note that Oryall and Brimacombe [24] found that the apparent cone angle of an air jet injected into a liquid metal (mercury) was 155°.
2.2 Mass transfer models in non-ferrous metallurgy

Several investigators have used different models to characterize the mass-transfer coefficients, the gas-liquid interfacial areas and the efficiencies of gas-liquid reactions that occur in the industrial practice. These models may be grouped into three categories: high temperature experiments, physical modelling and mathematical modelling.

2.2.1 High temperature experiments

The important feature of high temperature experiments is that the thermal conditions in the model are similar to actual industrial practice. Themelis and Schmidt [25] injected a jet of CO vertically upwards into a copper melt at 1170°C. The effects of submersion, orifice diameter, and gas velocity were examined. The rate of deoxidation of liquid copper (0.1 < percent oxygen < 1) was controlled by gaseous mass transfer and the mass transfer parameter \( k_g a \), the product of mass transfer coefficient in the gas phase and the interfacial area per unit length of the jet trajectory) varied from about 40 to 240 cm\(^2\)s\(^{-1}\). The rate of reduction was not affected by the change in melt oxygen content from 1% to less than 0.1%.

Nanda and Geiger [26] studied the kinetics of deoxidation of molten copper with CO at 1135°C by monitoring the oxygen content of the bath. The gas, which formed bubbles in the melt, was injected through various-sized orifices. In this analysis, liquid phase control occurred at very low oxygen concentrations in the melt (wt% O < 0.05). It was also observed that \( k_l \) (mass transfer coefficient in the liquid phase) decreased with flow rate.

Fruehan [19] measured the mass transfer rate between submerged bottom-blown and top blown gas jets and liquid melts. At oxygen levels less than 0.025% in copper, the
rate was controlled by liquid-phase mass transfer. When the oxygen level was greater than 0.025% the rates were fast and essentially controlled by the rate of gas injection. The mass transfer rates increased with gas flow rate and the depth of jet submersion. This experiment was conducted with orifice diameters of 0.085 and 0.22 cm and gas flow rates varying from 1.8 to 18 cm$^3$s$^{-1}$.

Though high temperature experiments provide very useful information, it is difficult to gather precise data under such conditions.

2.2.2 Physical modelling

Most injection studies are conducted with clear liquids to facilitate optical observations and at ambient temperatures for ease of experimentation. In this type of modelling some principal characteristics of an existing industrial process are studied in a suitable model. The model may not reproduce the entire system but only the characteristic aspect under study based on appropriate similarity criteria.

Inada and Watanabe [27] used the NaOH-CO$_2$ system to study the efficiency of a bottom blown converter. They measured the rate of absorption of CO$_2$ in NaOH by monitoring the pH of the system. The test, which was conducted with pure CO$_2$ at Reynolds Numbers ranging from $10^3$ to $10^4$, showed mass transport control in the liquid phase. The volumetric mass transfer coefficient, $Ak_x$, was a function of the gas flow rate to the 0.65 power and increased with submergence. The nozzle diameter had little effect on the mass transfer parameter. In some of the experiments, the gas was injected horizontally as well as from the top. The highest volumetric mass transfer coefficient was obtained with the bottom injection followed by the horizontal. The efficiency was found to depend on submergence.
Taniguchi et al. [28] measured the volumetric mass transfer coefficient, $A_k$, in the bubble dispersed zone for the absorption of $CO_2$ in water in a cylindrical vessel. The gas was bottom injected through a 6 mm diameter nozzle and the flow rate ranged from 16.7 to 167 cm$^3$s$^{-1}$. The rate of absorption was controlled by liquid phase transport. The volumetric mass transfer coefficient decreased with increasing bath depth and vessel radius at a constant flow rate. It varied from 0.1 to 3 cm$^3$s$^{-1}$.

Haida and Brimacombe [29] evaluated the extent of solute inhomogeneity in a bath and the influence of the inhomogeneity on the efficiency of refining reactions. Pure $CO_2$ was injected into aqueous bath of 0.1NaOH solution. The NaOH concentration at different locations in the bath and the efficiency of $CO_2$ absorption were measured. The maximum efficiency obtained in the ladle shaped vessel was between 18.1 and 22.8%.

Brimacombe et al. [30] injected about 1% $SO_2$ gas into a solution of hydrogen peroxide to determine the rate of reaction between a horizontal submerged gas jet and a liquid. The study was undertaken to simulate the rates of reaction in a copper converter. Throughout the experiments mass transfer in the gas phase was found to be rate limiting. The absorption rate of $SO_2$ was measured as a function of jet Reynolds number ($10^4 - 4 \cdot 10^4$) and tuyere diameter ($0.238 < d_e < 0.476$ cm). The mass transfer parameter ($k_{SO_2}a$), which was assumed to be independent of the position along the jet trajectory, increased with Reynolds Number and the orifice diameter. Their analysis was based on steady state conditions where the fraction of gas absorbed was a function of the jet trajectory. The fraction of gas absorbed ranged from 0.59 to 0.91.

Rocha and Guedes de Carvalho [31] measured the gas-side mass transfer parameter with $NH_3-HCl$ system. $NH_3$ was top injected through a submerged lance at various depths. The absorption unit was divided into three sections: bubble formation, bubble rise and surface regions. The fraction of $NH_3$ absorbed was always above 0.92, even at the
minimum submersion (3 cm). Steady state conditions were assumed and the gas-side mass transfer parameters were obtained from a plot of the fraction that was not absorbed against the height of submersion by using an equation of the form:

$$\ln(1 - X) = \ln\left(1 - \frac{f_g}{Q}\right) - \left(\frac{k_g a}{Q}\right)y$$

(2.5)

$X$ is the fraction of gas absorbed and $f_g$ is the gas-side mass transfer coefficient for a forming bubble.

The correlation which was obtained showed that the mass transfer parameter was a function of the gas flow rate ($k_g a = 0.566Q^{0.9}$). The fraction of gas absorbed during bubble formation was reported as 0.9. The maximum $f_g$ value obtained using equation 2.5 and experimental data was 400 cm$^3$s$^{-1}$.

A $SO_2/N_2$ mixture was introduced into an agitated vessel of $NaOH$ solution by Chang and Rochelle [32] to measure the absorption rate of sulphur dioxide under steady state conditions. The rate was calculated from the liquid phase material balance. The mass transfer parameter $k_g a$, which was obtained from the rate, was found to be independent of the gas flow rate.

2.2.3 Mathematical modelling

In metallurgical processes, high temperatures are encountered and the actual chemical reactions are normally assumed to be fast. The rates may be controlled by transport processes either in the gas phase or the liquid phase and the reactions are said to be mass transfer limited. Depending on the nature of a process, mathematical expressions are derived to predict the parameters associated with that process. Experiments are usually conducted to confirm these predictions.
Below are examples of mathematical models developed by various investigators to predict some of the parameters associated with non-ferrous processes.

1. Mass transfer theory for a submerged jet was presented by Brimacombe et al. [30]. In this analysis, a reactant $A$, in the gas phase reacted at the gas-liquid interface with reactant $B$ in the liquid according to the equation below:

$$aA + bB \rightarrow \text{Products} \tag{2.6}$$

The equation below was used to predict which phase controls the rate of reaction, based on the assumption that the chemical reaction is instantaneous.

$$N = \frac{a(k_i a)C_i RT}{b(k_q a)P_g} \tag{2.7}$$

$P_g$ is the partial pressure of the soluble gas.

If $N > 1$, gas phase control prevails, while liquid transport is limiting for $N < 1$; the rate controlling step changes from one phase to the other when $N = 1$.

An experiment was performed by the same authors to determine the mass transfer parameter by injecting 1% $SO_2$ into $H_2O_2$ solution. Steady state conditions were assumed and the fraction of gas absorbed was found to be a function of the trajectory length. The mass transfer parameter, $k_{SO_2}a$, was calculated from the following relation:

$$-Q \ln \frac{P^{o}_{SO_2}}{P^{s}_{SO_2}} = k_{SO_2} aS_o \tag{2.8}$$

$P^{o}_{SO_2}, P^{s}_{SO_2}$ are partial pressures of $SO_2$ in the gas at the orifice and at the surface of the bath respectively. $S_o$ is the distance along the jet trajectory from orifice to the surface of the bath (calculated from the Themelis et al. [13] model).
The left hand-side of the above equation was plotted against $S_o$ and the slope of the straight line yielded $k_{SO_2}a$.

2. In the deoxidation of liquid copper by a submerged $CO$ jet Themelis and Schmidt [25] considered a differential element $dy$, in the vertical direction and equated the rate of decrease of $CO$ concentration ($C_{CO}$) to the rate of mass transfer across the gas film interface, i.e.,

$$-Qd(C_{CO}) = k_g a dy (C_{CO} - 0) \quad (2.9)$$

This equation was used to determine the gas phase mass transfer parameter assuming that $k_g a$ remains constant with distance from the orifice. The relation was also used to predict the $CO$ utilization efficiency.

Most of the models that predict the mass transfer rates with gas phase control are based on the tuyere submergence or the trajectory length of the jet. It is often desirable to understand what happens at the tuyere exit during bubble formation period.
3. In the model by Ashman et al. [10], the dynamics of bubble formation in a copper converter were examined. Mathematical equations were derived based on mass, heat and momentum balances on a gas bubble during the formation period. The resulting equations were solved with several assumptions in order to predict the effect of certain factors on bubble growth and detachment. The parameters that were considered are the gas flow rate, bath temperature, and tuyere diameter. The model also incorporates the effects of heat transfer to the bubble, chemical reaction between the bubble and the bath circulation velocity. These parameters were based on a standard set of operating conditions for an industrial practice as shown below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air flow rate per tuyere</td>
<td>$2.5 \times 10^5$ cm$^3$.s$^{-1}$</td>
</tr>
<tr>
<td>Inlet air temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Oxygen content of air</td>
<td>20.9%</td>
</tr>
<tr>
<td>Bath temperature</td>
<td>1200°C</td>
</tr>
<tr>
<td>Tuyere diameter</td>
<td>4 cm</td>
</tr>
<tr>
<td>Heat-transfer coefficient</td>
<td>0.029 W/cm$^2$.K</td>
</tr>
<tr>
<td>Mass-transfer coefficient</td>
<td>60 cm s$^{-1}$</td>
</tr>
</tbody>
</table>
The model was used to predict the concentration of $O_2$, temperature, volume and rise velocity of the bubble as a function of time. The mass transfer coefficient used in this model appeared to be quite arbitrary and it is likely that its value would change with injection conditions such as gas flow rate and tuyere diameter. During the bubble growth (0.1 s), the volume of the bubble increased to $4.4 \times 10^4$ cm$^3$ and a temperature of 312°C at a flow rate of about $3.33 \times 10^5$ cm$^3$s$^{-1}$. The partial pressure of $O_2$ dropped from 0.21 to 0.13. An increase in air flow rate from $1.67 \times 10^5$ to $3.33 \times 10^5$ cm$^3$s$^{-1}$ caused the bubble frequency to decrease from 12 to 9 s$^{-1}$ in contrast to the measurements of Bustos et al. [8]. Increasing the convective heat transfer coefficient caused the frequency to drop, with a corresponding increase in the bubble volume. An increase in the bath velocity from stagnant conditions to 240 cm s$^{-1}$ increases the bubble frequency from 3 to 15 s$^{-1}$. Although the model predicts that about 40% of the $O_2$ that enters the bubble is consumed during bubble formation, the model could not predict the total $O_2$ efficiency since the fraction of gas absorbed during bubble rise was not considered. Although these models provide some insight into converter operations, further work needs to be done in order to predict the entire fraction of gas that reacts during injection.

Table 2.1 is a summary of most of the mass transfer models discussed in the literature review.
### Table 2.1 Mass Transfer Models for Gas Injection Systems

<table>
<thead>
<tr>
<th>Injection System</th>
<th>Type of Injection</th>
<th>Parameter Studied</th>
<th>Rate Controlling Step</th>
<th>No. of Tuyeres</th>
<th>Tuyere Diameter (mm)</th>
<th>Gas Flow Rate (cm³/s)</th>
<th>N°</th>
<th>Nmo</th>
<th>Equations used</th>
<th>Purpose</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-Cu melt with 0.1-1%O</td>
<td>vertically upwards</td>
<td>( k_d ) (0.4-2.5 cm³/s)</td>
<td>gas phase</td>
<td>1-9.5</td>
<td>80-1670</td>
<td>1.4-417</td>
<td>1000-9100</td>
<td>( \ln(CO) = \frac{k_d}{y} ) ( \frac{Q}{V} )</td>
<td>Deoxidation of liquid copper</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CO-Cu melt with 0.05-0.005%O</td>
<td>vertically downwards</td>
<td>( k_d ) (0.4 cm/s) (max.)</td>
<td>liquid phase</td>
<td>1.6-4.8</td>
<td>0.4-15</td>
<td>1.5x10⁴-0.5</td>
<td>1-90</td>
<td>( \ln \left( \frac{C_2}{C_1} \right) = \frac{6k_dQ}{\delta V} )</td>
<td>Kinetics of deoxidation of molten copper</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>CO₂NaOH</td>
<td>vertical (torpedo and ladle shaped)</td>
<td>( k_d ) (0.043-0.076)</td>
<td>liquid phase</td>
<td>4</td>
<td>168-1325</td>
<td>1.6x10⁴ to 3.12x10⁴</td>
<td>2000-30000</td>
<td>Inhomogeneity of solute in a bath during gas injection</td>
<td>29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂NaOH</td>
<td>bottom</td>
<td>fraction absorbed</td>
<td>1</td>
<td>10</td>
<td>400-1300</td>
<td>0.47-5.0</td>
<td>7100-20000</td>
<td>Factors affecting rate of absorption between gas bubbles and liquid</td>
<td>33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂H₂O</td>
<td>bottom</td>
<td>( k_d ) (0.1-3x10⁻³)</td>
<td>liquid phase</td>
<td>6</td>
<td>16.7-166.7</td>
<td>0.011-1.1</td>
<td>426-4264</td>
<td>( \frac{dC}{dt} = k_dC - C )</td>
<td>Mass transfer in gas stirred systems</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>CO₂NaOH</td>
<td>top/ bottom side</td>
<td>( A_k = \beta Q^{0.38} )</td>
<td>liquid phase</td>
<td>1, 3, 5</td>
<td>1.3-5.5</td>
<td>1.67-83.3</td>
<td>0.09-229</td>
<td>( \ln \left( \frac{C_2}{C_1} \right) = \frac{A}{V} ) ( \frac{k_d}{V} )</td>
<td>Efficiency of gas-liquid reactions</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Air-Oil/H₂O with thymol</td>
<td>top/bottom</td>
<td>( k_d ) (1-60 cm³/s)</td>
<td>liquid phase</td>
<td>1-4</td>
<td>2, 4.8</td>
<td>16-167</td>
<td>( \frac{dC}{dt} = \frac{k_dA}{V} ) ( \frac{C-C_2}{C_1} )</td>
<td>Mass transfer between slag and steel</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar-metal/slag with Si</td>
<td>bottom</td>
<td>( k_d ) (cm/s) (0.01-0.05)</td>
<td>Si in the metal phase</td>
<td>1</td>
<td>1</td>
<td>3-100</td>
<td>0.54-414</td>
<td>( \ln \left( \frac{%Si}{%Si_2} \right) = k_w ) ( \frac{A}{V} ) ( \frac{t}{V} )</td>
<td>Mass transfer between slag and metal</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>Air H₂O/benzene with iodine</td>
<td>top/bottom</td>
<td>( k_d = 9.4Q^{0.38} ) (top) ( k_d = 18.2Q^{0.38} )</td>
<td>liquid phase</td>
<td>6</td>
<td>1</td>
<td>250, 417, 580</td>
<td>4.02 (avg.)</td>
<td>( V ) ( \frac{dC}{dt} = k_d(C - C) )</td>
<td>Q-BOP</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.1 continued.....

<table>
<thead>
<tr>
<th>Injection System</th>
<th>Type of Injection</th>
<th>Parameters Studied</th>
<th>Rate Controlling Step</th>
<th>No. of Tuyeres</th>
<th>Tuyere Diameter (mm)</th>
<th>Gas Flow Rate (cm³/s)</th>
<th>$N_p$</th>
<th>$N_a$</th>
<th>Equations used</th>
<th>Purpose</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ar-Ag$</td>
<td>top</td>
<td>$k_0$ (0-6cm³/s)</td>
<td>liquid phase</td>
<td>1</td>
<td>0.85, 2.2</td>
<td>1.8-18</td>
<td>.002-17.6</td>
<td>3-2500</td>
<td>$ln \left( \frac{C_0-C_s}{C_s-C_i} \right) = \frac{k_A}{V_s} t$</td>
<td>$O_2$ absorption in Ag. Deoxidation of Cu and Ag</td>
<td>19</td>
</tr>
<tr>
<td>$O_2-Ag$</td>
<td>bottom</td>
<td></td>
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<tr>
<td>$CO-Cu$</td>
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<tr>
<td>$SO_2-H_2O_2$</td>
<td>horizontal</td>
<td>$k_{so_2}$ (20-380cm³/s)</td>
<td>gas phase</td>
<td>1</td>
<td>2.38, 3.18, 4.76</td>
<td>125-3800</td>
<td>25-4000</td>
<td>$10^4-10^6$</td>
<td>$-Q \ln \left( \frac{P_i}{P_{so_2}} \right) = k_{so_2} S_o$</td>
<td>Copper Converting</td>
<td>30</td>
</tr>
<tr>
<td>$NH_3-HCl$</td>
<td>vertically downwards</td>
<td>$k_a = 10^4Q_s^2O_2^2$ (bubble rise)</td>
<td>gas phase</td>
<td>1</td>
<td>5-10</td>
<td>0-600</td>
<td>21.5 (max.)</td>
<td>8800 (max.)</td>
<td>$ln(1-X) = ln \left( 1 - \frac{f}{Q} \right) \frac{k_a}{Q}$</td>
<td>Mass transfer in Absorbers</td>
<td>31</td>
</tr>
</tbody>
</table>
CHAPTER 3

OBJECTIVES

It was concluded from the literature review that although mass transfer studies have been undertaken on side injection in non-ferrous systems, no thorough analysis of the copper/nickel converter has been done.

It was therefore important to consider the following objectives in this work.

1. To determine the mass transfer rates in a physical model similar to an industrial converter by considering the effect of variables such as bath depth, modified Froude number, gas flow rate and jet residence time.

2. To develop a model that will predict the fraction of gas absorbed and the subsequent efficiency in the system when the injection parameters are known.

3. To relate the findings of this investigation to experimental observations of other physical modelling studies and to copper converter practice.
CHAPTER 4

EXPERIMENTAL

4.1 Introduction.

Similarity criteria: Since the operating conditions and the physical properties of a model system differ from that of an industrial plant it is difficult to simulate an industrial process with a physical model. Similarity criteria are therefore used in the design of models for the study of an existing or a new process. The problem with physical modelling of a high temperature gas-liquid system lies in the number of physical parameters involved in the process. To attain fluid flow similitude between two gas-liquid systems, four conditions must be satisfied: dynamic, kinematic, geometric and thermal similarity. The use of these similarity criteria in the design and construction of a physical model of a copper converter have been discussed by Bustos [22]. His results have been employed in this work.

4.2 Gas injection system

The apparatus employed is illustrated in Figure 4.1. The equipment consisted of a converter shaped vessel which was a sectional, 1/4 scale Plexiglas model of a standard Peirce-Smith copper converter (diameter of 4 m and length 9 m) with five tuyeres. The converter-shaped vessel was constructed from a Plexiglas plate, 0.95 cm thick with internal diameter of 78 cm and length of 27 cm. An 8.5 by 30 cm opening was cut into the upper face of the model, where a fume hood was connected to exhaust excess $SO_2$. 


Figure 4.1  Schematic of the physical model.

1. Compressor
2. Globe Valve
3. Manometer
4. Plate Orifice
5. Sulphur Dioxide Gas
6. Rotameter
7. Tuyere Manifold
8. Tuyeres
9. Plexiglas Converter
10. Sampling Tube
11. Fume Hood
4.2.1 Tuyeres

The assembly consisted of a 5.8 x 7 x 24.8 cm Plexiglas block in which a 5 cm diameter hole was drilled. Into this hole was inserted a 33 cm long Plexiglas bar in which five threaded 7/8" NF holes, 5 cm apart had been drilled. The tuyeres of different diameters were made from 22.2 cm diameter brass rods in which a hole was drilled axially. The external surface was threaded with 7/8" NF thread to allow the tuyeres to be screwed into the tuyere assembly.

4.2.2 Gas delivery system.

4.2.2.1 Air

A Sutorbilt 4 MF air compressor, with a capacity of 0.08 m$^3$s$^{-1}$ at gauge pressure of 34.5 kPa (5 psig) was used as the air source. The gas flow rate which was measured by an orifice plate was controlled by a globe valve. The calibration of the flow rate is shown in Appendix A. A water manometer was used to record the air flow rate through the orifice. At the exit from the plate orifice the air entered a 51 cm long cylindrical copper manifold (7.5 cm in diameter) for distribution to the tuyeres.

4.2.2.2 Sulphur dioxide gas

The solute gas was delivered from a sulphur dioxide cylinder which was connected to a rotameter that measured the flow rate. The $SO_2$ flow rate was calibrated by using water displacement method as outlined in Appendix B. The $SO_2$ entered the main gas stream well before the manifold in order to ensure effective mixing with the air.
4.3 Method

SO₂/H₂O₂ system: It has been reported [10] that during converting the reactions that occur according to equations 1.1 and 1.3 are controlled by oxygen transport in the gas phase. A gas/liquid system that will produce an instantaneous, irreversible reaction with gas phase control was therefore required.

SO₂/H₂O₂ system, which has been used by Brimacombe et al. [30] for a similar purpose, was employed with an excess concentration of H₂O₂. This system has also been used by Chang and Rochelle [32] as a means of removing SO₂ from waste gases. Jean-Pierre Couilland et al. [38] used an aqueous solution of H₂O₂ to absorb SO₂ gas contained in a waste gas mixture. In this work a total absorption of the SO₂ gas was observed while the H₂O₂ concentration was in excess.

Other possible systems that could have been used are SO₂/NaOH, NH₃/H₂SO₄ or NH₃/HCl but these require high concentrations of NaOH and acids which would likely have ruined the tuyeres. CO₂/NaOH system could not be used since CO₂ does not react instantaneously with alkali solution but combines relatively slowly through an intermediate step which would have greatly complicated the analysis.

For the system selected, at the reaction plane, the concentration of SO₂ gas will be zero when the fraction of SO₂ in air is very low. The percentage of SO₂ in air varied from 0.03 to 1.0. The rate of reaction will then be equal to the rate at which the various components diffuse to the reaction plane. The actual kinetics of the chemical reaction is immaterial for such reaction [39]. The concentration profile may be represented by Figure 4.2, where the concentration of H₂O₂ is in excess. The reaction that occurs in the bath may be represented by the following equation:

\[ \text{SO}_2 + \text{H}_2\text{O}_2 = \text{H}_2\text{SO}_4 \]  

(4.1)
Figure 4.2 Interface concentration profile for the $SO_2/H_2O_2$ system.
Procedure: During injection, samples of solution were taken every two minutes. Each experiment lasted twenty minutes. The samples were then titrated against a standard solution of \(NaOH\) (1.0x10\(^{-5}\) to 1.3x10\(^{-4}\) mol cm\(^{-3}\)) to determine the concentration of sulphuric acid formed during injection in order to calculate the fraction of \(SO_2\) gas that reacted. Methyl red was used as the indicator. The titration reaction is represented below:

\[
H_2SO_4 + 2NaOH = Na_2SO_4 + H_2O
\]  

(4.2)

Since it was necessary to provide gas phase control in the system, four runs were done with different \(H_2O_2\) concentrations as indicated in Figure 4.3. The run with \(H_2O_2\) concentration of 9.7x10\(^{-5}\) mol cm\(^{-3}\) was selected for the subsequent experiments.

In one run, samples were taken from two different positions in the bath (bottom and central positions). The aim was to find out if the concentration of the acid formed varied from one position to another in the bath. This was also used to examine the nature of mixing in the bulk of the liquid phase. The results, as shown in Figure 4.4 indicate that there was virtually no difference in concentration at the two positions, and that mixing was effective. In all the experiments samples were taken from the central position.

It was important to determine how reproducible the experimental results were and therefore three experiments were run under the same conditions but on three different days. The results, as indicated in Figure 4.5 show good agreement.
Air flow rate = 15400 cm$^3$ s$^{-1}$
Percent filling = 30%

Figure 4.3 Concentration of sulphuric acid in the bath as a function of time at various hydrogen peroxide concentrations.
Figure 4.4  Concentration of sulphuric acid as a function of time at two sampling positions in the bath.
Figure 4.5  Plot showing the reproducibility of the experimental results.
4.4 Conditions for the Test

The tests were performed over a wide range of conditions to examine the influence of the following parameters on gas phase mass transfer in the system:

i. Tuyere diameter

ii. Tuyere submergence

iii. Gas flow rate

iv. Percent filling

v. Tuyere spacing

The range of variables are shown in Table 4.1.

4.5 Time exposure photographs

Time exposure photographs of the spout and the plume were taken under the conditions investigated to delineate the various regions of the gas-liquid zone including jet trajectory and spout height. One side of the vessel was lighted through translucent paper which acted as a diffuser. A Yashica camera set at an f stop of 22 and a shutter speed of 1/2 to 3/2 s was used with 32 ASA black and white film. Some instantaneous pictures were also taken.

4.6 Determination of the fraction of $SO_2$ absorbed ($X$).

A mole balance for sulphur dioxide gas was performed over the dispersed region (gas-liquid zone):

Rate at which $SO_2$ leaves the bath = Moles injected per unit time - Moles reacted per unit time

This is represented by the equation below:

$$(q_{SO_2})_f = q_{SO_2} - mV_b$$  (4.3)
Table 4.1. Range of Variables

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tuyere diameter, cm</td>
<td>1.6</td>
</tr>
<tr>
<td>Tuyere submergence, cm</td>
<td>0 to 13.1 (tuyere centre-line = 0)</td>
</tr>
<tr>
<td>Gas flow rate cm$^3$ s$^{-1}$</td>
<td>2x10$^3$ to 4.4x10$^4$</td>
</tr>
<tr>
<td>Modified Froude number</td>
<td>0.17 to 66</td>
</tr>
<tr>
<td>Number of tuyeres</td>
<td>1, 2, 3, 5</td>
</tr>
<tr>
<td>Tuyere spacing, cm</td>
<td>5, 10, 15</td>
</tr>
<tr>
<td>Percent filling, %</td>
<td>18.2 to 38.1</td>
</tr>
<tr>
<td>$SO_2$ flow rate, mol s$^{-1}$</td>
<td>6.54x10$^{-4}$ to 27.43x10$^{-4}$</td>
</tr>
</tbody>
</table>
where \( q_{SO_2} \): flow rate of \( SO_2 \) gas in moles per second.

\((q_{SO_2})_f\): moles of \( SO_2 \) that leaves the bath per second

\( m \): the slope of the \( H_2SO_4 \) versus injection time (\( t \)) plots (mol cm\(^3\)s\(^{-1}\)).

\( V_B \): bath volume (cm\(^3\))

For each experiment, the fraction of \( SO_2 \) absorbed was calculated as the ratio of the moles of \( SO_2 \) gas reacted to that injected, that is:

\[
X = \frac{m V_B}{q_{SO_2}}
\]  

(4.4)

where \( X \) is the fraction of gas absorbed.

### 4.7 Determination of the trajectory length (\( S_o \)) and the spout height (\( h \))

Figure 4.6 is a schematic diagram of the bath during gas injection. The diagram also shows the trajectory length and the spout height. The trajectory length up to the quiescent level was determined by solving equations (2.1) and (2.3). A fourth order Runge Kutta method for solving differential equations with double precision was used in this analysis. The procedure is summarized in Appendix C.

The spout height as indicated in Figure 4.6, was determined from the time-averaged photographs.
$X_p$: Horizontal distance determined from photographs as well as from the trajectory equation.

Figure 4.6  Diagram indicating some of the parameters employed in the analyses.
CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Observations of injection phenomena

A series of photographs showing the phenomena in the bath during gas injection are shown in Figure 5.1 and Figure 5.2. At lower modified Froude numbers, from visual and photographic examination, the gas entering the bath forms bubbles which break into smaller bubbles at a short distance from the tuyeres. As the modified Froude number is increased the phenomena at the tuyere exit becomes quite complicated. Thus the injection phenomena at the tuyere line is characterized by the generation of an unstable gas-filled packet or envelope which at certain instants may cover several of the tuyeres simultaneously indicating strong interaction between them. This unstable envelope breaks up to form a bubble dispersion zone directly above the tuyeres. In the bulk of liquid phase there was a clockwise recirculating flow which became violent as the gas flow rate increased. This can be observed in Figure 5.2 (b). The time averaged photographs shown in Figure 5.1 indicate a curve along the boundary of trajectory that separates the dispersed region from the rest of the bath. It was observed that at the prevailing modified Froude numbers \( N'_{Fr} < 14, \ d_o = 1.6 \text{ cm} \), the gas did not penetrate very far into the liquid before moving in the vertical direction. The surface of the bath formed a wave-like curvature with amplitude decreasing as the extreme end of the bath is approached (Figure 5.2 (a)).
Figure 5.1  Time-exposure photographs of the bath during gas injection
(a) $Q = 5000$ (b) $Q = 30900$ cm$^3$ s$^{-1}$; filling = 38.1%.
Figure 5.2  Photographs showing liquid circulation and slopping in the bath
(a) $t = 0.03$ s (b) $t = 0.017$ s; $Q = 9300$ cm$^3$ s$^{-1}$, filling = 35%
A spout with varying height was formed at all flow rates directly above the tuyeres. A horizontal distance $X_p$, as indicated in Figure 5.3 was measured from the time-averaged photographs and compared with the calculated values from the trajectory equation (2.2) to establish the validity of the use of the trajectory equation. To obtain $X_p$ from the trajectory equation, the following analyses based on Figure 5.3 were employed.

For an incremental value, $dx$, in the horizontal direction, $X_t$ and $X_p$ were calculated from the following equations:

$$X_t = \frac{d}{2} \cos(90 - \theta)$$

(5.1)

where $\tan(\theta) = \frac{dy}{dx}$

$$X_p = x + X_t$$

(5.2)

$Y_p$, which represents the vertical component of the jet trajectory, was used to calculate the length $y$ which corresponds to $X_p$, as indicated in equations 5.3 and 5.4.

$$Y_t = \frac{d}{2} \cos(\theta)$$

(5.3)

$$y = Y_p - Y_t$$

(5.4)

The values of $X_p$ and $y$ were computed for each incremental value of $x$, until a value of $y$ which represents the actual submergence used in the experiment was obtained. This final value of $X_p$ was then compared with that measured from the photographs. The jet cone angle was varied but those that gave comparable results were 20° and 30°. The results, as shown in Table 5.1, indicates that the differences between the values obtained from the two techniques are quite small, especially at higher percent filling. At lower percent filling the values predicted by using a cone angle of 30° seems to be quite good.
Figure 5.3  Diagram used in calculating $X_p$ from the trajectory equation.
Table 5.1  
Horizontal distance of jet as determined from photographs and trajectory equation (2.1) with a cone angle of 20° and 30°.

<table>
<thead>
<tr>
<th>$Q \times 10^3$ (cm$^3$s$^{-1}$)</th>
<th>35 percent filling</th>
<th>30 percent filling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_p$ (cm)</td>
<td>$X_p$ (cm)</td>
</tr>
<tr>
<td></td>
<td>Photograph</td>
<td>Trajectory equation</td>
</tr>
<tr>
<td></td>
<td>±0.5</td>
<td>20°</td>
</tr>
<tr>
<td>15.40</td>
<td>5.7</td>
<td>5.58</td>
</tr>
<tr>
<td>30.90</td>
<td>9.3</td>
<td>9.87</td>
</tr>
<tr>
<td>43.80</td>
<td>12.2</td>
<td>12.85</td>
</tr>
</tbody>
</table>


5.2 Trajectory length, spout height and spout area.

The results of these measurements for three different percent filling are shown in Tables 5.2, 5.3 and 5.4.

The spout height was found to increase with gas flow rate and tuyere submergence. As shown in Figure 5.4, at the same flow rate, the spout height increased with submergence. The vertical cross-sectional area of the spout, which was determined from the pictures, also increased with gas flow rate. At a flow rate of about $1.5 \times 10^4 \text{ cm}^3\text{s}^{-1}$, the rate of increase decreased (Figure 5.5). Sahajwalla [40] injected air through a nozzle located at the bottom of a physical model of a ladle furnace and measured the spout height and the potential energy in the spout as a function of flow rate. At an air flow rate of about $1350 \text{ cm}^3\text{s}^{-1}$, an abrupt increase in the slope of the curves were observed, which was quite different from the observations in this work.

In the present work, at lower flow rates the gas bubbles rise up close to the wall with little penetration. Thus the horizontal component of the gas jet is very small as compared to the vertical component. As the flow rate increases, the momentum of the jet also increases with a corresponding increase in the horizontal component. The horizontal component increases faster than the vertical component. The rate of increase in the vertical component starts to decrease at a flow rate of about $1.5 \times 10^4 \text{ cm}^3\text{s}^{-1}$. Thus the spout height tends to collapse as observed in Figure 5.4. In the work of Sahajwalla [40], as the gas flow rate increases, the spout height increases accordingly since there is no horizontal component. The abrupt decrease in the slope of the curve observed in the present work may be due to a "breakthrough effect" or gas channelling (accelerated escape of injected gas from the bath).
Table 5.2. (25% filling, tuyere submergence = 5.7 cm)

<table>
<thead>
<tr>
<th>Gas flow rate, $Q \times 10^3$ (cm$^3$s$^{-1}$)</th>
<th>Trajectory length, $S_0$ (cm)</th>
<th>Spout height, $h$ (cm)</th>
<th>$S_0 + h$ (cm)</th>
<th>Spout area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>5.9</td>
<td>2.2</td>
<td>8.1</td>
<td>27.3</td>
</tr>
<tr>
<td>6.80</td>
<td>6.0</td>
<td>2.5</td>
<td>8.5</td>
<td>41.6</td>
</tr>
<tr>
<td>8.73</td>
<td>6.2</td>
<td>3.1</td>
<td>9.3</td>
<td>55.9</td>
</tr>
<tr>
<td>9.30</td>
<td>6.3</td>
<td>3.4</td>
<td>9.7</td>
<td>62.4</td>
</tr>
<tr>
<td>10.92</td>
<td>6.5</td>
<td>4.2</td>
<td>10.7</td>
<td>82.6</td>
</tr>
<tr>
<td>15.40</td>
<td>6.9</td>
<td>5.7</td>
<td>12.6</td>
<td>97.5</td>
</tr>
<tr>
<td>30.90</td>
<td>8.7</td>
<td>7.6</td>
<td>16.3</td>
<td>116.1</td>
</tr>
<tr>
<td>43.80</td>
<td>11.0</td>
<td>9.6</td>
<td>20.6</td>
<td>161.4</td>
</tr>
</tbody>
</table>
Table 5.3.  
(30% filling, tuyere submergence = 8.6 cm)

<table>
<thead>
<tr>
<th>Gas flow rate, $Q \times 10^3$ (cm$^3$·s$^{-1}$)</th>
<th>Trajectory length, $S_o$ (cm)</th>
<th>Spout height, $h$ (cm)</th>
<th>$S_o + h$ (cm)</th>
<th>Spout area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>8.7</td>
<td>4.9</td>
<td>13.5</td>
<td>63.7</td>
</tr>
<tr>
<td>6.80</td>
<td>8.8</td>
<td>6.0</td>
<td>14.8</td>
<td>71.5</td>
</tr>
<tr>
<td>8.73</td>
<td>9.4</td>
<td>6.75</td>
<td>16.15</td>
<td>94.9</td>
</tr>
<tr>
<td>9.30</td>
<td>9.5</td>
<td>6.8</td>
<td>16.3</td>
<td>103.4</td>
</tr>
<tr>
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<td>9.9</td>
<td>7.2</td>
<td>16.8</td>
<td>117.0</td>
</tr>
<tr>
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<td>10.2</td>
<td>8.7</td>
<td>18.9</td>
<td>153.4</td>
</tr>
<tr>
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<td>12.9</td>
<td>10.3</td>
<td>23.2</td>
<td>202.6</td>
</tr>
<tr>
<td>43.80</td>
<td>14.1</td>
<td>14.1</td>
<td>28.2</td>
<td>254.3</td>
</tr>
</tbody>
</table>
Table 5.4.  \( (35\% \text{ filling, tuyere submergence} = 11.7 \text{ cm}) \)

<table>
<thead>
<tr>
<th>Gas flow rate, ( Q \times 10^3 ) (cm(^3)s(^{-1}))</th>
<th>Trajectory length, ( S_0 ) (cm)</th>
<th>Spout height, ( h ) (cm)</th>
<th>( S_0 + h ) (cm)</th>
<th>Spout area (cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>12.5</td>
<td>5.9</td>
<td>18.4</td>
<td>66.3</td>
</tr>
<tr>
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<td>12.7</td>
<td>7.0</td>
<td>19.7</td>
<td>85.8</td>
</tr>
<tr>
<td>8.73</td>
<td>12.9</td>
<td>8.0</td>
<td>20.9</td>
<td>105.0</td>
</tr>
<tr>
<td>9.30</td>
<td>13.1</td>
<td>8.4</td>
<td>21.5</td>
<td>109.8</td>
</tr>
<tr>
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<td>13.6</td>
<td>8.7</td>
<td>22.3</td>
<td>128.7</td>
</tr>
<tr>
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<td>14.5</td>
<td>9.1</td>
<td>23.6</td>
<td>200.0</td>
</tr>
<tr>
<td>30.90</td>
<td>16.8</td>
<td>14.9</td>
<td>31.7</td>
<td>308.1</td>
</tr>
<tr>
<td>43.80</td>
<td>17.7</td>
<td>17.1</td>
<td>34.8</td>
<td>430.0</td>
</tr>
</tbody>
</table>
Figure 5.4 Effect of gas flow rate on spout height at different percent fillings.
Figure 5.5  Effect of gas flow rate on the vertical cross-sectional area of the spout.
5.3 Determination of mass transfer parameter, $k_{SO_2}a$.

In order to determine $k_{SO_2}a$, a rate equation for the reaction within the jet and the spout was derived by considering a differential element $ds$ along the jet trajectory and equating the decrease of $SO_2$ concentration in the gas flow to the rate of mass transfer across the gas film interface. The equation, which is similar to that used by Themelis and Schmidt [25] and Brimacombe et al. [30] is given below:

$$-Qd[C_{SO_2}] = k_{SO_2}a ds ([C_{SO_2}]_o - [C_{SO_2}]_e)$$

(5.5)

where $[C_{SO_2}]_e = \text{equilibrium concentration at the reaction interface;}$

in this system $[C_{SO_2}]_e = 0$.

Rearranging equation (5.5) and integrating with the boundary conditions

$[C_{SO_2}] = [C_{SO_2}]_o, \ s = 0$ and $[C_{SO_2}] = [C_{SO_2}]_f, \ s = S_0 + h$ yields

$$\ln\left(\frac{[C_{SO_2}]_f}{[C_{SO_2}]_o}\right) = -\frac{k_{SO_2}a}{Q}(S_o + h)$$

(5.6)

According to equation (5.6), a plot of the left hand side against $S_o + h$ should yield a straight line of slope $-k_{SO_2}a/Q$ (assuming that $k_{SO_2}a$ does not change with position).

Since $[C_{SO_2}] / [C_{SO_2}]_o$ can be represented by $1-X$, equation (5.6) can be written as

$$\ln(1-X) = -\frac{k_{SO_2}a}{Q}(S_o + h)$$

(5.7)

where $X$ is the fraction of gas absorbed. Figure 5.6 is a plot resulting from equation (5.7) for three different flow rates. Analyses were done based on the trajectory length, $S_o$, alone but the correlation coefficients were not as good as those obtained using $(S_o + h)$. This may indicate that a significant amount of absorption occurs in the spout region.
Figure 5.6  Plot of ln(1-X) against (S_o + h) for different flow rates.
The mass transfer parameter, $k_{SO_2}a$, determined from the above relationship was plotted against the tuyere Reynolds Number, $N_{Re}$, as presented in Figure 5.7. Similar plots were obtained by [25] and [30]. As shown in the plot, $k_{SO_2}a$ values tend to increase with the tuyere Reynolds number.

5.4 Effect of tuyere submergence on the fraction of gas absorbed.

At a constant flow rate of $1.54 \times 10^4$ cm$^3$ s$^{-1}$, the tuyere submergence was varied from the tuyere centre-line (0 cm) to 13.1 cm. The fraction of gas absorbed increased with tuyere submergence as depicted in Figure 5.8. As the submergence is increased, the time spent by the gas in the bath also increases, resulting in an increase in the fraction of gas absorbed. The fraction of gas absorbed was very high at all the submergences studied. Even with the bath surface at the tuyere level the fraction of gas absorbed was quite substantial, about 45%.

5.5 Varying the number of tuyeres and tuyere spacing

The number of tuyeres were varied at a constant gas flow rate ($9.3 \times 10^3$ cm$^3$ s$^{-1}$) and a tuyere diameter of 1.6 cm. This is illustrated in Figure 5.9. There was a slight increase in the fraction of gas absorbed as the number of tuyeres decreased from three to one. With five tuyeres, the fraction of gas absorbed was slightly higher than that with three. The effect of tuyere spacing was observed when three tuyeres were used to conduct two experiments. In the first experiment, the three tuyeres were placed in the central positions of the tuyere assemblage with spacing of 5 cm. The tuyere spacing for the second experiment was 10 cm with two of the tuyeres close to the wall of the vessel. Though Figure 5.9 shows a slight decrease in the fraction of gas absorbed as the tuyere spacing is increased for the same number of tuyeres, the difference is not quite significant. Since
two of the tuyeres for the second experiment were close to the wall of the vessel, it is possible that the gas entering the bath through these tuyeres may have a reduced gas-liquid contact area.

5.6 Effect of gas flow rate

Detailed studies on the effect of gas flow rate on the fraction of gas absorbed were undertaken with 25%, 30% and 35% fillings. The gas issuing from the tuyeres did not form a continuous jet but a series of gas pulses which penetrated slightly in the horizontal direction before turning upward. The forward penetration increased slightly with the modified Froude number. The plume and the spout formed a dispersed region of gas bubbles and liquid solution which covered the region above the tuyeres. At constant $SO_2$ flow rate, increasing the air flow rate resulted in a decrease of the fraction of gas absorbed up to a certain flow rate and stayed almost constant at all higher levels (Figure 5.10).

The analyses based on the mass transfer parameter could not explain the observations in Figure 5.10. Equation (5.7) could not be used to explain some of the results that were obtained, and this may be due to the assumption that the mass transfer parameter does not change with position along the 'jet'. This assumption may be valid if the velocity of the jet were to remain constant throughout the system or the structure did not change. When the velocity profile ($u_v/u_e$) was calculated using the trajectory equation (2.2), a rapid drop was observed immediately in front of the tuyeres (Figure 5.11). (The constant, 2.8, that forms part of the horizontal axis appears during the derivation of the dimensionless horizontal length and represents the distance the jet cone extends into the tuyere). It was therefore decided to analyze the results in terms of the gas residence time.
Figure 5.7  Mass transfer parameter $k_{SO_2} a$, as function of tuyere Reynolds Number $N_{Re}$. 
Figure 5.8   Effect of tuyere submergence on the fraction of sulphur dioxide absorbed.
Figure 5.9 Effect of number of tuyeres and tuyere spacing on the fraction of sulphur dioxide absorbed.
Figure 5.10  Effect of gas flow rate on fraction of sulphur dioxide absorbed.
Figure 5.11 Plot of gas fraction and the velocity profile along the jet trajectory as a function of dimensionless horizontal distance.
6.1 Theoretical prediction of fraction of $SO_2$ absorbed ($X$) as a function of gas residence time.

This model presents a method of calculating the fraction of $SO_2$ absorbed within a bubble as it rises in the bath. The equations are based on the residence time of the bubble. The following assumptions were made:

1. The system is isothermal.
2. There is a constant flow of gas through the tuyeres.
3. The volume of the bubble does not change since the concentration of the reactive gas in the bubble is very small.
4. Reaction is irreversible and instantaneous.
5. The bubbles are spherical in shape and unaffected by adjacent bubbles.
6. The gas inside the bubble is back-mixed.

Figure 6.1 shows the gas bubble in contact with the hydrogen peroxide solution. The rate equation for the reaction between $SO_2$ in the bubble and the liquid can be derived by considering a differential time element $dt$, and equating the decrease in $SO_2$ concentration in the bubble to the rate of mass transfer to the gas-liquid interface.

Rate of $SO_2$ transfer to the gas-liquid interface is given by equation (6.1)
Figure 6.1  Gas bubble in contact with the liquid phase.
\[ n_{\text{SO}_2} = k_{\text{SO}_2} A \left( [C_{\text{SO}_2}] - [C_{\text{SO}_2}]_e \right) \]  

(6.1)

Rate of decrease of \( \text{SO}_2 \) in the bubble is represented by:

\[ n_{\text{SO}_2} = -V_b \frac{[dC_{\text{SO}_2}]}{dt} \]  

(6.2)

where \( V_b \) is the bubble volume. The other variables are as defined before.

Equating the two equations above gives

\[-V_b \frac{[dC_{\text{SO}_2}]}{dt} = k_{\text{SO}_2} A \left( [C_{\text{SO}_2}] - [C_{\text{SO}_2}]_e \right) \]  

(6.3)

Since the reaction is assumed to be instantaneous and irreversible, \( [C_{\text{SO}_2}]_e = 0 \).

Equation (6.3) was integrated with the following boundary conditions:

\([C_{\text{SO}_2}] = [C_{\text{SO}_2}]_o, \ t = 0 \) and \([C_{\text{SO}_2}] = [C_{\text{SO}_2}]_f, \ t = t_r\). This yields

\[ \ln \left( \frac{[C_{\text{SO}_2}]_f}{[C_{\text{SO}_2}]_o} \right) = -k_{\text{SO}_2} A \frac{t_r}{V_b} \]  

(6.4)

where \( t_r \) is the residence time of the bubble. This can also be expressed as

\[ \ln(1 - X) = -\frac{k_{\text{SO}_2} A}{V_b} t_r \]  

(6.5)

where \( X \) is the fraction of gas absorbed. Knowing the fraction of gas absorbed from experiments and the residence time, it is possible to determine the mass transfer parameter for each flow rate.

The above relationship indicates that the fraction of gas absorbed does not depend on the initial concentration of the gas. Some experiments were conducted by varying the flow rate of \( \text{SO}_2 \) gas. The results as indicated in Figure 6.2 shows that the fraction of gas absorbed remains almost constant with \( \text{SO}_2 \) flow rate.
Figure 6.2   Effect of sulphur dioxide flow rate on the fraction of gas absorbed.
6.2 Determination of 'bubble' residence time

An equation that expressed the residence time as a function of the horizontal distance of the jet was incorporated into the trajectory equation developed by Themelis et al.[13]. This was solved by using the same procedure for determining the trajectory length as outlined in Appendix C. The velocity of the jet and the gas fraction at any position were also determined. This procedure was used to calculate the residence time of the gas up to the quiescent level. It is necessary to note that residence time at a constant percent fill decreases with flow rate to an asymptote.

The residence time in the spout was obtained by dividing the spout height by the calculated velocity of the gas at the quiescent level based on the assumption that the gas travels with a constant velocity in the spout. The sum of the residence time up to the quiescent level and that of the spout gave the total residence time of the gas in the bath. The residence time was plotted against the gas flow rate as shown in Figure 6.3. This parallels the observed absorption of $SO_2$ in Figure 5.11. That is, the relationship between the fraction of gas absorbed and the gas flow rate indicated in Figure 5.11 is similar to that between the residence time and gas flow rate. At lower flow rates, the gas trajectory is almost vertical and the residence time tends to be inversely proportional to the flow rate. The residence time is expected to decrease at higher flow rates as well but at higher flow rates the gas penetrates further into the bath leading to a longer trajectory length which requires a longer residence time. The decrease in residence time with flow rate is balanced by a longer residence time required by longer trajectory length which leads to a constant residence time at high flow rates.
Figure 6.3  Effect of gas flow rate on the residence time.
6.3 Analysis based on the residence time

6.3.1 Relationship between the residence time and the fraction of gas absorbed

The plot in Figure 6.4 shows the fraction of gas that is not absorbed \((1-X)\) as a function of gas residence time for all the gas flow rates and percent fillings investigated in this work at a tuyere diameter of 1.6 cm (30 data points). Following equation 6.5, regression analysis of the plot resulted in an exponential curve that can be represented by the equation below:

\[
(1-X) = 0.255e^{-9.42r}
\]  

(6.6)

The correlation coefficient of equation 6.6 in logarithmic form is 0.974. This equation shows that the fraction of gas absorbed increases with gas residence time. Figure 5.11 indicates that for each percent filling the fraction of gas absorbed is maximum at lower flow rates which also correspond to maximum residence time.

The above relationship can be used to predict the fraction of gas absorbed if the gas residence time is known. Comparing equations (6.5) and (6.6), it can be seen that the pre-exponential constant has changed from 1 to 0.255. The value 0.255 indicates that when the residence time is zero part of the gas has been absorbed already. Further explanation of this result will be given in the next section.

The equation obtained from the experimental analysis was found to be similar to that for unsteady-state diffusion in a sphere as shown in Figure 6.5 [2]. As an example, the predictions of this analysis for flow rates ranging from 5000 to 30900 cm\(^3\) s\(^{-1}\) at 30 and 35 percent fillings are shown in Table 6.1.
Figure 6.4   Plot of (1-X) against gas residence time.
Figure 6.5  Unsteady state diffusion in a sphere [2].
Table 6.1. Comparison of measured and predicted $X$ values using diffusion analysis [2].

<table>
<thead>
<tr>
<th>X (Expt.)</th>
<th>X (Predicted)</th>
<th>X (Expt.)</th>
<th>X (Predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.982</td>
<td>1.000</td>
<td>0.940</td>
<td>0.970</td>
</tr>
<tr>
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<tr>
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<td>0.990</td>
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<td>0.945</td>
</tr>
<tr>
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<td>0.940</td>
</tr>
<tr>
<td>0.945</td>
<td>0.980</td>
<td>0.900</td>
<td>0.920</td>
</tr>
<tr>
<td>0.941</td>
<td>0.970</td>
<td>0.888</td>
<td>0.890</td>
</tr>
</tbody>
</table>
The parameter \( \sqrt{D_{SO_2-Air} t/R^2} \) was evaluated and used to determine \( X \) using Figure 6.5. \( D_{SO_2-Air} (0.139 \text{ cm}^2\text{s}^{-1}) \) is the diffusion coefficient of \( SO_2 \) in air which was calculated from the equation developed by Hirschefelder et al.[41], \( t \) is the gas rise time and \( R \) is the radius of gas bubble during its rise through the bath. \( R \) was determined from the correlation obtained by Liebson et al. [42] when they injected air into water at higher Reynolds numbers (\( N_{Re} > 10^4, R = 0.335N_{Re}^{0.5} \)). The average value of \( R \) was 0.225 cm. This approach was able to predict values close to those of the experimental results.

The actual equation for the diffusion curve shown in Figure 6.5 for a spherical bubble is given below [2]:

\[
X = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-D_{A-B} t/R^2}
\]  

(6.7)

The above equation can be simplified to the following form with little error, i.e,

\[
X = 1 - e^{-\lambda_r r}
\]  

(6.8)

where \( \lambda_r \) is a term that must be determined in order to represent equation (6.7) by equation (6.8). In this form it can easily be manipulated and compared to the earlier analysis.

In order to determine the form of \( \lambda_r \) various values of \( X \) were selected in Figure 6.5 and the corresponding values of \( \sqrt{D_{A-B} t/R^2} \) obtained. Different values of \( D_{A-B}/R^2 \) were chosen arbitrarily in order to calculate \( t \). The \( t \) values obtained this way were substituted in equation 6.8 and the corresponding \( \lambda_r \) were computed. A plot of \( \lambda_r \) values against \( D_{A-B}/R^2 \) yielded an equation of the form
\[ \lambda_r = 9.87D_{A-b}/R^2 \] (6.9)

with a correlation coefficient of 0.999. The constant 9.87 in equation 6.9 resulted whilst transforming equation 6.7 to equation 6.8. By comparing the equation obtained from experimental analysis (equation 6.6) to that of equation 6.8, the experimental one can be transformed to the following form:

\[ (1 - X) = 0.255e^{-\lambda_r t} \] (6.10)

where \( \lambda_r \) would equal 9.42. This equation can be used to predict the gas utilization efficiency of the system which is given by:

\[ \text{Gas Utilization Efficiency} = 100 \left( 1 - 0.255e^{-\lambda_r t} \right) \] (6.11)

### 6.3.2 Bubble formation analysis

From equation (6.10), at \( t_r = 0 \), \( 1 - X = 0.255 \), which indicates that the fraction of gas absorbed during formation is constant for the physical model at about 0.74. The bubble size and internal mixing tend to increase with gas flow rate. At higher flow rate mixing inside the bubble is vigorous but takes place over a large volume whilst at lower flow rate mixing is less vigorous but takes place over a smaller volume. This may be the reason why there is a constant value for gas absorption during bubble formation at different flow rates. Submergence may not have any effect on this constant value since the bubbles may have fully formed for all the submergences considered during this analysis. When calculating the gas residence time the bubble formation period was not considered. It was assumed that the bubble has already formed and that the time calculated was for bubble rise. During bubble formation, the absorption process is expected to be similar to that of bubble rise, that is, mass transfer inside a gas cavity. Assuming that the forming bubble is spherical, the mass transfer might be described by equation 6.10. A corresponding
equation can therefore be written for the reaction that occurs during this period i.e.,

\[ (1 - X_f) = e^{-\lambda_f t_f} \quad (6.12) \]

where \( X_f \) is the fraction of gas absorbed during formation, \( \lambda_f \) is a term similar to \( \lambda_c \) and \( t_f \) is the bubble formation time. \( \lambda_f \) is assumed to be a function of \( D_{SO_2-Air}/R_{av}^2 \), where \( R_{av} \) is the time-averaged bubble radius during formation. \( R_{av} \) was calculated from the procedure outlined below:

During bubble formation period, the volume of bubble is expected to change with time. Therefore at any time, \( t \), the volume of bubble is given by

\[ V_b = Qt \quad (6.13) \]

The instantaneous radius of bubble can be evaluated as

\[ R = \left( \frac{3Qt}{4\pi} \right)^{1/3} \quad (6.14) \]

The area of bubble can be represented by

\[ A = 4\pi \left( \frac{3Qt}{4\pi} \right)^{2/3} \quad (6.15) \]

The time-average area is therefore calculated as

\[ A_{av} = \frac{1}{\int_0^{t_f} A dt} \quad (6.16) \]

The time-average radius, \( R_{av} \), is determined from \( A_{av} \) as

\[ R_{av} = \sqrt{\frac{A_{av}}{4\pi}} \quad (6.17) \]
The bubble formation time, \( t_f \), in equation 6.16 was obtained from the results of Bustos work on bubble frequency analysis for similar range of gas flow rates in the same physical model [22]. \( \lambda_f \) was represented by the equation below:

\[
\lambda_f = KD_{SG_2-Air}/R_{av}^2
\]  

(6.18)

To determine \( K \), \( \lambda_f \) was calculated as

\[
\lambda_f = -\frac{1}{t_f} \ln(0.225)
\]  

(6.19)

The constant \( K \) was calculated for all the measured flow rates and was termed as the "enhancement factor" during bubble formation.

During gas injection, power for stirring in the bath and gas phase is supplied by the injected gas. At high velocities the kinetic energy of the injected gas will enhance mixing in the bath and the gas phase. If bubbles are formed during injection, some fraction of kinetic energy will show up inside the bubble as internal mixing and gas circulation. It has been reported by Humphrey et al. [43] that circulation inside a bubble which depends on the momentum of injected gas entering the bubble have an important effect on the rate of mass transfer in bubbles forming from tuyeres. The rate at which the gas jet transfers kinetic energy to the bubbles can be represented by equation 6.20.

\[
\varepsilon_p = \frac{1}{2.10^4 W A_s^2} \rho_s Q^3
\]  

(6.20)

\( \varepsilon_p \): Specific power density due to kinetic energy of the gas (watts/kg).

\( \rho_s \): Density of gas (g/cm\(^3\))

\( A_s \): Cross sectional area of the tuyere (cm\(^2\))

\( W \): Mass of the gas bubble (g)
The specific power density was computed for each gas flow rate employed in the physical model. Since the kinetic energy contributes to mixing at higher flow rates, the power density may therefore influence the enhancement factor during bubble formation. Figure 6.6 shows a plot of the enhancement factor against the specific power density. Equation 6.21 provides a good fit between the enhancement factor and the power density with a correlation coefficient of 0.99.

\[ K = 71e^{0.343} \]  

(6.21)

As will be seen in section 6.7 it was necessary to use such relationship to predict the enhancement factor for various industrial data. Though equation 6.21 indicates a good fit it predicts low \( K \) values for the industrial data. Equation 6.22 is another fit for Figure 6.6.

\[ K = 742.1 + 0.057e_p \]  

(6.22)

with a correlation coefficient of 0.96. Though equation 6.22 has a lower correlation coefficient it is able to predict good \( K \) values for the industrial data.

The above analyses based on bubble formation and bubble rise can be used to describe the absorption phenomena in the bath during injection. Thus equation 6.12 represents absorption during bubble formation period, whilst equation 6.10 describes that of bubble rise. This phenomena is illustrated in Figure 6.7.

The above results indicate that the fraction of gas absorbed during bubble formation forms a higher percent of the total fraction of gas absorbed. Other investigators have also observed similar behaviour. Clift et al. [21] have reported that a very significant fraction of the total mass transfer in industrial extraction or absorption operations occurs during bubble formation. Transfer tends to be particularly favourable because of the exposure of fresh surface with vigorous internal circulation during bubble formation period. Rocha and Carvalho [31] observed that the fraction of gas absorbed during bubble formation in
the NH₃/HCl system when gas phase control prevailed was 90%. The mathematical model presented by Ashman et al. [10] also predicted 40% of absorption during bubble formation in a copper converter. In most absorption analyses based on the jet model a lumped value for the mass transfer parameter, \( k_g a \) has been used to describe absorption from bubble formation to bubble rise. This seems to be inappropriate since it has been realized from the present work that the absorption rate during the bubble formation period differ from that during bubble rise where no internal circulation takes place inside the bubble.

6.4 Effect of injection parameters on the fraction of gas absorbed

Due to the low modified Froude numbers used, the gas did not penetrate very far into the liquid before turning in the vertical direction. This resulted in the formation of a dispersed region above the tuyeres and close to the wall of the vessel. This dispersed region which may form in an industrial converter is likely to contribute to tuyere erosion and refractory wear.

The spout height measured in this work increased with gas flow rate. It formed a significant percentage of the "total trajectory length", and in some of the measurements, the percentage was as high as 50%. When the spout height was included in the total trajectory length, a good correlation was obtained between the fraction of gas absorbed and the total trajectory length, indicating that part of the absorption also occurs in the spout. Previous analyses have neglected the spout height [30, 25]. As the spout height increases, splashing is also expected to increase accordingly. From visual observation, bath slopping, which is an unfavourable phenomena during injection, was also found to increase with spout height. The effect of tuyere submergence on fraction of gas absorbed as shown in Figure 5.8 is quite remarkable. As the submergence is increased from the
tuyere centre-line to 13.1 cm (18.2% to 38.1% filling), the fraction of gas absorbed is increased from 0.445 to about 0.99. It is clear that the fraction of gas absorbed when the submergence was at the tuyere center-line (0.445) is different from the extrapolated value during bubble formation (0.74). This is due to the fact that at the tuyere center-line, the bubbles are not fully formed and also a fraction of the injected gas escapes through the surface of the bath without complete reaction. The increase in absorption with tuyere submergence is related to the gas residence time in the bath. There is more contact between the solute gas and the liquid as tuyere submergence is increased.

6.5 Mass transfer parameter, \( k_{SO_2} a \)

The mass transfer parameter, \( k_{SO_2} a \), as defined in equation 5.3 and calculated from plots similar to Figure 5.5, varied from 1100 to 2560 cm\(^2\)s\(^{-1}\). The purpose was for comparison with the results of previous investigators. Brimacombe et al. [30], using a single tuyere obtained \( k_{SO_2} a \) values that ranged from about 20 to 380 cm\(^2\)s\(^{-1}\). In the work of Themelis and Schmidt [25], the mass transfer parameter, \( k_{CO} a \), ranged from 40 to 230 cm\(^2\)s\(^{-1}\) when CO gas was injected into liquid copper. In all the above results, \( k_g a \) increased with the tuyere Reynolds number, \( N_{Re} \). The effect of \( N_{Re} \) on \( k_g a \) is presented in Figure 6.8. The results of the present work are much higher than that of the other investigators due to the high flow rates used in this work.

6.6 Gas residence time and the fraction of gas absorbed

The analysis which involves the mass transfer parameter indicates that high mass transfer coefficients and interfacial areas are obtained as the gas flow rate is increased. This may therefore lead to higher absorption, contrary to the present results (Figure 5.10). It was observed in Figure 5.10 that as the gas flow rate is increased, the fraction of gas
absorbed decreases up to a certain value where it remains almost constant. However, the fraction of gas absorbed increases with the gas residence time as indicated in Figure 6.4. From Figure 6.3, as the flow rate is increased, the gas residence time also decreases and tends to flatten out as higher flow rates are approached. Therefore the fraction of gas absorbed is apparently dependent on the gas residence time only. The lower fraction of gas absorbed at higher flow rates are thus due to the shorter residence time of the gas. Since it was possible to express the results of the experiments in terms of the residence time with one equation, this provides an alternative route to evaluate the fraction of gas absorbed in an industrial converter by using the trajectory equation to determine the residence time as shown in the next section. This method of analysis may be simpler since it does not involve the mass transfer parameter, which is difficult to evaluate for an industrial practice.

6.7 Efficiency analysis on industrial data

Data on efficiency and other operating parameters for various copper converters are listed in Table 6.2 to Table 6.4.

The bubble rise time for each data point was calculated using the trajectory equations presented in Appendix C. Two different cone angles were used in the analysis. The first one was a cone angle of 155° which has been reported by Oryall and Brimaconbe [24]. The rise time obtained varied from 45 to 80 seconds which from the practical point is too long. With this cone angle the jet expands quickly leading to a sudden drop in the gas velocity which results in a longer rise time. The second was an angle of 20° which has been used by Themelis et al. [13]. The values were mostly less than a second which were quite reasonable. Since the values of the spout height for the industrial data have not been measured, they were not included in the determination of
the gas rise time. The two equations derived for absorption during bubble formation
period and bubble rise time were employed in calculating the oxygen utilization
efficiency during converting, that is,

\[
\text{Oxygen Utilization Efficiency} = 100 \left(1 - e^{-\lambda_f} e^{-\lambda_r}\right) \tag{6.23}
\]

where \(\lambda_r = 9.87 D_{O_2-Air}/R^2\), \(D_{O_2-Air}\) is the diffusion coefficient of oxygen in air and \(R\) is
the radius of bubble during its rise. \(R\) was calculated from equation 6.24 developed by
Sano and Mori [45] for bubble swarms when nitrogen was injected into mercury.

\[
R = 0.0455 (\sigma/\rho_f)^{0.5} u_s^{0.44} \tag{6.24}
\]

where \(\sigma\) is surface tension of liquid and \(u_s\) is the superficial gas velocity.

\(\lambda_f\) in equation 6.23 is given by the relation below:

\[
\lambda_f = KD_{O_2-Air}/R^2 \tag{6.25}
\]

The specific power density, \(\varepsilon_p\), was calculated for the industrial data and was used
to determine \(K\) by employing equation 6.22. Figure 6.9 shows \(K\) values of the physical
model and that of the Magma data. The bubble frequency for the industrial data was
assumed to be 10 s\(^{-1}\) based upon the work of Hoefele and Brimacombe [9].

Figure 6.10 shows a plot of the predicted efficiency against the actual efficiency for
the Magma data. The figure indicates a good agreement between the predicted and the
actual values. This indicates that the analysis based on residence time is very useful in
predicting efficiencies. The procedure based on the physical model where the bubble
formation period and the gas rise time are used to determine the efficiencies is
strengthened by this results. When the bubble frequency and the tuyere submergence are
known, it is possible to calculate the total residence time and the efficiency of gas
utilization. The slightly lower predicted values may be due to the fact that the spout
height was not included in the analysis. Figure 6.11 is a plot of the predicted efficiency against the actual efficiency for the Johnson's data on most plants around the world [12]. As can be observed in the figure, most of the predicted efficiencies are lower than the reported values. Bustos [22] observed that there was absolutely no correlation between the efficiencies of Johnson's industrial data and other parameters like tuyere diameter, tuyere submergence, bath depth and gas flow rate. It must be emphasized that in predicting the efficiencies, these parameters were employed in the calculation of the gas residence time.
Table 6.2. The Noranda process (1-ton pilot plant) [44]

(a) Conversion of white metal with slag.

<table>
<thead>
<tr>
<th>$N_{Re}$</th>
<th>Tuyere velocity (cm/s)</th>
<th>$N'_{Fr}$</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tuyere submergence</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>bath depth</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.6 cm</td>
</tr>
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<td>13880</td>
<td>94.1</td>
<td>51, 55, 70</td>
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<td>18510</td>
<td>167.3</td>
<td></td>
</tr>
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<td>20830</td>
<td>211.9</td>
<td></td>
</tr>
<tr>
<td>53000</td>
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<td>80, 88</td>
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</table>

(b) Conversion of white metal without slag.

<table>
<thead>
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<th>$N_{Re}$</th>
<th>Tuyere velocity (cm/s)</th>
<th>$N'_{Fr}$</th>
<th>Efficiency (%)</th>
</tr>
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<td></td>
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<td></td>
<td>Tuyere submergence</td>
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<td>bath depth</td>
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<tr>
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<td>3899.0</td>
<td></td>
</tr>
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</table>

Tuyere diameter, $d_o = 0.3175$ cm
Table 6.3. Copper converter operating practice from most plants around the world [12].

<table>
<thead>
<tr>
<th>Plant</th>
<th>Blowing rate (SCFM)</th>
<th>No. Of tuyeres</th>
<th>Tuyere diameter (in)</th>
<th>Efficiency (%)</th>
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</thead>
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<tr>
<td>Mount Isa</td>
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<td>54</td>
<td>2</td>
<td>85</td>
</tr>
<tr>
<td>Port Kembla</td>
<td>14000</td>
<td>30</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>Hoboken</td>
<td>16000</td>
<td>18</td>
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</tr>
<tr>
<td>Gaspe</td>
<td>22000</td>
<td>50</td>
<td>1.9</td>
<td>80</td>
</tr>
<tr>
<td>Hudson Bay</td>
<td>20000</td>
<td>38</td>
<td>2</td>
<td>76</td>
</tr>
<tr>
<td>Copper Cliff</td>
<td>18000</td>
<td>48</td>
<td>1.9</td>
<td>93</td>
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<tr>
<td>Noranda</td>
<td>23000</td>
<td>48</td>
<td>1.9</td>
<td>95</td>
</tr>
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<td>Chuquicamata</td>
<td>20000</td>
<td>52</td>
<td>2</td>
<td>98</td>
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<td>Caledones</td>
<td>18000</td>
<td>45</td>
<td>2</td>
<td>82</td>
</tr>
<tr>
<td>Ronnskar</td>
<td>16000</td>
<td>48</td>
<td>1.9</td>
<td>95</td>
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<td>Ghatisla</td>
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<td>83</td>
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<tr>
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<td>14000</td>
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<td>1.6</td>
<td>90</td>
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Table 6.4. Oxygen utilization data from Magma Copper Company (San Manuel) [12]

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<tr>
<th>Blows</th>
<th>Tuyere air flow rate (SCFM)</th>
<th>Tuyere velocity (ft/s)</th>
<th>$N'_{re}$</th>
<th>Efficiency (%)</th>
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</table>
Figure 6.6  Plot of enhancement, $K$, factor against the specific power density (The straight line represents equation 6.22).
Figure 6.7  Plot showing the proposed absorption phenomena during gas injection for the physical model.
Figure 6.8  Comparison of the mass transfer parameter, $k_g \alpha$, obtained from the present work with that of other investigators.
Figure 6.9  Prediction of the enhancement factor for the Magma data from the physical model.
Figure 6.10 Predicted efficiency versus actual efficiency for the Magma data in Table 6.4 (slag blow).
Figure 6.11  Predicted efficiency versus actual efficiency for Johnson’s industrial survey presented in Table 6.3.
CHAPTER 7

SUMMARY AND CONCLUSIONS

The fraction of gas absorbed during horizontal gas injection in a system similar to the copper converter has been determined by using $SO_2/H_2O_2$ system. It was observed that the gas entering the bath forms large bubbles which break into smaller bubbles a short distance from the tuyeres. For a constant $SO_2$ flow rate, the fraction of gas absorbed decreased with air flow rate up to a certain value and stayed almost constant at all higher flow rates. The spout height which increased with air flow rate formed a high percentage of the total trajectory length. It was included in the analysis since it is believed that part of the absorption takes place in the spout. The fraction of gas absorbed increased with tuyere submergence and percent filling from 0.445 to about 0.99. A substantial fraction of gas (0.445) was absorbed at zero submergence (tuyere center-line).

In analysing the results, the mass transfer parameter, $k_{SO_2}a$, was initially evaluated. It was found to increase with the tuyere Reynolds number and gas flow rate. Though the mass transfer parameter increased with gas flow rate, the fraction of gas absorbed did not increase with the gas flow rate. It was therefore not possible to use this parameter to explain the results. With this approach, the different zones that exist in the bath cannot be separated.

The second method for analysing the results was based on bubble formation and rise periods. The bubbles are formed at the tuyeres and a high percentage of the gas is
absorbed during bubble formation. This was attributed to the vigorous internal mixing and gas circulation inside the bubble. The absorption phenomena during bubble formation and bubble rise was considered to be an "enhanced" diffusion process. The gas rise time was calculated by applying the trajectory equations outlined in Appendix C. This analysis resulted in a single equation which could be used to determine the fraction of gas absorbed for a known gas flow rate and tuyere submergence. It was observed that the fraction of gas absorbed increased with the total gas residence time. Since there was a parallel between the effect of gas flow rate on residence time and effect of gas flow rate on the fraction of gas absorbed, it was possible to explain the effect of gas flow rate on the fraction of gas absorbed with this approach. From this method, it is possible to determine the utilization efficiency during gas injection when the gas residence time and the bubble formation time is known. Thus for a horizontal injection process similar to the converter, a substantial part of the reaction is likely to occur at the tuyere.

This method was extended to the analysis of industrial data for the comparison of measured and predicted oxygen utilization efficiencies. The predicted efficiencies for some cases were very good whilst in others, there appeared to be no direct correlation between the gas residence time and efficiency. For an industrial practice, the absorption rate and gas utilization efficiency for gas-metal reactions will depend on the gas flow rate, the bubble formation period, bubble rise time and the tuyere submergence.
REFERENCES


APPENDIX A

Calibration of Orifice Plate

The air flow rate was measured with a thin square-edged orifice plate. The diameter for the plate was made to be equal to that of the nominal internal diameter of the pipe in which it was installed. Two pressure taps were located one inch (flange taps) from the inlet and the outlet faces of the orifice plate. Tubes were connected to a water manometer from the taps which measured the differential and upstream pressures of the air passing through the orifice plate. The recommendations of A.S.M.E. report on fluid meters [46] were considered and related to the design of the orifice plate. The ratio between the orifice diameter and the inside diameter of the pipe, was designated as $\beta$. Two $\beta$ values were used. For relatively higher flow rates, $\beta$ was equal to 0.6 and for lower flow rates, $\beta$ was 0.4. The dimensions of the device are listed in Table A1.

<table>
<thead>
<tr>
<th>Inside diameter of pipe, $D_p$ (cm)</th>
<th>5.04</th>
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</thead>
<tbody>
<tr>
<td>Orifice diameter ($\beta = 0.4$), $D_\circ$ (cm)</td>
<td>2.02</td>
</tr>
<tr>
<td>Orifice diameter ($\beta = 0.6$), $D_\circ$ (cm)</td>
<td>3.02</td>
</tr>
<tr>
<td>Plate thickness (cm)</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The downstream face of the plate orifice was bevelled at 45° as recommended by the A.S.M.E. report [46]. The theoretical rate of flow of a compressible fluid is given by the equation below:
The actual rate of flow is given by

\[ M_{\text{actual}} = C_D M_{\text{ideal}} \]  

(A2)

The values for the discharge coefficient, \( C_D \), were obtained from the relationship given below, that is

\[ C_D = C_0 + \Delta C \left( \frac{10^4}{N_{Re}} \right)^a \]  

(A3)

where \( C_0 \) and \( \Delta C \) represent the discharge coefficient when the throat Reynolds number tends to infinity and the increase in the discharge for an arbitrary Reynolds number change from \( 10^4 \) to infinity respectively.

The exponent \( a = 1 \) for flange taps.

For \( \beta = 0.4 \), \( C_0 = 0.60139 \) and \( \Delta C = 0.01809 \)

For \( \beta = 0.6 \), \( C_0 = 0.60799 \) and \( \Delta C = 0.03920 \) [22]

Equation A1 was combined with the experimental measurements of the upstream and downstream pressures to determine the flow rate. The relationship between the air
flow rate $Q$, and the pressure drop across the orifice plate are shown in Figure A1 and Figure A2. It was possible to express the air flow rate as a function of the pressure drop in the form of exponential relation:

$$\beta = 0.4, \quad Q = 2780H^{0.48} \text{ with a correlation coefficient of 0.998.}$$

$$\beta = 0.6, \quad Q = 6670H^{0.48} \text{ with a correlation coefficient of 0.999.}$$

These equations were then used to calculate the air flow rate at any known pressure drop $H$. 
Figure A1  Air flow rate against differential pressure for the orifice plate with a diameter ratio of 0.4.
Figure A2  Air flow rate against differential pressure for the orifice plate with a diameter ratio of 0.6.
Calibration of Rotameter

The rotameter used in the experiments was No. 603 (Model 7600) by Matheson. The tube consisted of a cylindrical glass graduated from 0 to 150 mm and contained two floats - a stainless steel and a pyrex. The calibration was done with the two balls simultaneously by using a water displacement method. An inverted, graduated cylindrical container was filled with water which was covered with a little oil. The rotameter was then connected to the inverted cylinder as shown in Fig. B1. The $SO_2$ was supplied from a gas cylinder at a pressure of 65.5 kPa (9.5 psig). The positions of the balls as well as the volume of water displaced were recorded when the gas was turned on for a certain time interval. The flow rate of the gas at each position of the balls was calculated by dividing the volume of water displaced by the time of injection. The calculated flow rates were plotted against the various positions of the balls (Fig B2). When the $SO_2$ flow rates were correlated with the height of the balls the following equations resulted:

Steel ball  
\[ q_{SO_2} = 7.8 \times 10^{-5}H_b^{0.75} \]  
with a correlation coefficient of 0.999.

Pyrex ball  
\[ q_{SO_2} = 4.5 \times 10^{-5}H_b^{0.73} \]  
with a correlation coefficient of 0.994

Since the correlations obtained were very good, the above equations were used to determine the $SO_2$ flow rates in the experiments.
Figure B1  Schematic of sulphur dioxide calibration set-up.
Figure B2 Calibration curves for sulphur dioxide gas.
APPENDIX C

Determination of jet trajectory length ($S_o$) and residence time ($t$).

The jet trajectory length was calculated by using the theoretical expression derived by Themelis et al. [13] and Engh et al. [23]. The general equation relating the vertical and the horizontal components of the jet trajectory as indicated in Figure C1 is given below:

$$d^2y_r = 4N_{Fr}^{-1} \left[ \tan^2(\theta/2) \right] \left[ 1 + \left( \frac{dy_r}{dx_r} \right)^2 \right] x_r^2 C$$  (C1)

$x_r = x/d_o$ : dimensionless horizontal distance of jet.

$y_r = y/d_o$ : dimensionless vertical distance of jet.

$C$ : gas fraction in the jet.

$N_{Fr}$ : modified Froude number.

For an incremental distance, $dx$, in the horizontal direction, the incremental distance, $ds$, along the axis of the jet trajectory is given by

$$ds = \sec \theta dx$$  (C2)

Since $\sec \theta = \left[ 1 + (dy/dx)^2 \right]^{1/2}$, the equation for the trajectory length can be written as

$$\frac{ds}{dx} = \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{1/2}$$  (C3)

In dimensionless form, equation C3 can be represented by C4.

$$\frac{dS_r}{dx_r} = \left[ 1 + \left( \frac{dy_r}{dx_r} \right)^2 \right]^{1/2}$$  (C4)

where $S_r = s/d_o$ is the dimensionless distance along the axis of the jet trajectory.
The time it takes for a bubble to travel an incremental length $ds$, along the axis of the jet trajectory is given by equation C5.

$$\frac{dt}{ds} = \frac{ds}{u_x}$$  \hspace{1cm} (C5)

where $u_x$ is the velocity of the gas along the jet trajectory for that short distance. Equation C5 can be written as

$$\frac{dt}{ds} = \frac{1}{u_x}$$  \hspace{1cm} (C6)

Since $dt/ds = (dt/dx)(dx/ds)$, it implies that,

$$\frac{dt}{dx} = \frac{dt}{ds} \cdot \frac{ds}{dx}$$  \hspace{1cm} (C7)

Substituting C3 and C6 into C7 gives equation C8.

$$\frac{dt}{dx} = \frac{1}{u_x} \left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{1/2}$$  \hspace{1cm} (C8)

If $t_i$ is the time the gas travels the initial distance $d/o/2 \tan(\theta_c/2)$ before it enters the bath with the nominal tuyere velocity $u_o$, and $t$ is the time it takes to travel a distance $s$, along the jet trajectory, then $t$ can be written in dimensionless form as

$$t_r = t/t_i$$. Therefore $dt = t_i dt$,

In dimensionless form equation C8 can be written as

$$\frac{dt_r}{dx_r} = \frac{d_o}{t_i u_x} \left[ 1 + \left( \frac{dy_r}{dx_r} \right)^2 \right]^{1/2}$$  \hspace{1cm} (C9)

The velocity along the jet trajectory is represented by equation C10.
\[ u_s = \frac{u_0 d_0^2}{C d^2} \]  

where \( d \) is the diameter of the jet trajectory at any point as indicated in Figure C1.

\[ d = 2d_0 S_t \tan(\theta_c/2) \]  

The gas fraction in the jet is given by C12.

\[ C = \left(1 - \frac{P_t}{P_v}\right) + \left[\left(\frac{P_t}{P_v} - 1\right)^2 + 16 \frac{P_t}{P_v} S_t^2 \tan^2(\theta_c/2)\right]^{1/2} \]

Equations C1, C4 and C9 were solved numerically using a fourth order Runge-Kutta method to obtain the trajectory coordinates, the trajectory length and the residence time.
Figure C1  Schematic of a jet with a rising trajectory.