Gas Quality Control in Oxy-Fuel Technology for Carbon Capture and Storage: Scrubbing of CO₂ Prior to Compression

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By

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Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to the final version of my thesis being made available worldwide when deposited in the University’s Digital Repository, subject to the provision of the Copyright Act 1968.

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Abstract

Oxy-fuel combustion is an emerging technology intended to mitigate CO$_2$ emissions from power plants. Compared with other CO$_2$ capture technologies, non-CO$_2$ components in Oxy-fuel flue gas are highly concentrated, among which SO$_2$ is of concern. Sodium based quench units have been used in Oxy-fuel projects to directly cool the gas prior to compression and to also remove SO$_2$. However, the high concentration of CO$_2$ in the flue gas can interfere with the capture of SO$_2$.

This study considers the mechanisms by which SO$_2$ in CO$_2$ is absorbed by sodium containing liquids, using laboratory experimentation and experiments at the Callide Oxy-fuel Project. Conditions for the operation of Oxy-fuel scrubbers are recommended, including operational pH levels based on both the SO$_2$ absorption rate and the effective use of Na$^+$ in liquid.

In the laboratory evaluation, dynamic experiments were designed to elucidate the reaction mechanisms of SO$_2$ absorption from gas mixtures of SO$_2$/N$_2$, SO$_2$/CO$_2$, SO$_2$/N$_2$/O$_2$ and SO$_2$/CO$_2$/O$_2$ when introduced into solutions of NaOH, Na$_2$CO$_3$ and NaHCO$_3$ with known initial concentrations and pH. Correspondingly, the steady state experiments were designed to understand the absorption rate of SO$_2$ from gas mixtures of SO$_2$/CO$_2$ when introduced into sodium solutions with known mixtures of NaHCO$_3$ and NaHSO$_3$. The SO$_2$ concentration of the exhaust gas and the changes in the pH of the liquid were obtained during experiments in both dynamic and steady state processes. The changes in both parameters were recorded during experiments for dynamic processes; whereas both parameters were controlled to reach target values during experiments for steady state processes. Additionally, liquid samples were obtained on a regular basis for the analysis of HCO$_3^-$, S (IV) and S (VI) in both dynamic and steady state processes.

The absorption rate of SO$_2$ in dynamic experiments was found to be reduced in CO$_2$ in the gas phase controlled region primarily due to the reduced diffusivity of SO$_2$ in CO$_2$ and reduced kinematic viscosity of CO$_2$ compared to N$_2$. The dynamic absorption results for gas mixtures of SO$_2$/CO$_2$ demonstrated three pH regions of absorption rate behaviour and the absorption rate of SO$_2$ was correlated with speciation in these regions, as pH decreased during the experiments.

The steady state experiments of SO$_2$ absorption into mixtures of NaHCO$_3$ and NaHSO$_3$ investigated solution chemistry at various pH values, the significance of solution pH and the concentration of SO$_2$ on the absorption rate of SO$_2$. The absorption rates of SO$_2$ obtained in steady state experiments were predicted by the model based on the instantaneous reaction
assumption. The model generally overestimates the absorption rates of SO$_2$ at pH values below pH 6 indicating a kinetic limitation of SO$_2$ and water reaction at low pH values.

Experiments at the Callide Oxy-fuel Project yielded both gas and liquid analyses. Gas analysis for SO$_2$, CO$_2$, O$_2$, CO, NO and NO$_2$ were obtained at three positions: before, at the intermediate location of, and after the atmospheric scrubbing system. Liquid analysis for dissolved CO$_2$, HCO$_3^-$, S (IV) and S (VI) was obtained from two columns. From the gas analysis, it could be observed that the initial Quencher column captured most of the SO$_2$ (97%) and the subsequent low pressure (LP) scrubber captured a limited amount of the SO$_2$ (1%). Thus, from the liquid analysis, the amount of total sulfur measured in the liquid discharge from the Quencher is therefore 100 times higher than the total sulfur measured in the liquid obtained from the LP scrubber.

This work has implications for the absorption of SO$_2$ into sodium solutions in a spray tower. Simulations on the absorption rate of SO$_2$ into droplets were conducted based on the instantaneous reaction model and demonstrated the impacts of pH, SO$_2$ concentration, droplet size, droplet position and gas phase CO$_2$ on the absorption rate of SO$_2$. More importantly, simulations revealed the three pH regions for droplets in a spray tower. In region 1, the absorption rate of SO$_2$ is the highest; however, a large amount of CO$_2$ is absorbed instead of SO$_2$. In region 2, the absorption rate of SO$_2$ is moderate and Na$^+$ is effectively utilised. In region 3, the absorption rate of SO$_2$ is low and dissolved SO$_2$ is not fixed.

The operational pH of the sodium based quench unit is recommended to be in region 2, where a high absorption rate of SO$_2$ and low sodium losses are expected. The operational window is primarily related to the concentration of sodium solutions and the window narrows at high sodium solution concentrations (refer to dynamic experiments). The operational window is secondarily related to the concentration of SO$_2$ (refer to dynamic experiments). This operational pH region is also related to droplet position and droplet size (refer to droplet simulations).

The operational pH region 2 can be further divided into three sub regions. Three sub regions are defined as follows. Region 2-1 is the pH region where the absorption rates of SO$_2$ at intermediate to high concentrations from 600ppm to 1500ppm are moderate; region 2-2 is the pH region where the absorption rates of SO$_2$ at all concentrations are moderate; region 2-3 is the pH region of minimal Na$^+$ waste for CO$_2$ capture. In the region 2-1, the absorption rate is moderate, but there is a large amount of Na$^+$ consumed for CO$_2$ capture. In the region 2-2, there is moderate consumption of Na$^+$ for CO$_2$ capture. In the region 2-3, Na$^+$ consumed for CO$_2$ capture is minimized, but the effective ratio of Na$^+$ is still not 100%. The operational pH region graph can be used to optimise the operation of a spray tower.
This work also has implications for the disposal of waste liquids and use of reagents. The disposal of waste liquids should take into consideration the presence of HCO$_3^-$ in liquids and the effect on the final pH for extended exposure of liquid solutions to air. In the presence of HCO$_3^-$, the final pH reached will be pH around 8 and in the absence of HCO$_3^-$, the final pH will reach around 4. The cost of reagents should also be considered. Using soda ash instead of caustic soda and sodium bicarbonate could reduce costs by 58-79%.
Acknowledgement

It has been a long but a remarkable journey for me to come here and work for four years for my PhD. It has marked two things in my life. One is a good completion of the journey as a student; the other one is the opportunity to experience education in Australia. Within this journey, there are so many people who have given me help.

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Publications

Journals


Conference Papers

Liu, D., Y. Liu, and T. Wall, CO\textsubscript{2} quality control in oxy-fuel combustion: A dynamic study on the absorption of SO\textsubscript{2} into sodium based aqueous solutions relevant to scrubbing prior to CO\textsubscript{2} compression, The 37th International Technical Conference on Clean Coal & Fuel Systems, 3-7 June 2012, Clearwater, Florida, USA.


Liu, D., T. Wall, and Y. Liu, A dynamic study on the impacts of CO\textsubscript{2} on SO\textsubscript{2} absorption into sodium based aqueous solutions in an oxy-fuel scrubber. Australian Combustion Symposium, 6-8 November, 2013, Perth, WA, Australia.
Reports

Liu, Y., D. Liu, and T. Wall. Reporting of well stirred scrubber results: scrubbing of SO$_2$ and CO$_2$ by caustic solutions at atmospheric pressure. 


Nomenclature

$A$ interfacial area between gas and liquid, cm$^2$

$A^*$ interfacial concentration of dissolved gas A, mole/cm$^3$

$A^0$ average concentration of dissolved gas A in bulk liquid, mole/cm$^3$

$[A]_i$ concentration of A at the gas liquid interface, mole/L; Here, A refers to Na$^+$, H$^+$, OH$^-$, SO$_2^-$, HSO$_3^-$, SO$_3^{2-}$, CO$_2^-$, HCO$_3^-$, HCl, CO$_3^{2-}$ and total S

$[A]_0$ concentration of A in the bulk liquid, mole/L; Here, A refers to Na$^+$, H$^+$, OH$^-$, SO$_2^-$, HSO$_3^-$, SO$_3^{2-}$, SO$_4^{2-}$, CO$_2^-$, HCO$_3^-$, HCl, CO$_3^{2-}$ and total S

$[A]_{i0}$ concentration of A at the discrete point 0

$[A]_a$ concentration of A in the bulk liquid, mole/L; Here, A refers to Na$^+$, H$^+$, OH$^-$, SO$_2^-$, HSO$_3^-$, SO$_3^{2-}$, SO$_4^{2-}$, CO$_2^-$, HCO$_3^-$, HCl, CO$_3^{2-}$ and total S

$a$ interfacial area to volume ratio, cm$^{-1}$ or cm$^2$/L

$B^0$ concentration of B in bulk liquid, mole/cm$^3$

$C_D$ drag coefficient

$D$ diffusivity of gases in liquid, cm$^2$/s

$D_A$ diffusivity of gas A in liquid, cm$^2$/s; Here, A refers to Na$^+$, H$^+$, OH$^-$, SO$_2^-$, HSO$_3^-$, SO$_3^{2-}$, CO$_2^-$, HCO$_3^-$, and CO$_3^{2-}$

$D_G(T_1)$ diffusivity of a gas at a temperature $T_1$

$D_G(T_2)$ diffusivity of a gas at a temperature $T_2$

$D_L(T_1)$ diffusivity of a gas in liquid at a temperature $T_1$

$D_L(T_2)$ diffusivity of a gas in liquid at a temperature $T_2$

$D_{SO_2-H_2O}$ diffusivity of SO$_2$ in water, cm$^2$/s;

$D_{CO_2-H_2O}$ diffusivity of CO$_2$ in water, cm$^2$/s.

$d$ stirring diameter, cm

$d_p$ equivalent diameter of a droplet, cm

$E_i$ enhancement factor for instantaneous reactions

$E$ enhancement factor

$F_a$ faraday constant, 96488 C/g-equiv

$f$ oscillation frequency of a droplet, 1/s

$H_a$ Hatta number, $\sqrt{M}$

$H_e$ Henry’s constant, atm cm$^3$/mole for P/A$^*$ or mole/L-atm for A$^*$/P$^*$
h  solubility factor, L/mole
I  ionic strength of an electrolyte solution, g ion/L
K  equilibrium constant, mole/L
$K_G$  overall mass transfer coefficient based on gas side mole/cm$^2$ s atm
$K_L$  overall mass transfer coefficient based on liquid side, cm/s
$k_L$  liquid phase mass transfer coefficient, cm/s
$k_2$  kinetic constant for a second order reaction, L/mole·s or cm$^3$/mole·s
$k_G$  gas side mass transfer coefficient, mole/cm$^2$·s·atm or m/s;
$k_{L,a}$  liquid side overall volumetric mass transfer coefficient, h$^{-1}$ or s$^{-1}$
$k_{l,SO_2-H_2O}$  liquid side mass transfer coefficient for SO$_2$ in water, cm/s
$k_{l,CO_2-H_2O}$  liquid side mass transfer coefficient for CO$_2$ in water, cm/s
$k_1$  forward rate constant for SO$_2$ reaction with H$_2$O , s$^{-1}$
$k_{-1}$  backward rate constant for SO$_2$ reaction with H$_2$O, L/mole·s
$M$  $M = \frac{D_A k_2 B_0}{k_2^2}$  for a 2nd order (1,1 order) reaction
the molecular weight of the solvent, 18g/mole
MFC  Mass Flow Controller
m  mass of a droplet, $(\pi / 6)d_p^3 \rho_p \cdot g$
total flow rate of gases passing through CPU, kmol/h
$m_L$  flow rate of discharged liquid, L/h
$m_{A,in}$  mole flow rate of A at the inlet of a scrubber, kmole/h; Here, A refers to SO$_3$, SO$_2$, NO$_2$ and H$_2$O in the gas phase.
$m_{A,out}$  mole flow rate of A at the outlet of a scrubber, kmole/h;
$m_B$  mole flow rate of B in the liquid phase with B representing NaOH, Na$_2$SO$_4$, NaHSO$_3$ and NaNO$_3$.
N  absorption rate, mole/cm$^2$·s or mole/L·s
n  rotation speed, s$^{-1}$ or rpm
P$_i$  concentration of a gas above interface, atm
P  concentration of gases, ppm or atm
$P_{in}$  concentration of gases at the inlet of WSR, atm
$P_{out}$  concentration of gases at the outlet of WSR, atm
R  gas constant, 8.315J/K g-mol
$\bar{R}$  average gas absorption rate, mole/cm$^2$s
\( \text{Re}_* \) interfacial Reynolds number, \( \text{Re}_* = \frac{u_* d}{v} \)

\( \text{Re} \) gas Reynolds number, \( \text{Re} = \frac{\rho_G d_p u_p}{\mu_G} \)

Reynolds number, \( \text{Re} = \frac{d^2 \times n \times \rho_G}{\mu_G} \)

\( R_s \) gas side resistance ratio

\( R_L \) liquid side resistance ratio

\( \gamma_i \) activity coefficient of ion i

\( \text{Sc} \) liquid Schmidt number, \( \text{Sc} = \frac{V_L}{D} \)

\( \text{Sc} \) gas Schmidt number, \( \text{Sc} = \frac{\mu_G}{D_G \rho_G} \)

\( \text{Sh} \) liquid Sherwood number \( \text{Sh} = \frac{d_p k_L}{D} \)

\( \text{Sh} \) gas Sherwood number \( \text{Sh} = \frac{k_g d}{D_g} \)

\( S(\text{IV}) \) the total concentration of \( \text{HSO}_4^- \), \( \text{SO}_3^{2-} \) and \( \text{SO}_2 \)

\( T \) temperature, K

\( T_c \) Celsius temperature

\( t \) time, min

\( u_* \) interfacial velocity, cm/s

\( u_p \) droplet velocity, cm/s

\( u_\infty \) droplet terminal velocity, cm/s

\( \Delta V_{HCl} \) HCl added between two valley points for dpH/dt, mL

\( V \) molecular volume of the solute at the normal boiling point with 34cm\(^3\)/mole for CO\(_2\) and 44.8cm\(^3\)/mole for SO\(_2\)

flow rate of inlet gas stream, L/min or L/s

\( V_L \) kinematic viscosity of liquid, cm\(^2\)/s

\( V_G \) kinematic viscosity of gases, cm\(^2\)/s

\( V \) initial volume of the solution mixture, mL

\( X_{\text{SO}_2} \) mole fraction of \( \text{SO}_2 \), %

\( X_{\text{CO}_2} \) mole fraction of \( \text{CO}_2 \), %
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\chi$</td>
<td>an association factor, 2.6 for water</td>
</tr>
<tr>
<td>$z_j$</td>
<td>the valency</td>
</tr>
<tr>
<td>$z^0$</td>
<td>equivalent ion conductance, cm$^2$/mole/ohm</td>
</tr>
<tr>
<td>$\theta$</td>
<td>exposure time at the interface, s</td>
</tr>
<tr>
<td>$\delta$</td>
<td>thickness of the liquid film, cm</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>surface tension of liquid, dyne/cm</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>density of the droplet liquid, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_G$</td>
<td>gas density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>liquid density, g/cm$^3$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>distortion parameter, $\varepsilon = 0$ or $\varepsilon = 3$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>a constant, here $\omega = 1$.</td>
</tr>
<tr>
<td>$\nu_m$</td>
<td>molar volume of gas mixture, taken as 22.4L/mole at the standard temperature and pressure</td>
</tr>
<tr>
<td>$\mu_G$</td>
<td>gas viscosity, g/cm s</td>
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