

GHGT-9

Low energy packed tower and caustic recovery for direct capture of CO₂ from air.

Mahmoudkhani M.^{a,*}, Heidel K.R.^a, Ferreira J.C.^a, Keith D.W.^a, Cherry R.S.^b

^a Energy and Environment System Group, Institute for Sustainable Energy Environment and Economy
University of Calgary, Alberta, CANADA

^b Idaho National Laboratory, Idaho Falls, ID, USA

Abstract

We used a 6.5 m tall packed tower prototype to study the capturing rate of CO₂ from air. The tower was operated at a pressure drop of less than 27 pa in the packing at 0.7m/sec air speed with a counter current flow mode and with NaOH or KOH solution as the absorbent. The tower consumed an average of ~30 kJe per mole CO₂. We found that via an intermittent operation with a 5% duty cycle, the fluid pumping work reduced by 90%. A novel process for removing carbonates ions from alkaline solutions based on titanate compounds is compared to the traditional lime cycle for the caustic recovery. The titanate process reduces the high-grade heat requirement by ~50%. The results from experimental data of leaching and precipitation test support process design of the titanate cycle. In this paper, we also present the chemical process design.

© 2009 Elsevier Ltd. All rights reserved.

Keywords: air capture; packed tower; direct causticization; titanate; leaching; precipitation;

1. Introduction

To avoid dangerous climate change, the growth of atmospheric concentrations of greenhouse gases must be halted, and may have to be reduced. The concentration of carbon dioxide, CO₂, the most dominant greenhouse gas, has increased from 280ppm in the pre-industrial age to more than 380ppm now and is now increasing by more than 2ppm per year driven by global CO₂ emissions that are now increasing at more than 3.3% per year (Canadell et al. [1]). Carbon capture and storage (CCS) technologies target CO₂ removal from large fixed-point sources such as power plants, however fixed point sources emit approximately half of global CO₂ emissions leaving small and dispersed emissions unabated. Direct capture of CO₂ from ambient air or “air capture”, is one of the few methods capable of systematically managing dispersed emissions. Therefore, while air capture is expected to be more

* Corresponding author. Tel.: +1-403-210-9137; fax: +1-403-210-3894.

E-mail address: maryam@ucalgary.ca.

expensive than capture from large point sources it remains important as it will primarily compete with emission reductions from dispersed sources such as transportation which can be very expensive to mitigate.

Carbon dioxide absorption from atmospheric air using alkaline solution has been explored for half a century (Spector and Dodge [2], Tepe and Dodge [3]). Large scale scrubbing of CO₂ from ambient air for climate mitigation was first suggested by Lackner in the late 1990's (Lackner et al.[4]). In wet scrubbing techniques, CO₂ is absorbed into a solution of sodium hydroxide, NaOH, creating an aqueous solution of sodium hydroxide and sodium carbonate, Na₂CO₃. The contactor, as the component of the system that provides the contact between CO₂ and sodium hydroxide, has thus far been a point of contention. Large convective tower (Lackner et al. [4]), and packed scrubbing towers (Bacocchi et al. [5] and Zeman [6]) have been the most frequently suggested forms of the contactor. A packed tower equipped with Sulzer Mellapak has been theoretically investigated by Bacocchi et al.[5] to absorb CO₂ from air with an inlet concentration of 500ppm to an outlet concentration of 250ppm using a 2M NaOH solution. Zeman [6], however, selected a chamber filled with packing material that provides sufficient surface area for 50% capture rate from air with inlet concentration of 380ppm with 1M sodium hydroxide solution. Zeman [6] estimated a total energy requirement of 380 kJ/molCO₂ for the capture and chemical recovery using a modified lime cycle as for the chemical recovery.

An alternative strategy, analyzed by Stolaroff et al. [7], is to generate a fine spray of the absorbing solution to provide a large surface to the air flow through an open tower. This strategy could have the potential to operate with a small pressure drop in air and avoids the capital cost of packing material. However, while the spray contactor can achieve low pumping energy, it does so only by reducing flow rate to reduce coalescence which in turn reduces capture rate per unit area and so drives up the capital cost component of total contactor cost. The packed tower design reported here has a capture rate per unit area about an order of magnitude larger than in the spray tower design while maintaining a similarly low energy cost.

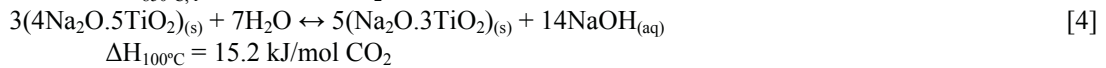
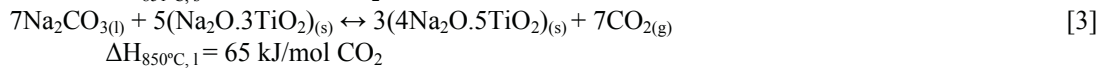
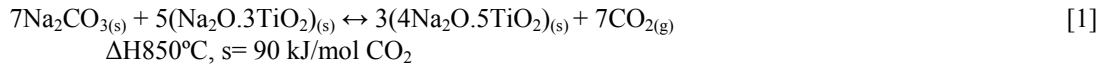
Water loss was a major concern in the spray system, it was addressed and found that the water loss could be managed by adjusting of the NaOH concentration with temperature and humidity of air, i.e. the higher the concentration of sodium hydroxide, the lower the water loss, e.g. using ~7.2M NaOH, at 15°C and 65% relative humidity, water loss is eliminated (Stolaroff et al. [7]).

All of these processes create a mixed sodium carbonate/sodium hydroxide solution which must be converted back to sodium hydroxide solution and carbon dioxide gas to have a closed loop process. Conversion of sodium carbonate into sodium hydroxide, so-called causticization, is one of the oldest processes in pulp and paper industry. To convert sodium carbonate and recover NaOH the conventional causticization using lime has been used on a continuous basis for more than 80 years.

In air capture process, the aqueous solution of sodium carbonate and concentrated sodium hydroxide must be converted to fresh sodium hydroxide and gaseous CO₂ to be used for disposal or fuels. To convert sodium carbonate to sodium hydroxide and regenerate the feed solution, a conventional causticization technique using lime has been addressed (Bacocchi, et al. [5], Stolaroff et al.[7] and Zeman [6]). In conventional chemical recovery, Na₂CO₃ is causticized with lime to form NaOH and lime mud (CaCO₃). The conversion of Na₂CO₃ to NaOH and regeneration of lime is a series of liquid-solid reactions. To convert calcium carbonate to lime the thermodynamic minimum required energy is 179 kJ/mol CO₂.

The enthalpy of the reaction for absorption of CO₂ from air into sodium hydroxide solution for a nominal 1 molar solution and at 298K and a pressure of 1 bar is -109.4 kJ/mol CO₂ which implies that to go from sodium carbonate to sodium hydroxide the thermodynamic minimum required energy is 109.4 kJ/mol CO₂ (Zeman and Lackner [8]). Comparing the high temperature energy required regenerating NaOH using conventional causticization with the thermodynamic minimum required energy given by the enthalpy of the reaction for absorption of CO₂ from air into sodium hydroxide solution, it can be seen that the required energy for conventional causticization is far beyond the thermodynamic minimum.

Studies of the direct causticization of sodium carbonate with titanium dioxide, as an advanced causticization method, have been carried out by Chen and van Heiningen [9], Kiiskilä [10], [11], Nohlgren [12], Palm and Theliander [13], Zeng and van Heiningen [14] and Zou [15]. It has been found that the main decarbonization reaction in the direct causticization based on TiO_2 is the reactions between Na_2CO_3 and $\text{Na}_2\text{O}\cdot 3\text{TiO}_2$, i.e. *Reactions [1] and [3]*. The high temperature reaction in this method would require almost half of what is reported for the conventional causticization method, i.e. 90 as compared to 179 kJ/mol CO_2 .



The formed sodium penta-titanate, $4\text{Na}_2\text{O}\cdot 5\text{TiO}_2$, is then hydrolyzed, Equation [4], in a leaching unit at a temperature of about 100°C , to sodium hydroxide and sodium tri-titanate, which the latter is recycled to the causticization unit.

The conventional titanate process cannot be directly applied to air capture; however, because it requires pure and dry anhydrous sodium carbonate. Separation of anhydrous sodium carbonate from Na_2CO_3 - NaOH feed solution, and preparation of a well-mixed stream of solid sodium carbonate and sodium tri-titanate, the latter is the reagent for decarbonizing of sodium carbonate via reactions [1] and [2] is the crucial step necessary for applying the titanate process to air capture. Mahmoudkhani and Keith (2008) studied the regeneration of NaOH via direct causticization using titanate and presented an end-to-end energy and exergy analysis. In this paper we summarize some results from our earlier studies (Mahmoudkhani and Keith [16]) and present a preliminary chemical process design and experimental results on important chemical reactions and on a packed-tower contactor.

2. Contactor

The CO_2 capture experimental apparatus, referred to as the contactor, (Figure 1, Table 1) uses the fan to draw air in, push it up through the packing, and out the top of the tower.

Table 1: Contactor Specifications

Specifications		Short Stack	Tall Stack
Dimensions	Height (m)	4.8	6.0
	Tower Diameter (m)	1.22	
	Inlet Diameter (m)	0.61	
Packing Height, m		1.5	2.6
Operating Volume, L		350 to 450	
Fluid Flow Range, L/s		1.9 to 6.3	
Air Velocity Range, m/s		0.5 to 3	
Packing Type		Sulzer 250X	

At the same time the pump is cycling the caustic fluid from the basin at the bottom of the tower up to a distribution system directly above the packing. As the fluid flows down it coats the sulzer 250X packing, which has 250m^2 surface area per m^3 of packing, in a thin film of fluid that interacts with the passing air. The Sulzer 250X packing was chosen by Renato Bacicchi so that the tower would remove half of the ambient CO_2 if the air was

passing through the packing at 1 m sec^{-1} . A sensor suite recorded the rotational frequency of the pump and the fan, inlet temperature, inlet relative humidity, inlet carbon dioxide concentration, outlet temperature, outlet relative humidity, and outlet carbon dioxide concentration.

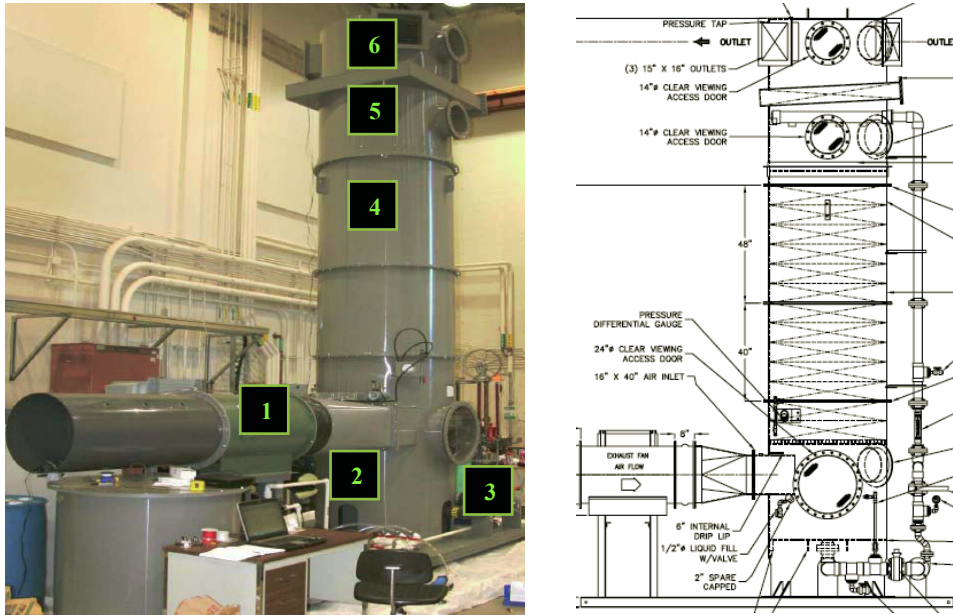


Figure 1: The packed tower consists of:

1. Air Driver(fan) 2. Fluid Basin 3. Fluid Pump 4. Packing 5. Fluid Distributor 6. Air Outlet with Demister

2.1. Contactor experimental results

For the experiments, we chose to consider the PV work performed since on the full scale contactor components with different efficiencies would be used. All of the tests measurements were taken at our chosen operating point of 0.7 m/s air speed and $3.6 \text{ L/m}^2\cdot\text{s}$ through the packing. The first test performed used a 3 molar NaOH solution and the CO_2 concentration across the tower decreased by 68%. Using this solution the system was consuming $177 \text{ kWhr/ton CO}_2$ with 2.6m of packing and $136 \text{ kWhr/ton CO}_2$ with 1.5m of packing. The goal of our second major experiment (see Figure 2) was to determine how changing the fluid affects the capture rate of the contactor. When we ran the experiment we found that the KOH captured 27% more CO_2 and was using $125 \text{ kWhr/ton CO}_2$.

During our initial testing we noticed that if the pump was shutdown and the fan was left running the system had an extremely slow decay, as seen in Figure 2. It was capturing 80% what it would normally capture even after the pump had been off for ten minutes. We performed tests to determine how much fluid if any remained in the packing and found that on average 30 litres was held up by the packing. Our next goal was to determine how the system would run with the pump on for 30 seconds and off for 600 seconds (see Figure 3). We ran the contactor in this manner for over an hour and there did not seem to be any detrimental effects.

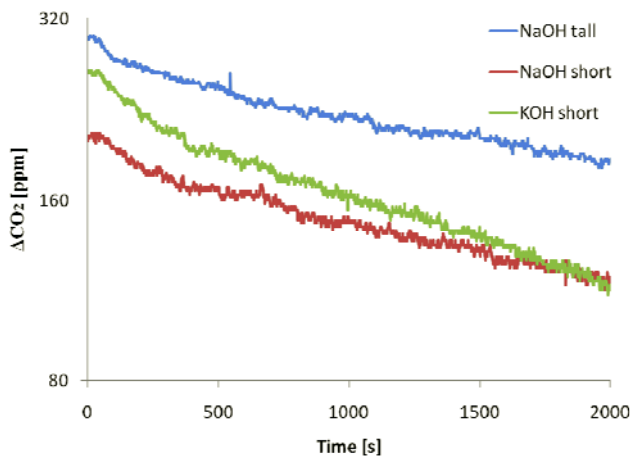


Figure 2: Capture performance of KOH vs. NaOH; pump was shut off after 30 seconds of stable running. Note that the y-axis is displayed in log scale. Note how after 100 seconds the lines are linear showing that the decay of the capture rate is exponential.

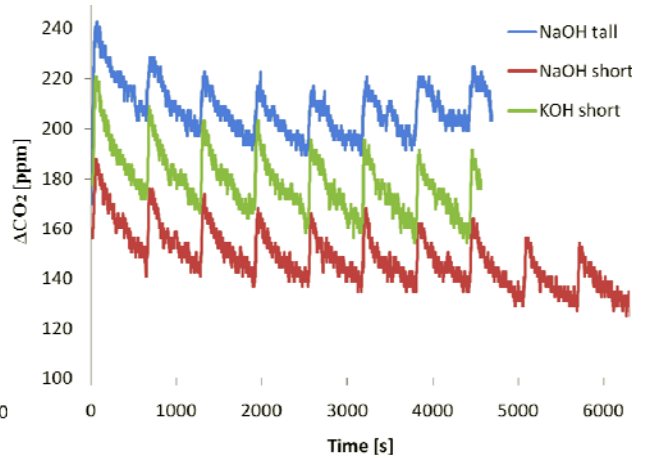


Figure 3: Long test of cyclic pumping with pump on for 30 seconds and off for 600 seconds. Note how there is no drastic decrease in the capture rate from one cycle to the next. A decrease does occur but it was expected as the chemical solution is depleted.

As seen in Table 2, at least 85% of the contactors energy requirements are due to the pump, large savings could be achieved if the pump was not run continuously.

Table 2: Summary of the systems energy requirements. All data is in kWhr/ton CO₂.

	Complete System		Fluid		Air	
	Base	Cyclic Pump	Base	Cyclic Pump	Base	Cyclic Pump
NaOH tall	177	30	158	9	19	21
NaOH short	136	29	116	6	20	23
KOH short	125	25	107	6	18	18

2.2. Full scale contactor design

Based on the results of our experiments a new design (see Figure 4) for the contactor has been developed. The new contactor is a cross flow slab design.

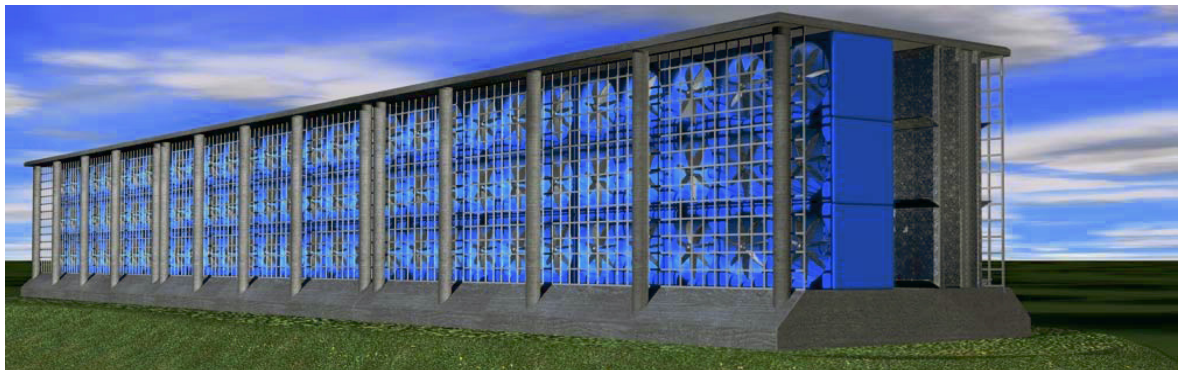


Figure 4: Artistic rendering of how the full scale contactor may look.

This system should reduce the air handling costs since the air will not need to be accelerated to 4 times the desired velocity in the packing which keeps the operating costs low. The system will also have a much higher capture per square meter because about half the footprint is area where the air contacts the fluid. So the contactor will require less land and will have lower capital costs.

3. Chemical recovery cycle

In our process, capturing CO₂ from air is viewed as a three step process requiring, the CO₂ capture, a precipitation and a decarbonization step (Mahmoudkhani and Keith [8]). The precipitation unit is a two-stage crystallization unit for precipitating anhydrous sodium carbonate from concentrated alkaline aqueous solution. In the first crystallization stage, sodium carbonate decahydrate (Na₂CO₃·10H₂O) is crystallized from concentrated alkaline aqueous solution by ~10°C temperature swing. The solubility curve for sodium carbonate in presence of sodium hydroxide in the solution follows the same pattern as the solubility curve for Na₂CO₃-water system. The higher concentration of NaOH, as expected, significantly lowers the solubility. This allows us to precipitate anhydrous sodium carbonate below the boiling point of the solution. In the second stage anhydrous sodium carbonate is crystallized from a saturated sodium carbonate aqueous solution at elevated temperature and concentration of sodium hydroxide by means of solubility swing. Earlier, Mahmoudkhani and Keith [16] presented the detailed process description on sodium carbonate precipitation in presence of sodium hydroxide. The solid anhydrous sodium carbonate is then causticized using direct causticization with sodium tri-titanate, in the kiln where CO₂ is liberated from sodium carbonate and sodium hydroxide is regenerated and recycled to the contactor.

3.1. Process simulation

We used VMGSim™ for building a process flowsheet for the entire process. VMGSim™ is the process simulation system that integrates a state of the art flowsheeting kernel with Visio™ for ease-of-use and powerful graphics capability and Excel™ for seamless bidirectional spreadsheet calculations. The power of VMG's thermodynamic packages drives the core of VMGSim (www.virtualmaterials.com). Figure 5 demonstrates the process flowsheeting made by VMGSim for the CO₂ capture and caustic recovery process.

VMGSim was essentially developed for process simulations deal with oil and natural gas compounds, and therefore, the titanate compounds are seldom included in process simulators database. Because of this, we built a custom thermodynamics model which includes thermodynamical properties for the six hypothetical compounds (sodium hydroxide, sodium carbonate in solid and aqueous state, sodium carbonate decahydrate, sodium tri-titanate, sodium penta-titanate). The thermo-chemical properties of these compounds were created based on data available in the literature, e.g. molecular weight, liquid density, enthalpy of formation. The simulation is inter-linked to Excel™ in order to perform the solubility calculations based on a macro code calculating the sodium carbonate solubility at various concentration of aqueous sodium hydroxide. The process simulation is based on capturing rate of 1 Mtonne of CO₂ per year.

3.2. Simultaneous leaching/precipitation results

A key step in caustic recovery is leaching sodium hydroxide out from sodium penta-titanate, reaction [4]. In our proposed process, Mahmoudkhani and Keith [16], the leaching of sodium hydroxide occurs simultaneously with the precipitation of anhydrous sodium carbonate. A number of leaching tests were therefore performed for simultaneous leaching of sodium penta-titanate and precipitation of anhydrous sodium carbonate. Various amounts of sodium penta-titanate were used to obtain various concentrations of sodium hydroxide. The solubility of sodium carbonate would therefore shift by changes in concentration of sodium hydroxide which would in turn lead to different precipitation efficiencies. Figure 6 shows a summary of this data. As shown, the experimental results are in good agreement with the expected theoretical values obtained from the both the solubility data of sodium carbonate in an alkaline solution and the reaction stoichiometry (reaction [4]). A few scattered data at a concentration of 3M for

sodium hydroxide might be an indication of interference between the two reactions (i.e. reaction [4] and precipitation of Na_2CO_3). This will be discussed in a separate paper.

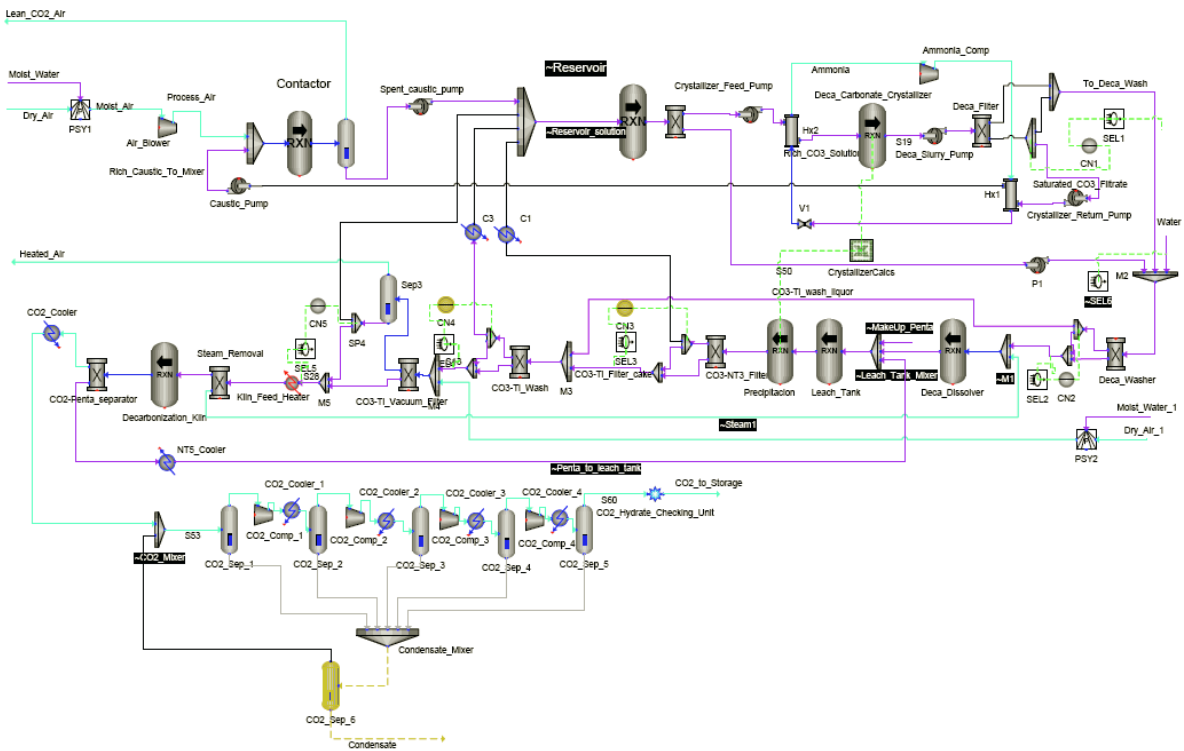


Figure 5: Process flowsheet for the CO₂ capture and caustic recovery

Flowsheet includes the contactor, crystallization cycle, leaching cycle, decarbonization and compression section. The green dash lines represent the inter-links to Excel. The pink lines represent the material streams for slurry/liquid components (vapour fraction = 0). The blue lines represent material stream for the components at mixed phase components (0 < vapour fraction < 1). The cyan lines represent the material stream for the gaseous phase components (vapour fraction = 1)

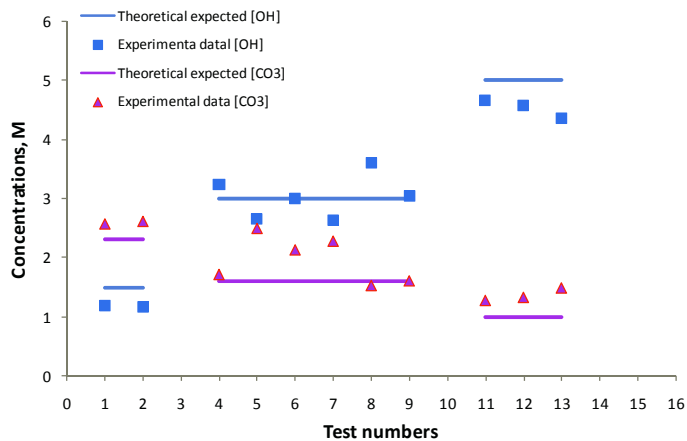


Figure 6: Experimental results on simultaneous leaching of NaOH and precipitation of Na_2CO_3

4. Conclusion

An energy efficient process for capturing CO₂ from atmosphere using packed tower and an energy efficient process for recovering sodium hydroxide was assessed in this paper. The contactor is designed as to capture at least 50% of CO₂ at each run. It was found that at least 85% of the contactors energy requirements are due to the pump, large savings could be achieved if the pump was not run continuously. Via an intermittent operation of the contactor with a 5% duty cycle, the fluid pumping work reduced by 90%. The proposed chemical recovery process requires about half of the high temperature heat requirement for the conventional causticization process using lime. A key step in the caustic recovery is the leaching of hydroxide from the titanate compound and precipitate out sodium carbonate. Experimental results of simultaneous leaching and precipitation are in good agreement with the theoretical expected values. All together makes the CO₂ capture from air using an alkaline based system to be a plausible process to consider as for the mitigation of climate change.

5. Acknowledgment

The authors would like to acknowledge Mike Foniok and Brandon Hart for performing the CO₂ capturing experimental tests in the scrubber, Alessandro Biglioli for managing the scrubber setting up, Dr. Frank Zeman for helping with the design of the scrubber and his insights on chemical engineering aspects of the capturing process, and Dr. Christelle Guillermier for developing the Labview code to record data from the sensors. We also acknowledge Carolyn Ladd for performing experimental works on simultaneous leaching and precipitation, Dr. Curtis Berlinguette for the fruitful discussion on leaching chemistry and experimental set up, Maurice Shevalier and Michael Nightingale for their insights in samples analysis and Dr. Marco Satyro for providing us VMGSim software to do process simulation,

References

1. Canadell J.G. et al., 2007. Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity and efficiency of natural sinks. *Proceedings of the National Academy of Sciences*. 104(47), 18866-18870.
2. Spector N.A., Dodge B.F., 1946. Removal of carbon dioxide from atmospheric air. *Trans. Am. Inst. Chem. Eng.* 42, 827-848.
3. Tepe J.B., Dodge B.F., 1943. Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. *Trans. Am. Inst. Chem. Eng.* 39, 255-276.
4. Lackner K.S., Grimes P., Zioc H.J., 1999. Capturing carbon dioxide from air. 24th Annual Technical Conference on Coal Utilization: Clearwater, FL.
5. Baciocchi R Storti, G, Mazzotti M., 2006. Process design and energy requirement for the capture of carbon dioxide from air. *Chemical Engineering and Processing*. 45, 1047–1058.
6. Zeman F., 2007. Energy and material balance of CO₂ capture from ambient air. *Environmental Science & Technology*. 41, 7558-7563.
7. Storaloff J. K., Keith D.W., Lowry G.V., 2008. Carbon dioxide capture from atmospheric air using sodium hydroxide spray. *Environmental Science & Technology*, 42: 2728-2735.
8. Zeman F. and Lackner K., 2004. Capturing carbon dioxide directly from the atmosphere. *World Resource Review*. 16(2), 157-172.
9. Chen X. And van Heiningen A.R.P., 2006. Kinetics of the direct causticizing reaction between sodium carbonate and titanium dioxide or sodium tri-titanate. *Journal of Pulp and Paper Science*. 32(4), 245-251.
10. Kiiskilä E. 1979a. Recovery of sodium hydroxide from alkaline pulping liquors by smelt causticizing, Part II. Reactions between sodium carbonate and titanium dioxide. *Paperi ja Puu, Papper och Trä*. 5, 394-401.
11. Kiiskilä E., 1979b. Recovery of sodium hydroxide from alkaline pulping liquors by smelt causticizing, Part III. Alkali distribution in titanium dioxide causticizing. *Paperi ja Puu, Papper och Trä*. 6, 453-464.
12. Nohlgren I., 2002. Recovery of kraft black liquor with direct causticization using titanates. PhD thesis. Lulea University of Technology, Lulea, SWEDEN.
13. Palm M. and Theliander H., 1997. Kinetic study of the direct causticization reaction involving titanates and titanium dioxide. *Chemical Engineering Journal*. 68, 87-94.
14. Zeng L. and van Heiningen A.R.P., 1997. Pilot fluidized-bed testing of kraft black liquor gasification and its direct causticization with TiO₂. *Journal of Pulp and Paper Science*. 23 (11), J511-J516.
15. Zou X., 1991. Recovery of Kraft Black Liquor Including Direct Causticization. Ph.D. Thesis. McGill University, Montreal, Quebec.
16. Mahmoudkhani M. and Keith D.W. 2008, Low-energy sodium hydroxide recovery for CO₂ capture from air. *International Journal of Greenhouse Gas Control Technologies*, In review .