



# Carbon dioxide absorption into unpromoted and borate-catalyzed potassium carbonate solutions

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## ABSTRACT

Potassium carbonate based solvents have the potential for capturing  $CO_2$  from emission sources such as power stations burning fossil fuels. However, due to poor reaction kinetics a rate promoter is considered necessary to improve the rate of reaction of  $CO_2$  with the solvent. Using a characterized wetted-wall column, we have studied the reaction kinetics of  $CO_2$  into unpromoted and borate-promoted 30 wt% potassium carbonate solutions. Results presented here show that, at 80 °C, addition of small amounts of boric acid (0.2 M, 0.6 M and 1.5 M) accelerate the overall absorption process of  $CO_2$  in carbonate solvents by 3%, 10% and 29% respectively. The Arrhenius expression for the reactions  $CO_2 + OH^-$  and  $CO_2 + B(OH)_4^-$  are  $k_{OH} [M^{-1} s^{-1}] = 2.53 \times 10^{11} \exp(-4311/T [K])$  and  $k_{borate} [M^{-1} s^{-1}] = 5.5 \times 10^{11} \exp(-6927/T [K])$ ; and the activation energies are 35.8 kJ mol<sup>-1</sup> and 57.6 kJ mol<sup>-1</sup> respectively. Experiments were conducted between 40 °C and 80 °C and at a bulk partial pressure of  $CO_2$  of 90 kPa.

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## 1. Introduction

It is widely accepted that the increase in the carbon dioxide ( $CO_2$ ) emissions to our atmosphere is the major contributor to global climate change. Numerous methods for reducing greenhouse gases to our atmosphere have been proposed including carbon capture and sequestration (CCS). Reactive absorption into a solvent is the benchmark technology for  $CO_2$  removal from the flue gas of coal fired power stations [1,2].

The basic principle behind all solvent absorption processes is the mass transfer of a solute (e.g.  $CO_2$ ) from a gas stream to a liquid solvent in a gas–liquid contacting absorber. The  $CO_2$  loaded solution is subsequently fed to a high temperature and/or low pressure regenerator that releases the  $CO_2$  which can then be used for other purposes such as sequestration in the case of carbon capture and storage. The 'lean' solvent is returned back to the absorber. The absorption of  $CO_2$  into carbonate–bicarbonate solutions is a widely known process [3]. German patents exploring hot carbonate absorption of  $CO_2$  exist as early as 1904 [4]. In the 1950s Benson and Field developed the Benfield process which used hot potassium carbonate as a  $CO_2$  absorption solvent to reduce the costs of synthesis gas purification for the production of liquid fuel from coal [5–7].

In comparison to the benchmark industrial solvent for  $CO_2$  absorption, monoethanolamine (MEA), potassium carbonate

processes require less energy as the heat of absorption is 37% that of MEA [5]. Furthermore, MEA degrades at high temperatures as well as in the presence of oxygen, forms corrosive and toxic organic products, and requires pre-treatment processes for sulphur dioxide removal [8–10]. Despite its immunity to these constraints, a key limitation for a carbonate based solvent is the slow rate of reaction with  $CO_2$ . Promoters such as piperazine [11], amino acids [12–14], arsenious acid [15,16], amine derivatives [17–19], carbonic anhydrase [20–22], and boric acid [20,23] have been suggested to enhance the reaction kinetics. Of these, boric acid  $B(OH)_3$  is attractive because it is relatively benign and economically affordable, and is not expected to interact with species such as sulphur dioxide or oxygen often present in the flue gas from power stations [24].

In basic solutions (pH > 9), where pre- and post-combustion carbon capture normally takes place [1,2], the reaction of  $CO_2 + H_2O$  forming  $HCO_3^-$  can be neglected [25], and the predominant equilibrium reactions are as follows (NB: in this work all species are aqueous unless otherwise stated):



It is well established that the rate-limiting reaction in chemical absorption of  $CO_2$  into carbonate solutions is the formation of the bicarbonate ion, Eq. (1) [26].

It has been reported that  $B(OH)_3$  and  $B(OH)_4^-$  are the predominant boron species at boron concentrations and pH range relevant to carbon capture systems [20,27]. Using a stopped flow

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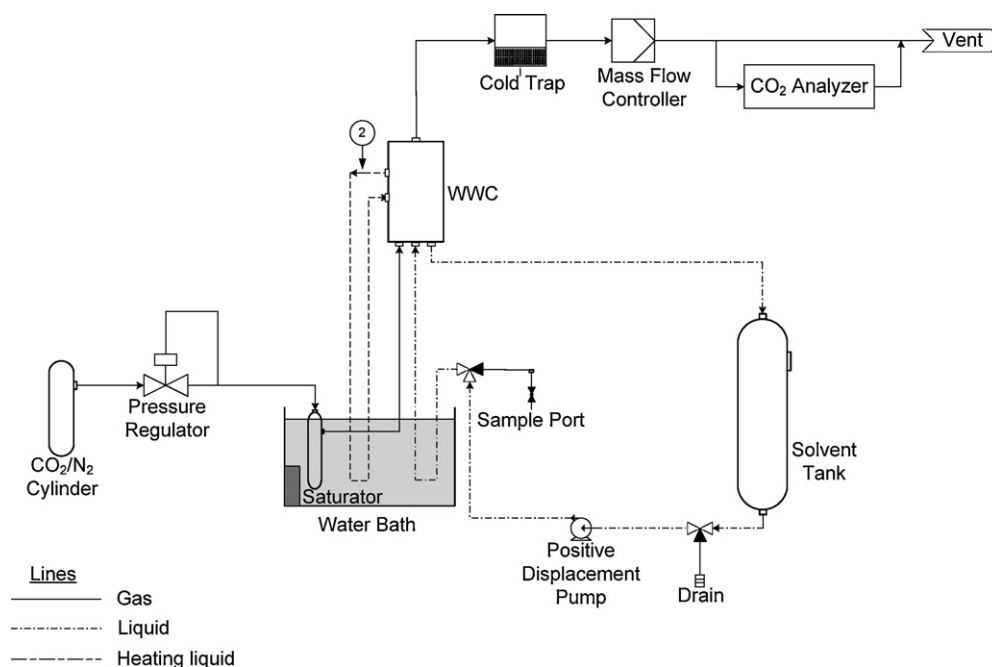
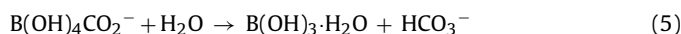


Fig. 1. Process flow diagram of the wetted-wall column.

indicator technique, results from our previous work [20] showed that, at total boron concentrations from 4 to 12.5 mM and a temperature range 25–40 °C,  $B(OH)_4^-$  is the active form of boron, and that it catalyzes  $CO_2$  hydration via the same fundamental mechanism as the enzyme carbonic anhydrase:



In this study we aim to extend our previous work [20] by investigating the effect of boric acid on  $CO_2$  absorption in potassium carbonate solutions at significantly higher boron concentrations and temperatures, which are closer to the conditions encountered in industrial carbon capture systems [24,28]. Therefore we have studied the kinetics of  $CO_2$  reacting with  $B(OH)_4^-$  using a wetted-wall column (WWC). This work has implications for the operation of borate-promoted potassium carbonate solvent systems for carbon capture and sequestration, and more specifically allows accurate design of absorber and regenerator units.

## 2. Materials and methods

The kinetics of reactions  $CO_2 + OH^-$  and  $CO_2 + B(OH)_4^-$  were studied using a wetted-wall column (WWC), a device that allows contact between a gas and a liquid phase with a controlled and measurable surface area for mass transfer, and thus, accurate measurements of the flux of  $CO_2$  into un-promoted and borate-promoted potassium carbonate solvents.

All chemicals employed in this study were of analytical reagent grade and used as supplied without further purification. Potassium Carbonate ( $\geq 99\%$ , Thasco Chemical Co. Ltd.) and potassium bicarbonate ( $\geq 99\%$ , Sigma) were weighed to prepare a chemical equivalent of a 30 wt%  $K_2CO_3$  solution with known  $CO_2$  loading. The promoter boric acid ( $\geq 99.5\%$ ) was purchased from Chem-Supply.  $CO_2/N_2$  gas mixtures (10.2% and 89.8%  $CO_2$  in  $N_2$  obtained from BOC Gases Australia Limited) were used for all experiments and for

the calibration of a MGA3000C  $CO_2$  gas analyser (ANRI Instrument and Control Pty. Ltd.).

The WWC technique as presented by Bishnoi and Rochelle [29] and Cullinane and Cullinane [30] was adopted as described in our previous work [23], to study both promoted and un-promoted absorption of  $CO_2$  into potassium carbonate solutions. Modifications were made for this work to enable continuous monitoring of the gas outlet concentration. These modifications included installing a series of cold traps and a  $CO_2$  gas analyser. A process flow diagram of the full experimental setup is shown in Fig. 1.

The WWC, as shown schematically in Fig. 2, consists of a stainless steel tube 115 mm long with a 13 mm outer diameter. The total contact area, 4840 mm<sup>2</sup>, was calculated as the longitudinal area of the tube, 4590 mm<sup>2</sup>, and the area of the top of the column, 250 mm<sup>2</sup>, which was considered a hemisphere due to the shape of liquid film. The column was enclosed by a thick-walled steel cylinder with an outside diameter of 25 mm to provide a gas–liquid contact chamber. The hydraulic diameter of the enclosure is 13 mm, giving a cross sectional area for gas flow of 380 mm<sup>2</sup>. The chamber was housed inside a second thick-walled steel chamber (102 mm outside diameter) that served as an insulating bath with circulating heat transfer liquid.

The liquid solvent was contained in a stainless steel reservoir with a total volume of 3000 cm<sup>3</sup>. The fluid was pumped from the reservoir to the gas–liquid contact chamber. The fluid flowed up through the middle of the column, overflowed at the top, and was evenly distributed on the outer surface of the column. The liquid was collected at the bottom of the column and pumped back to the solution reservoir by a positive displacement IDEX micropump (Process Pump Pty. Ltd.). A typical liquid flowrate used in this experiment was 100 mL/min.

The gas flowrate was manually controlled by an outlet needle valve and monitored using an Aalborg flowmeter (0–250 mL/min) (Pryde Measurement Pty. Ltd.). The gas was saturated with water at the operating temperature of the column in a sealed vessel immersed in a heat bath in order to avoid the gas absorbing liquid within the WWC. After saturation, the gas was introduced to the bottom of the column through a 1/4 inch tube. It subsequently flowed counter-currently past the liquid film. The gas exited the top of the

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