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# Simultaneous removal of CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub> using single stage absorption column

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## ABSTRACT

Capturing flue gases often require multiple stages of scrubbing, increasing the capital and operating costs. So far, no attempt has been made to study the absorption characteristics of all the three gases (NO, SO<sub>2</sub> and CO<sub>2</sub>) in a single stage absorption unit at alkaline pH conditions. We have attempted to capture all the three gases with a single wet scrubbing column. The absorption of all three gases with sodium carbonate solution promoted with oxidizers was investigated in a tall absorption column. The absorbance was found to be 100% for CO<sub>2</sub>, 30% for NO and 95% for SO<sub>2</sub> respectively. The capture efficiency of sodium carbonate solution was increased by 40% for CO<sub>2</sub> loading, with the addition of oxidizer. Absorption kinetics and reaction pathways of all the three gases were discussed individually in detail.

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## Introduction

Capturing CO<sub>2</sub>, NO<sub>x</sub> and SO<sub>x</sub> together has never been done before, but capturing them separately incurs a huge plant capital and operational costs. Capturing flue gases from power plants is a multi-step process. This is usually done in three stages: (1) Selective catalytic reduction (SCR) for the removal of NO<sub>x</sub>. (2) Flue gas desulfurization (FGD) for the capture of SO<sub>2</sub> and (3) CO<sub>2</sub> capture (Astarita et al., 1981; Barzagli et al., 2017; Deshwal et al., 2008a; Kawatra et al., 2011; Kawatra, 2020; Xie et al., 2015; Yang et al., 2008). Capturing CO<sub>2</sub> separately from other gases requires an additional 20% footprint for each capture unit operation (Berghout et al., 2015), making it difficult for power plants with space constraints and also increasing the capital and operational costs for each individual unit operation. If these processes could be combined into single capture column, the problems mentioned above could be resolved. In a recent study conducted by Li et al. (2016) at 650-

MW coal fired power plant, concluded that total cost of flue gas removal could be reduced by 13.1% by just integrating FGD and CO<sub>2</sub> capture into single stage. If all the three processes can be combined into one step with the help of non-toxic reagents like sodium carbonate, further cost savings could be achieved, making flue gas removal more economical and environment friendly.

To date, minimal attempts have been made to combine all three processes into a single step. Santos et al. (2016) have previously proposed a method to capture all the three gases through chemical absorption with ozone as the oxidizing agent, but they never reported any absorption efficiencies for all the three gases. Few authors have previously studied the combined removal of NO<sub>x</sub> and SO<sub>x</sub> under acidic pH conditions (Chu et al., 2001; Deshwal and Hyung-Keun, 2009; Kouravand et al., 2018; Krzyzyska and Hutson, 2012; Santos et al., 2016). Deshwal and Hyung-Keun (2009) were able to achieve SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies of 100% and 70% respectively with the help of aqueous euechlorine, which is a significant removal, but only the addition of oxidant is not adequate for a system of flue gas with variable concentrations of CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>.

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Other researchers (Chu et al., 2001; Guo et al., 2010; Kouravand et al., 2018) have tried similar approaches for capturing  $\text{NO}_x$  and  $\text{SO}_x$  in a combined system before scrubbing  $\text{CO}_2$ . In the current paper, we have investigated sodium carbonate solution enhanced with rate promoters ( $\text{H}_2\text{O}_2/\text{NaOCl}$ ) for the absorption of the three gases  $\text{CO}_2$ ,  $\text{NO}$  and  $\text{SO}_2$  in a single scrubbing column. This will eliminate the need for additional capital and operating costs.

The choice of oxidant is based on the fact that  $\text{H}_2\text{O}_2$  is a very strong oxidizer and has high nucleophilic reactivity for carbonyl carbon (Edwards and Pearson, 1962).  $\text{H}_2\text{O}_2$  is a very strong oxidizing agent but is also more expensive than other oxidizers, hence substituting it with  $\text{NaOCl}$  will reduce the reagent cost slightly. The reason for selecting  $\text{NaOCl}$  instead of  $\text{NaClO}_2$  and  $\text{NaClO}_3$  is based on the previous observations that  $\text{ClO}^-$  acts as a better nucleophile compared to the other two species (Guo et al., 2010; Wei et al., 2009).

The use of low-cost reagents like sodium carbonate is of great importance for reducing the cost of post combustion  $\text{CO}_2$  capture. The carbonate solution also has other advantages such as low toxicity compared to amines, less solvent loss and no thermal degradation (Barzagli et al., 2017). The absorption of carbon dioxide by carbonate solutions is limited at ambient temperature and is governed solely by the rate of physical mass transfer (Astarita et al., 1981; Barzagli et al., 2017). Even at temperatures above 378 K, the reactions are not fast enough to make the absorption instantaneous (Hu et al., 2016). Therefore, the use of rate-enhancing agents such as piperazine (PZ), monoethanolamine (MEA), boric acid, carbonic anhydrase (CA), polyglycol ethers, hydrogen peroxide and sodium hypochlorite are of great importance (Ramazani et al., 2016; Valluri and Kawatra, 2021). But some of these rate-enhancing agents have disadvantages, for example PZ and MEA are volatile and would make heat stable salts in presence of  $\text{SO}_2$ . Enzymatic catalysts like carbonic anhydrase are very sensitive to presence of  $\text{NO}_x$  and  $\text{SO}_x$  (Sahoo et al., 2018), hence not recommended in a combined capture system. Carbonic anhydrase also loses catalytic activity at temperatures greater than 314 K (Floyd et al., 2013).

The composition of  $\text{NO}_x$  in flue gas is mostly 90% inactive  $\text{NO}$  and the remainder is  $\text{NO}_2$  (Deshwal et al., 2008b).  $\text{NO}$  is problematic because it is very inactive in the absorbent solution and has very low water solubility.  $\text{NO}_2$  dissolves readily in water, but  $\text{NO}$  must be oxidized to  $\text{NO}_2$  in order to implement the wet scrubbing process (Baveja et al., 1979). In the past, oxidative absorbents such as chlorine dioxide, boric acid,  $\text{KMnO}_4$ , hydrogen peroxide and several others have been tested in aqueous solutions (Baveja et al., 1979; Chu et al., 2001; Chang and Rochelle, 1981; Deshwal et al., 2008a; Deshwal and Kundu, 2015; Ghosh et al., 2009; Guo et al., 2010; Myers Jr and Overcamp, 2002; Phan et al., 2014; Wei et al., 2009), to study the absorption kinetics of  $\text{NO}$  in water. Reagents such as sodium hypochlorite have good oxidizing properties at lower pH, which are converted to good absorbing properties at higher pH, due to high nucleophilic reactivities achieved under alkaline conditions. The majority of recent research has attempted to use these oxidizers alone at acidic pH in aqueous solutions where the reaction rate is higher at acidic pH and the rate progressively decreases at higher pH levels (Baveja et al., 1979; Deshwal et al., 2008b; Deshwal and Kundu, 2015).

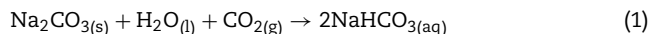
In this study we have examined the absorption efficiency of sodium carbonate solution promoted with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and sodium hypochlorite ( $\text{NaOCl}$ ) on  $\text{NO}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  under alkaline conditions, at pH ranging from 11 to 12. This process with respect to  $\text{NO}$  is similar to selective non-catalytic reduction (SNCR) at ambient temperature. While sodium carbonate displays slower absorption kinetics for  $\text{CO}_2$  absorption compared to traditional amines, adding these rate promoters can enhance the absorption kinetics greatly making its absorption performance surpass that of amines.  $\text{SO}_2$  is instantaneously absorbed into aqueous sodium carbonate solutions. The uniqueness of our work is that we have examined the absorption of all three gases with a single stage of sodium carbonate absorption supported with  $\text{H}_2\text{O}_2/\text{NaOCl}$ . We also analyzed the absorption kinetics of both  $\text{H}_2\text{O}_2$  and  $\text{NaOCl}$  with all three gasses individually. The primary focus of our paper is to explore the absorption characteristics of combined gas system and how the absorption kinetics of each individual gas is affected by the rate promoter.

### Theory

Low cost reagents like sodium carbonate are gaining attention in post combustion  $\text{CO}_2$  capture. The reason for adding rate promoters is because the sodium carbonate has slower kinetics compared to amines and other alkali absorbents like  $\text{NaOH}$ . There are several rate promoters that will increase the kinetics as well as aid in using low concentrations of the reagents by achieving high mass transfer ratio in less time.

#### $\text{CO}_2$ absorption in aqueous solution

When  $\text{CO}_2$  is introduced in aqueous solution, the first step is hydration where gas phase  $\text{CO}_2$  is transferred to liquid phase  $\text{CO}_2$  then it forms carbonic acid, which reacts with sodium carbonate to form sodium bicarbonate. The reaction between sodium carbonate and  $\text{CO}_2$  are shown in Eqs. (1)–(4) below:



Eq. (1) represents the overall reaction between aqueous sodium carbonate and  $\text{CO}_2$  forming sodium bicarbonate, with the following reaction Intermediates.



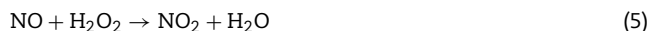
Step (3) is the slowest and rate determining step, so adding a rate promoter would enhance the reaction kinetics and improve the absorption efficiency of carbonate solution. All previous research was unquestionably in agreement that the rate of reaction of  $\text{CO}_2$  in alkaline solutions follow first order kinetics (Astarita et al., 1981; Hu et al., 2016; Xie et al., 2015). Enhancing the reaction kinetics for  $\text{CO}_2$  absorption in carbonate solution can be done with the help of several rate promoters like vanadate, hypochlorite, piperazine etc. Boric acid, arsenous acid and MEA are among other homogeneous rate enhancing reagents explored previously (Ghosh et al., 2009; Hu et al., 2016; Phan et al., 2014). Arsenous acid gave very good

performance for increasing absorption kinetics of CO<sub>2</sub> hydration, but due to toxic and carcinogenic effects of arsenite it is no longer explored as a rate promoter for CO<sub>2</sub> capture. Other reagents like piperazine and boric acid does not have oxidative properties like hypochlorite to enhance NO absorption.

#### NO absorption in aqueous solution

NO has very low solubility in water (0.0056 mg/100 mL at 293 K). While NO<sub>2</sub> hydrolyses readily in water, if NO can be oxidized to NO<sub>2</sub> then it can be easily absorbed into aqueous solutions. There are several oxidizing agents like H<sub>2</sub>O<sub>2</sub>, NaClO, NaClO<sub>2</sub>, KMnO<sub>4</sub> etc. Other previously studied absorbents include Na<sub>2</sub>SO<sub>3</sub>, FeSO<sub>4</sub>, EDTA and urea. In most of these studies the reaction was found to follow first order kinetics. Many of these reagents have disadvantages pertaining to mixed gas system. For example, the use of potassium permanganate was known to produce brown precipitates, due to the formation of manganese dioxide (Chu et al., 2001). These precipitates clog the packing material in the scrubbing column, and also causes problems in the pumping system. Urea is certainly out of question because of its dormant activity for CO<sub>2</sub> and SO<sub>2</sub>.

NO absorption in aqueous solutions after being oxidized to NO<sub>2</sub> is shown below and the overall reaction of NO and H<sub>2</sub>O<sub>2</sub> in the aqueous phase is as follows:



Reactions scheme with NaOCl is as follows:



#### SO<sub>2</sub> absorption in aqueous solution:

Although different methods have been proposed over the years, wet scrubbing process is the commonly used process for removing SO<sub>2</sub> from flue gas. The following reaction pathways should be considered when sulfur dioxide is introduced into aqueous solutions of NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub>:



Reaction (10) has very fast kinetics, with a forward rate constant of  $3.40 \times 10^6 \text{ sec}^{-1}$  (Chang and Rochelle, 1981). Reactions (11) and (12) can be regarded as almost instantaneous, since they are based on simple transfer of H<sup>+</sup>. The mass transfer coefficient of SO<sub>2</sub> in aqueous solutions is correlated to temperature and with increase in temperature it increases, at the operating temperature of around 318 K the mass transfer coefficient of SO<sub>2</sub> in aqueous solution is two times higher than at 293 K (Chang and Rochelle, 1981). Owing to high mass transfer

coefficient and instantaneous reactions, SO<sub>2</sub> can be absorbed readily into sodium carbonate solution with or without the presence of rate enhancing reagents.

#### Kinetic measurements

Dankwerts surface renewal model is the widely accepted kinetic model for the absorption of gases in liquid solutions (Danckwerts and Lannus, 1970). Based on the Danckwerts film renewal model the rate of absorption of NO is given by:

$$N_{\text{NO}} = \frac{k_g}{RT} (p_{\text{NO}} - p_{\text{NO}_i}) \quad (14)$$

where R is universal gas constant,  $k_g$  (m/sec) is gas phase mass transfer coefficient, T is the temperature and  $p_{\text{NO}}$  is partial pressure of NO.  $p_{\text{NO}_i}$  is the interfacial pressure of NO in the aqueous solution that can be obtained by Henry's law:

$$p_{\text{NO}_i} = H_{\text{NO}} c_{\text{NO}} \quad (15)$$

where,  $H_{\text{NO}}$  (Pa·m<sup>3</sup>/mol) is Henry's law constant,  $c_{\text{NO}}$  (mol/m<sup>3</sup>) is the concentration of NO at the gas-NaClO/Na<sub>2</sub>CO<sub>3</sub> solution interface, and is directly associated with the solution's ionic strength. This relationship is shown in the following expression (Onda et al., 1970a):

$$\log \left( \frac{c_{\text{NO}}}{c_{\text{NO}_w}} \right) = -(k_{\text{NaClO}} I_{\text{NaClO}} + k_{\text{OH}^-} I_{\text{OH}^-}) \quad (16)$$

where  $k_{\text{NaClO}}$  and  $k_{\text{OH}^-}$  are the salting-out parameters of NaClO and OH<sup>-</sup>, respectively, I (mol/L) is the ionic strength of the solution, and  $c_{\text{NO}_w}$  (mol/m<sup>3</sup>) is the interfacial concentration of NO at the gas-water interface. The salting out parameters of an electrolyte solution can be obtained by adding their anion, cation and gas contribution numbers respectively, as shown in the equation below.

$$k = x_a + x_c + x_g \quad (17)$$

where  $x_a$  is contribution by anions,  $x_c$  is contribution by cations and  $x_g$  by gas, respectively in mol/L.

The individual x values can be identified from previous literature (Onda et al., 1970b; Sada et al., 1978, 1986). But,  $x_{\text{ClO}^-}$  is not mentioned in the literature so it is presumed that the role of hypochlorite ion is the same as that of chlorite i.e.  $x_{\text{ClO}^-} = 0.3497$  (Chang and Rochelle, 1981).

The rate at which CO<sub>2</sub> is absorbed into carbonate solutions can be described as follows:

$$R_{\text{CO}_2} = \frac{dc}{dt} = k_L a (c^* - c) = k [\text{CO}_2] \quad (18)$$

where  $k_L$  is mass transfer coefficient, a is gas-liquid interfacial area,  $c^*$  is CO<sub>2</sub> concentration at saturation i.e. the solubility of CO<sub>2</sub>, c is bulk concentration of CO<sub>2</sub> dissolved, and k is the rate constant assuming first order kinetics (Danckwerts and Lannus, 1970).

The percentage concentration of gases going in and out of the scrubbing column is continuously monitored by the gas analyzer. The absorption efficiency (AE, %) or percentage of absorbance (PA, %) for each gas (CO<sub>2</sub>, NO and SO<sub>2</sub>) is calculated individually by the following equation:

$$\text{AE} = \text{PA} = \frac{Y_{\text{in}} - Y_{\text{out}}}{Y_{\text{in}}} \times 100\% \quad (19)$$

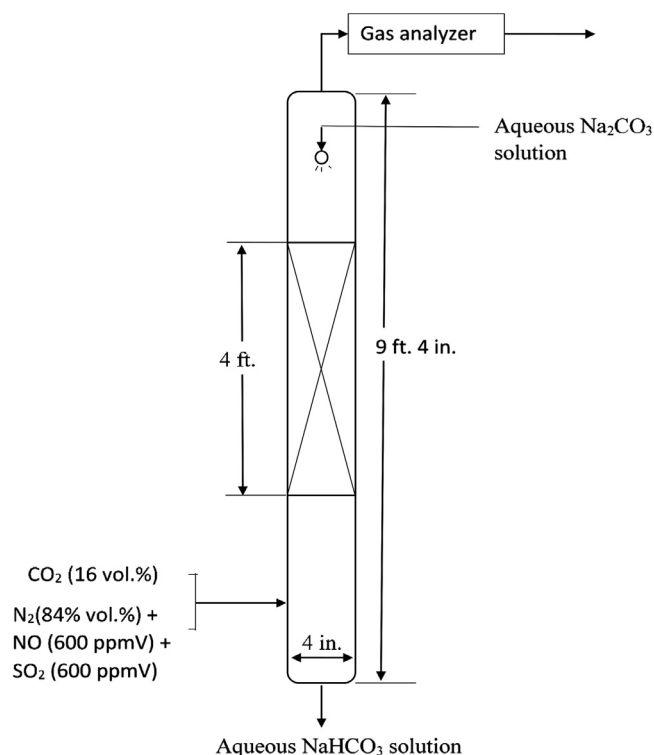


Fig. 1 – Dimensions of pilot scale CO<sub>2</sub> capture column.

where  $Y_{in}$  is number of moles of the gas going into the scrubbing column and  $Y_{out}$  is number of moles of the gas coming out of the scrubbing column.

## 1. Materials and methods

### 1.1. Column properties

A CO<sub>2</sub> capture column has been designed and built as shown in Fig. 1. The packing material used to fill the scrubber column is polypropylene pall rings 0.5 inch × 0.5 inch. The height of a packed bed scrubbing column ( $Z$ ) is calculated using the contact tower design equation (Eq. (20)).  $G_s$  represents molar flow of solute-free gas per cross-sectional area of the column.  $a$  is the interfacial area available for mass transport.  $K_y$  accounts for overall gas phase mass transfer coefficient.  $Y$  is the fraction of moles of gas phase solute per moles of solute-free gas, and  $Y^*$  denotes the gas phase mole fraction in equilibrium with the liquid phase. The denominator of the integral represents the driving force for mass transfer and is integrated over the condition of the gas phase from the top to the bottom of the column (Geankoplis, 1997).

$$Z = \frac{G_s}{K_y} \times \frac{Y_1}{a} \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*} \quad (20)$$

Given that the interfacial area  $a$  is in the denominator of the design equation, it is advantageous to have a large amount of interfacial area within the scrubbing column. This is the reason most scrubbing columns are filled with packing.

### 1.2. Experimental

The pilot scale scrubbing column shown in Fig. 1 was used to conduct experiments on absorbance of CO<sub>2</sub>, NO and SO<sub>2</sub> with sodium carbonate solution in the presence of oxidizer. The top portion of the capture column (7 ft) is made of transparent poly acrylic plastic, and the bottom portion is made of steel to ensure robustness. The packed-bed absorption column (Packing: Polypropylene pall rings 0.5 inch × 0.5 inch) in Fig. 1 is used as a counter-current absorption column, where flue gas enters from the bottom of the column, then the gas flows up through the packed bed where it contacts the scrubbing liquid. The scrubbing liquid removes the contaminant and exits out the bottom. Clean gas then exits out from top of the column. In order to simulate the flue gas, a gaseous mixture containing 16 vol.% CO<sub>2</sub>, 600 ppmV NO, 600 ppmV SO<sub>2</sub> and remainder nitrogen was continuously fed into the bottom of the scrubbing column with the help of a gas diffuser.

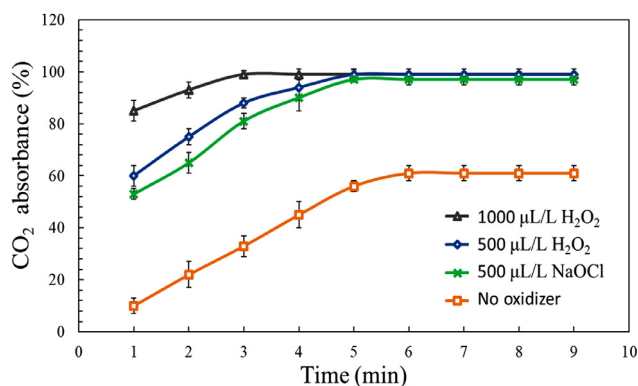
For the absorption experiments, Na<sub>2</sub>CO<sub>3</sub> (99.8% pure) was obtained from Genesis Alkali, H<sub>2</sub>O<sub>2</sub> and NaOCl (reagent grade) were obtained from Sigma-Aldrich. All gas cylinders were obtained from Air-products. Gas flow rate was maintained at 21 L/min. Gas flow rates were measured with gas flow meters (Model 7520, OMEGA, USA) equipped with gas controllers (Model 316, McMaster-Carr, USA). Separate flow meters were installed for the mixed gases to measure the volumetric flow and to control the percentage of CO<sub>2</sub> in the gas stream. We suggest using stainless steel for the column and piping to avoid any equipment corrosion due to caustic pH.

The composition of gases exiting out from the top of the column is measured with a Nova Multi-Gas Analyzer fitted with nondispersive infrared (NDIR) and electrochemical sensors, calibrated with CO<sub>2</sub>/NO/SO<sub>2</sub>/N<sub>2</sub> reference gases. A range of concentrations for the oxidizer (H<sub>2</sub>O<sub>2</sub>/NaOCl) starting from 500 to 1500 μL/L were tested. The pH measurements were taken at regular intervals with Oakton hand held pH meter. The percentage of absorbance data was continuously recorded by the data logger connected to the gas analyzer. After each experiment the data logger was connected to the computer and the graph generated from it was integrated to calculate the total moles of CO<sub>2</sub> absorbed per minute for measuring the kinetic data. The accuracy of the data was ensured by repeating these experiments in triplicates. The operating conditions of the column shown in Fig. 1 were: liquid/gas-ratio 4.3, scrubbing solution flowrate 2 gallons/min, gas inlet temperature 313 K, scrubbing solution inlet temperature 318 K, gas composition 16 vol.% CO<sub>2</sub>, 600 ppmV NO, 600 ppmV SO<sub>2</sub>, and rest N<sub>2</sub>.

## 2. Results and discussion

Along with replacing three stage flue gas capture with single stage, we also aim at reducing the reagent costs by switching from amines to dilute sodium carbonate solution enhanced with rate promoters. CO<sub>2</sub> capture with dilute sodium carbonate solution was first patented by Kawatra et al. (2011). Later there were several improvements made for this process, most recently Barzaghi et al. (2017) have tested dilute sodium carbonate solution for CO<sub>2</sub> capture and were able to achieve 80% CO<sub>2</sub> absorption efficiency. We have tested various concentra-





**Fig. 2 – Absorbance of CO<sub>2</sub> vs time in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution + varying H<sub>2</sub>O<sub>2</sub>/NaOCl at 318 K with the error bars representing standard error (n = 3).**

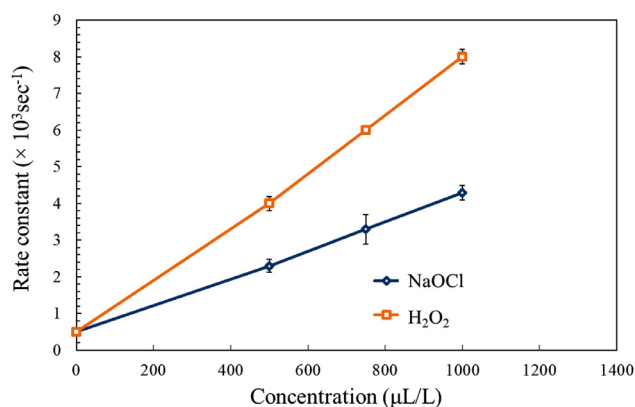
tions of sodium carbonate solution ranging from 0.1 to 0.4 mol/L with the addition of H<sub>2</sub>O<sub>2</sub>/NaOCl ranging from 500 to 1000 μL/L. Starting with a 50-gallon solution, the scrubbing solution was recycled through the scrubber for a total duration of 87 min before it is completely loaded with bicarbonate. After performing several experiments, the optimum concentration was noted to be 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution + 750 μL/L H<sub>2</sub>O<sub>2</sub>, achieving 99.7% absorbance for CO<sub>2</sub>, 31% for NO and 97% for SO<sub>2</sub> respectively. The experimental uncertainty is calculated and the error bars are plotted within the 95% confidence interval. These results, along with reaction kinetics are discussed in detail in further sections.

### 2.1. CO<sub>2</sub> absorption

Curves in Fig. 2 show the absorbance of CO<sub>2</sub> in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution enhanced with H<sub>2</sub>O<sub>2</sub>/NaOCl. The percentage of absorbance (%) reached 80% in the first 1 min with the addition of H<sub>2</sub>O<sub>2</sub>/NaOCl and finally reaching 99.7% in 5 min after reaching steady state. The absorbance with Na<sub>2</sub>CO<sub>3</sub> solution alone is only 61%, but after the addition of oxidizer the absorbance increased to 100%. The rate of absorption increased with increasing H<sub>2</sub>O<sub>2</sub> and NaOCl concentrations. Initially with increase in concentration of the oxidizer from 500 to 1000 μL/L showed increased kinetics of CO<sub>2</sub> absorption, but after reaching steady state in 5 min, 750 and 1000 μL/L oxidizer gave almost similar absorption efficiency, with 1000 μL/L concentration showing 0.2% higher absorption than 750 μL/L. While performing the experiment we have observed effervescence in the liquid solution, though barely visible. In addition to potential chemical kinetic effects, the effervescence is believed to have led to additional bubble formation, increasing the mass transfer area of contact between the gas and the liquid. In Eq. (18) increasing the interfacial area (*a*) will increase the absorption rate.

#### CO<sub>2</sub> absorption kinetics

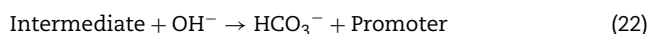
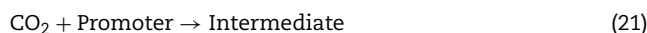
The reaction intermediates for CO<sub>2</sub> absorption into sodium carbonate solution are given below (Steps (2)–(4)). Step (3) is the rate determining step, since the rest of the reactions are almost instantaneous.



**Fig. 3 – Rate constant vs concentration for CO<sub>2</sub> absorption in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>/NaOCl solution with the error bars representing standard error (n = 3).**

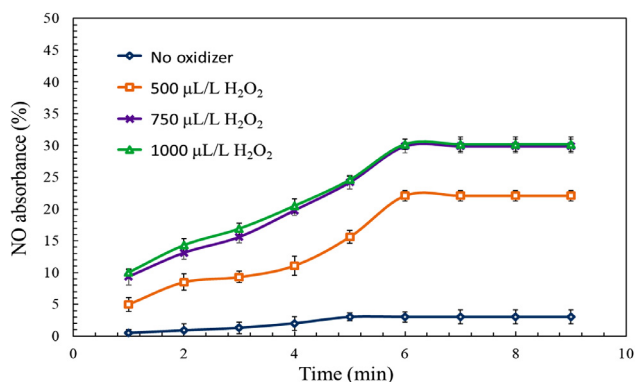


Adding a small amount of rate promoters can enhance the CO<sub>2</sub> absorption capacity of carbonate solutions significantly at lower temperatures (Chu et al., 2001; Dennard and Williams, 1966; Edwards and Pearson, 1962; Jencks and Carriolo, 1960; Wise and Houghton, 1968). Since CO<sub>2</sub> is a Lewis acid, Lewis bases with O<sup>−</sup> or OH groups can act as rate promoters. The enhanced CO<sub>2</sub> absorption rate in Fig. 2 can be attributed to the rate enhancing activity of H<sub>2</sub>O<sub>2</sub>/NaOCl on the equilibrium rate determining reaction (3). The time required to establish equilibrium was reduced after the addition of H<sub>2</sub>O<sub>2</sub>/NaOCl. Whether its organic or inorganic additive, both follow a mechanism suggested by Astarita et al. (1981) as shown below:

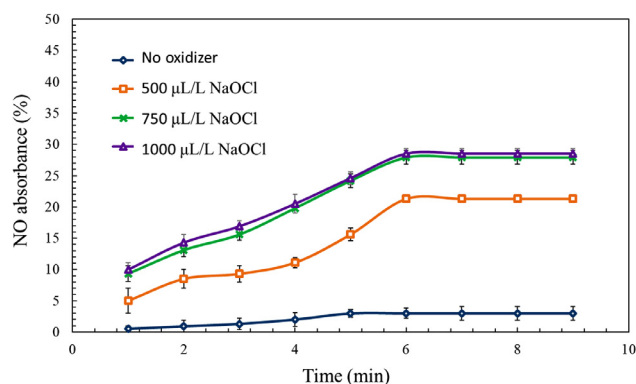


For the homogeneous activity with H<sub>2</sub>O<sub>2</sub> and NaOCl, carbonyl carbon acts as the substrate. This reaction scheme can be seen below. In case of homogeneous catalysis in the presence of H<sub>2</sub>O<sub>2</sub>/NaOCl, step (22) follows step (21) immediately. In a broader view these additives do not undergo any major chemical transformation, but rather increase the overall mass transfer phenomenon. Reaction mechanisms can be seen in Schemes 1 and 2 based on the alpha effect theory proposed by Edwards and Pearson (1962).

Rate of reaction was estimated by calculating the slope of number of moles of CO<sub>2</sub> absorbed vs time. Number of moles absorbed was calculated by performing trapezoidal integration on the graph generated by the data logger on the gas analyzer. The rate constant shown in Fig. 3 was estimated from the rate of reaction in Eq. (18) assuming first order kinetics. The observed rate constant represents that H<sub>2</sub>O<sub>2</sub> is



**Fig. 4 – Absorbance of NO vs time in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution + H<sub>2</sub>O<sub>2</sub> at 318 K with the error bars representing standard error ( $n = 3$ ).**



**Fig. 5 – Absorbance of NO vs time in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution + NaOCl at 318 K with the error bars representing standard error ( $n = 3$ ).**

a better homogeneous catalyst than NaOCl. In alkaline pH conditions certain nucleophiles like peroxide and hypochlorite react very rapidly. This nucleophilic substitution is described as “Alpha Effect” by Edwards and Pearson (1962). In this scenario, carbonyl carbon acts as the substrate, so under these conditions the rate constants (rate constants of H<sub>2</sub>O<sub>2</sub>  $2 \times 10^5 \text{ mol}^{-1} \cdot \text{min}^{-1}$ , rate constants of NaOCl  $1.6 \times 10^3 \text{ mol}^{-1} \cdot \text{min}^{-1}$  (Edwards and Pearson, 1962; Jencks and Carriolo, 1960)) clearly indicate that peroxide has higher absorption kinetics compared to hypochlorite. We have observed a similar trend in case of CO<sub>2</sub> absorption kinetics with H<sub>2</sub>O<sub>2</sub> and NaOCl as shown in Fig. 3, which supports the theory. Few researchers have previously tested ClO<sub>2</sub> and ClO<sub>3</sub> as well (Guo et al., 2010; Wei et al., 2009). From our point of view, the reason that ClO functions as a stronger nucleophile compared to ClO<sub>2</sub> and ClO<sub>3</sub> is because the exchange of electrons on the oxygen atom in ClO<sub>*n*</sub> occurs at a faster rate with a lower *n* value and thus Cl having a lower oxidation state. Overall H<sub>2</sub>O<sub>2</sub> gave slightly better kinetics compared to NaOCl as shown in Fig. 3.

Although we have not performed liquid analysis, depending on the molar ratio of CO<sub>2</sub> converted and sodium carbonate used (0.2 mol/L), the fraction of sodium carbonate converted to bicarbonate is only 0.45 without the rate promoter, due to slower absorption kinetics. The conversion increased to 82% after the addition of the rate promoter. Which corresponds to an increase of 45.1%.

## 2.2. NO absorption

Figs. 4 and 5 show the percentage absorbance of NO in 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution enhanced with 500 to 1500 μL/L H<sub>2</sub>O<sub>2</sub> and NaOCl respectively. The percentage of absorbance reached 10% in the first 1 min with the addition of H<sub>2</sub>O<sub>2</sub> and finally reaching 31% in 5 min after reaching steady state. The percentage of absorbance reached 9% in the first 1 min with the addition of NaOCl and finally reaching 29% in 5 min after reaching steady state. The NO absorption efficiency increased with increase in oxidizer concentration from 500 to 750 μL/L. The absorbance increased only slightly thereafter and reached an asymptotic maximum at 1000 μL/L concentration. It can be noted that H<sub>2</sub>O<sub>2</sub> gave better absorption kinetics than NaOCl,

which is discussed in detail in Section 2.2.1. The absorption performance of both rate promoters is limited at ambient conditions in the absence of a heterogeneous catalyst. We were able to achieve 30.2% absorbance with 0.2 mol/L Na<sub>2</sub>CO<sub>3</sub> solution + 1000 μL/L H<sub>2</sub>O<sub>2</sub> at pH 11.45 and temperature 318 K.

Since the NO oxidation reaction is limited after a certain value at 318 K, increasing temperature might increase the absorption performance, but due to other mixed gases and physical limitations of our system, we cannot increase the temperature of the absorbent solution. One other possibility is adding a heterogeneous catalyst like platinum to reduce the activation energy and promote the reaction rate at 318 K.

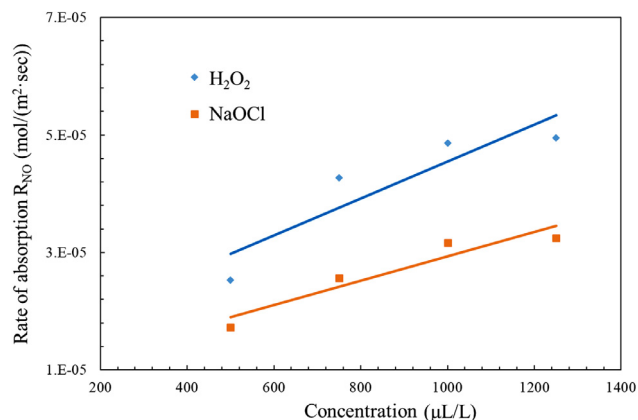
Also, pH plays a crucial role in limiting the NO absorption efficiency of the solution. At pH of ~11.5 reaction tend to limit itself after certain interfacial concentration is reached (Chu et al., 2001; Chang and Rochelle, 1981; Guo et al., 2010; Myers and Overcamp, 2002). So, the absorbance stopped at 30.2%. In retrospect NO oxidation continues to increase with increased oxidizer at lower pH values of around 5 (Deshwal and Kundu, 2015).

### 2.2.1. NO absorption kinetics

The absorption rate of NO can be expressed by Eq. (23), based on the gas-liquid mass transport theory proposed by Dackwerts and Lannus (1970).

$$R_{\text{NO}} = \sqrt{\frac{2}{m+1}} \times k_{m,n} \times D_{\text{NO}} \times C_{\text{NO}}^{m+1} \times C_{\text{NaOCl}}^n \quad (23)$$

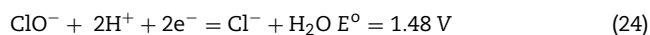
where  $R_{\text{NO}}$  is the rate of absorption of NO,  $k_{m,n}$  is the rate constant and  $D_{\text{NO}}$  is the diffusion coefficient of NO in water, which can be considered as  $2.076 \times 10^{-9} \text{ m}^2/\text{sec}$  at 318 K (Wise and Houghton, 1968).  $C_{\text{NO}}$  is the interfacial concentration of NO, which can be obtained from Eq. (16). Baveja et al. (1979) studied the absorption kinetics of nitric oxide in hydrogen peroxide solution and concluded that first-order kinetics followed. The reaction was found to follow first-order kinetics with NaOCl as well (Chu et al., 2001). So, the values of *m*, *n* are considered to be *m* = 1 and *n* = 1. The rate constant was estimated from Arrhenius equation, where the activation energy (*E<sub>a</sub>*) and frequency factor (*A*) are *E<sub>a</sub>* = 57.3 kJ/mol, *A* =  $6.52 \times 10^9 \text{ m}^3/(\text{mol} \cdot \text{sec})$  and *E<sub>a</sub>* = 28.15 kJ/mol,



**Fig. 6 – Effect of oxidizer concentration on the absorption rate of NO at 318 K.**

$A = 7.96 \times 10^8 \text{ m}^3/(\text{mol} \cdot \text{sec})$  for  $\text{H}_2\text{O}_2$  and  $\text{NaOCl}$ , respectively (Baveja et al., 1979; Deshwal and Kundu, 2015).

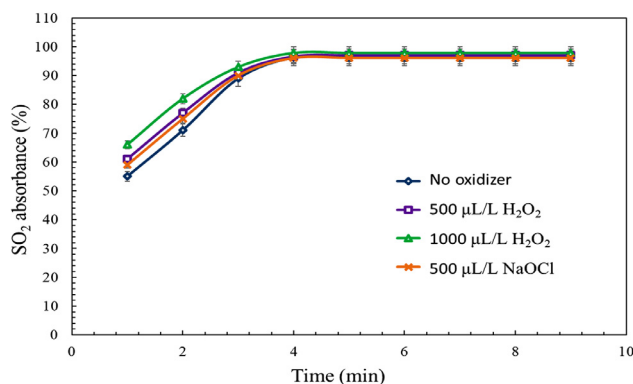
The effect of oxidizer concentration on the rate of absorption of NO at 318 K and 0.2 mol/L  $\text{Na}_2\text{CO}_3$  concentration can be seen in Fig. 6. The rate of absorption of NO initially increases with increasing oxidizer concentration and attains a steady state after 1000  $\mu\text{L/L}$  for both  $\text{NaOCl}$  and  $\text{H}_2\text{O}_2$ . This can be attributed to the fact that rate constant reaches a limiting value at higher pH levels beyond certain concentration of the rate promoter (Deshwal and Kundu, 2015). At  $\text{pH} > 10$  the absorption efficiency decreases due to decrease in oxidizing potential of the catalyst. We have observed a slowdown of absorption of NO because of the decrease in oxidizing ability of  $\text{NaOCl}$  at higher pH values. The potential for the half cell reaction of  $\text{NaOCl}$  in alkaline pH conditions can be seen below:



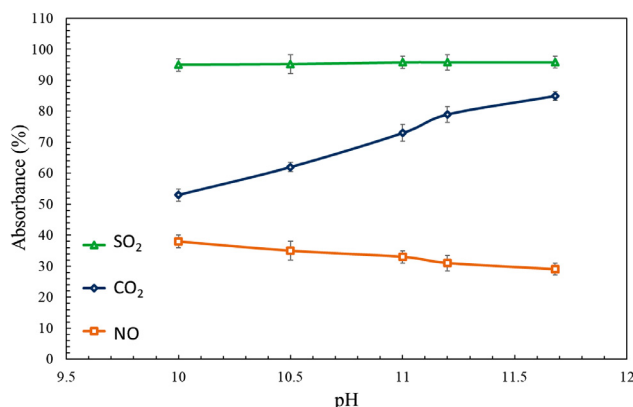
where  $E^\circ$  is the standard oxidation potential. According to Nernst equation higher  $\text{H}^+$  concentration implies higher potential ( $E$ ) and hence higher oxidizing ability. So, at higher pH values the oxidizing power reduces rapidly. Concentration of  $\text{Na}_2\text{CO}_3$  also has a direct effect on NO absorption efficiency. With increase in  $\text{Na}_2\text{CO}_3$  concentration from 0.2 to 0.3 mol/L the rate of reaction of NO drastically reduced. Wei et al. (2009) have also observed reduced NO absorption rate with increase in sodium carbonate concentration from 0.01 to 0.05 mol/L with  $\text{NaClO}_2$  as the rate promoter. The same applies for other alkali absorbent solutions as well. In case of  $\text{NaOH}$  as the absorbent solution Sada et al. (1978) have observed an exponential decrease in rate of reaction.

### 2.3. $\text{SO}_2$ absorption

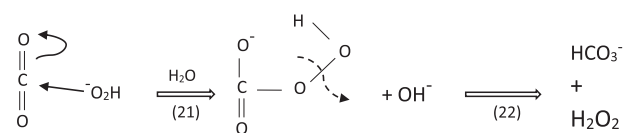
Since the reactions (10)–(13) are almost instantaneous, the rate of absorption of  $\text{SO}_2$  is very high compared to  $\text{CO}_2$  and NO in aqueous medium. Fig. 7 shows the absorbance of  $\text{SO}_2$  in 0.2 mol/L  $\text{Na}_2\text{CO}_3$  solution enhanced with  $\text{H}_2\text{O}_2/\text{NaOCl}$ . The absorbance reached 65% in the first 1 min and finally reaching 97% in 5 min after reaching steady state. The oxidizer did not show any major effect. Absorbance reached 95% very fast, hitting a maximum value of 96.2%. The rate promoters show



**Fig. 7 – Absorbance of  $\text{SO}_2$  vs time in 0.2 mol/L  $\text{Na}_2\text{CO}_3$  solution +  $\text{H}_2\text{O}_2/\text{NaOCl}$  with the error bars representing standard error ( $n = 3$ ).**



**Fig. 8 – Absorbance vs pH with 750  $\mu\text{L/L}$   $\text{H}_2\text{O}_2$  concentration at 318 K at 5 min interval with the error bars representing standard error ( $n = 3$ ).**

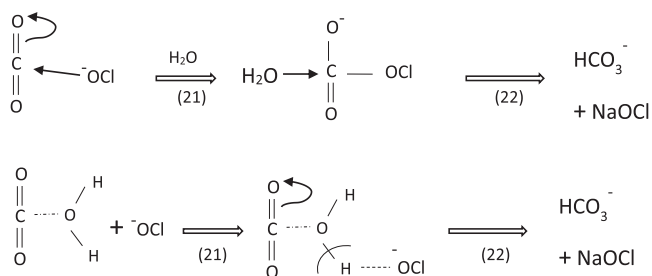


**Scheme 1 – Proposed theoretical mechanism with  $\text{H}_2\text{O}_2$ .**

almost negligible/minimal effect on absorption performance of  $\text{SO}_2$  in aqueous  $\text{Na}_2\text{CO}_3$  solution. These rate promoters do increase the absorbance of  $\text{SO}_2$  but since it is already readily absorbed, this difference is minute. Presence of  $\text{NO}_2$  from NO oxidation have not shown any significant effect on the absorption performance of  $\text{SO}_2$ .

### 2.4. Effect of solution pH on absorption efficiencies of $\text{CO}_2$ , NO and $\text{SO}_2$

Initial pH of the absorbent solution plays a crucial role in determining the mass transfer rate of gases into liquids. The pH of the solution was varied from 10.62 to 11.73 by changing the  $\text{Na}_2\text{CO}_3$  concentration. Fig. 8 shows the effect of pH on the absorbance of all the three gases at 750  $\mu\text{L/L}$   $\text{H}_2\text{O}_2$  concentration



**Scheme 2 – Proposed theoretical mechanisms with NaOCl.**

after 5 min of reaching steady state. The absorbance of SO<sub>2</sub> remained mostly unaffected, while that of CO<sub>2</sub> reduces rapidly at lower pH values due to low H<sup>+</sup> buffering capacity of the solution. The absorption efficiency for NO increases slightly at lower pH values. As evidenced by previous literature, where they studied NO absorption in acidic pH and observed that with increase in pH, absorption lowered.

Few researchers have previously studied the NO absorption characteristics in acidic pH conditions and observed a decrease in NO oxidation rate with increased pH (Baveja et al., 1979; Deshwal et al., 2008b; Krzyzyska and Hutson, 2012; Myers and Overcamp, 2002). We have observed quite a similar trend in our study in the pH range of 10 to 12, where the rate of absorption of NO decreased with increased pH, because of the weak ability of H<sub>2</sub>O<sub>2</sub>/NaOCl to act as an oxidizer in alkaline conditions. Since the primary goal of this unit is to capture CO<sub>2</sub>, operating at a pH of 11.6 or higher is ideal.

Our scrubber system is not a substitute for current SCR, but can definitely be used in industrial flue gas treatment with lower concentrations of NO<sub>x</sub> and SO<sub>x</sub>. It is also suggested that wherever the NO<sub>x</sub> percentage is higher, an additional scrubbing column should be included in series combination with the original scrubber, so that whatever NO<sub>x</sub> is left unabsorbed in the first column is absorbed by the second column.

Further investigation is needed into studying the overall feasibility of the process on a full plant scale unit. Next steps would be to build a full pilot scale continuous capture unit at a power plant to capture flue gas from a single boiler and test the feasibility of the overall process and also doing cost and sensitivity analysis for commercial applicability of this technology, which is beyond the scope and funding of this paper.

### 3. Conclusions

The present investigation suggests that it is possible to capture CO<sub>2</sub>, NO and SO<sub>2</sub> with a single scrubbing column. The efficacy of our system is clearly higher with a CO<sub>2</sub> absorption efficiency of 99.7%, compared to previous studies on CO<sub>2</sub> capture using low cost dilute sodium carbonate solution. Absorbance of CO<sub>2</sub> in a sodium carbonate scrubber column increased from 61% to 99.7% after the addition of H<sub>2</sub>O<sub>2</sub> or NaOCl. NO was also absorbed, but was limited by the alkaline pH to less than 31% absorbance. Lowering the pH decreased CO<sub>2</sub> absorption while increasing NO absorption. Excessive supply of oxidizer did not improve the absorption efficiency of NO. SO<sub>2</sub> absorption reached 95% almost instantaneously, with or with-

out the addition of oxidizer. H<sub>2</sub>O<sub>2</sub> acted as better rate enhancing agent than NaOCl. Enhancing the dilute sodium carbonate solution with H<sub>2</sub>O<sub>2</sub> increases its CO<sub>2</sub> absorption performance reducing the need for additional alkaline reagent.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### REFERENCES

- Astarita, G., Savage, D.W., Longo, J.M., 1981. Promotion of CO<sub>2</sub> mass transfer in carbonate solutions. *Chem. Eng. Sci.* 36 (3), 581–588.
- Barzaghi, F., Giorgi, C., Mani, F., Peruzzini, M., 2017. CO<sub>2</sub> capture by aqueous Na<sub>2</sub>CO<sub>3</sub> integrated with high-quality CaCO<sub>3</sub> formation and pure CO<sub>2</sub> release at room conditions. *J. CO<sub>2</sub> Util.* 22, 346–354.
- Baveja, K.K., Rao, D.S., Sarkar, M.K., 1979. Kinetics of absorption of nitric oxide in hydrogen peroxide solutions. *J. Chem. Eng. Jpn.* 12 (4), 322–325.
- Berghout, N., Kuramochi, T., van den Broek, M., Faaij, A., 2015. Techno-economic performance and spatial footprint of infrastructure configurations for large scale CO<sub>2</sub> capture in industrial zones: a case study for the Rotterdam Botlek area (part A). *Int. J. Greenh. Gas Control* 39, 256–284.
- Chang, C.S., Rochelle, G.T., 1981. SO<sub>2</sub> absorption into aqueous solutions. *AIChE J.* 27 (2), 292–298.
- Chu, H., Chien, T.W., Li, S.Y., 2001. Simultaneous absorption of SO<sub>2</sub> and NO from flue gas with KMnO<sub>4</sub>/NaOH solutions. *Sci. Total Environ.* 275 (1–3), 127–135.
- Danckwerts, P.V., Lannus, A., 1970. Gas-liquid reactions. *J. Electrochem. Soc.* 117 (10), 369C.
- Dennard, A.E., Williams, R.J.P., 1966. The catalysis of the reaction between carbon dioxide and water. *J. Chem. Soc. A* 812–816.
- Deshwal, B.R., Kundu, N., 2015. Reaction kinetics of oxidative absorption of nitric oxide into sodium hypochlorite solution. *Int. J. Adv. Res. Sci. Technol.* 4, 313–318.
- Deshwal, B.R., Jin, D.S., Lee, S.H., Moon, S.H., Jung, J.H., Lee, H.K., 2008a. Removal of NO from flue gas by aqueous chlorine-dioxide scrubbing solution in a lab-scale bubbling reactor. *J. Hazard. Mater.* 150 (3), 649–655.
- Deshwal, B.R., Lee, S.H., Jung, J.H., Shon, B.H., Lee, H.K., 2008b. Study on the removal of NO<sub>x</sub> from simulated flue gas using acidic NaClO<sub>2</sub> solution. *J. Environ. Sci.* 20 (1), 33–38.
- Deshwal, B.R., Hyung-Keun, L., 2009. Mass transfer in the absorption of SO<sub>2</sub> and NO<sub>x</sub> using aqueous euclorine scrubbing solution. *J. Environ. Sci.* 21 (2), 155–161.
- Edwards, J.O., Pearson, R.G., 1962. The factors determining nucleophilic reactivities. *J. Am. Chem. Soc.* 84 (1), 16–24.
- Floyd III, W.C., Baker, S.E., Valdez, C.A., Stolaroff, J.K., Bearinger, J.P., Satcher Jr, J.H., et al., 2013. Evaluation of a carbonic anhydrase mimic for industrial carbon capture. *Environ. Sci. Technol.* 47 (17), 10049–10055.



- Ghosh, U.K., Kentish, S.E., Stevens, G.W., 2009. Absorption of carbon dioxide into aqueous potassium carbonate promoted by boric acid. *Energy Procedia* 1 (1), 1075–1081.
- Guo, R.T., Gao, X., Pan, W.G., Ren, J.X., Wu, J., Zhang, X.B., 2010. Absorption of NO into NaClO<sub>3</sub>/NaOH solutions in a stirred tank reactor. *Fuel* 89 (11), 3431–3435.
- Hu, G., Nicholas, N.J., Smith, K.H., Mumford, K.A., Kentish, S.E., Stevens, G.W., 2016. Carbon dioxide absorption into promoted potassium carbonate solutions: a review. *Int. J. Greenh. Gas Control* 53, 28–40.
- Jencks, W.P., Carriuolo, J., 1960. Reactivity of nucleophilic reagents toward esters. *J. Am. Chem. Soc.* 82 (7), 1778–1786.
- Kawatra, S.K., 2020. *Advanced Coal Preparation and Beyond: CO<sub>2</sub> Capture and Utilization*. CRC Press.
- Kawatra, S.K., Eisele, T.C., Simmons, J.J., Michigan Technological University, 2011. Capture and sequestration of carbon dioxide in flue gases. US Patent 7,919,064.
- Kouravand, S., Kermani, A.M., 2018. Clean power production by simultaneous reduction of NO<sub>x</sub> and SO<sub>x</sub> contaminants using Mazut Nano-Emulsion and wet flue gas desulfurization. *J. Clean. Prod.* 201, 229–235.
- Krzyzynska, R., Hutson, N.D., 2012. Effect of solution pH on SO<sub>2</sub>, NO<sub>x</sub>, and Hg removal from simulated coal combustion flue gas in an oxidant-enhanced wet scrubber. *J. Air Waste Manag. Assoc.* 62 (2), 212–220.
- Li, K., Yu, H., Yan, S., Feron, P., Wardhaugh, L., Tade, M., 2016. Technoeconomic assessment of an advanced aqueous ammonia-based postcombustion capture process integrated with a 650-MW coal-fired power station. *Environ. Sci. Technol.* 50 (19), 10746–10755.
- Myers Jr, E.B., Overcamp, T.J., 2002. Hydrogen peroxide scrubber for the control of nitrogen oxides. *Environ. Eng. Sci.* 19 (5), 321–327.
- Onda, K., Sada, E., Kobayashi, T., Kito, S., Ito, K., 1970a. Salting-out parameters of gas solubility in aqueous salt solutions. *J. Chem. Eng. Japan* 3 (1), 18–24.
- Onda, K., Sada, E., Kobayashi, T., Kito, S., Ito, K., 1970b. Solubility of gases in aqueous solutions of mixed salts. *J. Chem. Eng. Jpn.* 3 (2), 137–142.
- Phan, D.T., Maeder, M., Burns, R.C., Puxty, G., 2014. Catalysis of CO<sub>2</sub> absorption in aqueous solution by inorganic oxoanions and their application to post combustion capture. *Environ. Sci. Technol.* 48 (8), 4623–4629.
- Ramazani, R., Mazinani, S., Jahanmiri, A., Van der Bruggen, B., 2016. Experimental investigation of the effect of addition of different activators to aqueous solution of potassium carbonate: absorption rate and solubility. *Int. J. Greenh. Gas Control* 45, 27–33.
- Sada, E., Kumazawa, H., Hikosaka, H., 1986. A kinetic study of absorption of nitrogen oxide (NO) into aqueous solutions of sodium sulfite with added iron (II)-EDTA chelate. *Ind. Eng. Chem. Fundam.* 25 (3), 386–390.
- Sada, E., Kumazawa, H., Kudo, I., Kondo, T., 1978. Absorption of NO in aqueous mixed solutions of NaClO<sub>2</sub> and NaOH. *Chem. Eng. Sci.* 33 (3), 315–318.
- Sahoo, P.C., Kumar, M., Puri, S.K., Ramakumar, S.S.V., 2018. Enzyme inspired complexes for industrial CO<sub>2</sub> capture: opportunities and challenges. *J. CO<sub>2</sub> Util.* 24, 419–429.
- Santos, S., Duarte, A.P., Bordado, J., Gomes, J., 2016. New process for simultaneous removal of CO<sub>2</sub>, SO<sub>x</sub> and NO<sub>x</sub>. *Ciênc. Tecnol. dos Mater.* 28 (2), 106–111.
- Valluri, S., Kawatra, S.K., 2021. Use of frothers to improve the absorption efficiency of dilute sodium carbonate slurry for post combustion CO<sub>2</sub> capture. *Fuel Process. Technol.* 212, 106620.
- Wei, J.C., Yu, P., Cai, B., Luo, Y.B., Tan, H.Z., 2009. Absorption of NO in aqueous NaClO<sub>2</sub>/Na<sub>2</sub>CO<sub>3</sub> solutions. *Chem. Eng. Technol.* 32 (1), 114–119.
- Wise, D.L., Houghton, G., 1968. Diffusion coefficients of neon, krypton, xenon, carbon monoxide and nitric oxide in water at 10–60°C. *Chem. Eng. Sci.* 23 (10), 1211–1216.
- Xie, H., Wang, P., He, N., Yang, X., Chen, J., 2015. Toward rational design of amines for CO<sub>2</sub> capture: Substituent effect on kinetic process for the reaction of monoethanolamine with CO<sub>2</sub>. *J. Environ. Sci.* 37, 75–82.
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R.B., Bland, A.E., et al., 2008. Progress in carbon dioxide separation and capture: a review. *J. Environ. Sci.* 20 (1), 14–27.