

DUAL ALKALINE APPROACHES FOR THE CAPTURE AND DISPOSAL OF CO₂

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Abstract

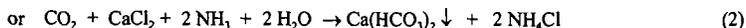
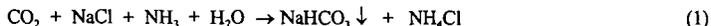
A new method being investigated to capture CO₂ uses a dual alkaline approach with the use of chloride salts in an alkaline solution. The capture of CO₂ leads to the precipitation of environmentally benign bicarbonate salts, which can be safely disposed of in the ground or ocean. A secondary alkaline is then employed to regenerate the first alkaline at ambient temperatures. During regeneration of the secondary alkaline, hydrochloric acid is produced which is subsequently injected into the ground to produce calcium chloride. The aqueous solution of calcium chloride can be either safely stored in the ground or pumped out as a salt source for the initial capture step. Another source of salt is the sodium chloride naturally available in the ocean. The dual alkaline approach offers an alternative method for CO₂ capture, separation, and disposal with the advantage of being able to avoid any new environmental problems that might occur as a result of the storage of supercritical CO₂ liquid.

1. Introduction

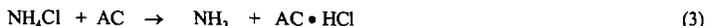
The existing approach for the sequestration of CO₂ from stationary power plants involves two steps: 1. The use of an amine (as an alkaline) to capture CO₂ from flue gas followed by steam stripping of the absorbed CO₂ at high temperatures, 2. The concentrated CO₂ gas is then pressurized to a supercritical CO₂ liquid for disposal in geologic formations and/or the deep ocean. It is known that both steps are energy intensive, especially the first step which accounts for two thirds to three fourths of the entire cost. Also, the reagent loss is substantial if flue gas contains a large amount of SO₂ and NO_x due to the difficulty in regenerating amines from heat stable salts such as amine sulfates or nitrates. Additional energy is also needed to pressurize the CO₂ gas into supercritical liquid for injection into the ground or deep-ocean. Besides the high cost of implementing the existing CO₂ sequestration approach, there is a concern about the ecological consequence resulting from the storage of CO₂ in the ocean and geological formations.

An alternative approach is the conversion of CO₂ to carbonate salts that can be safely returned to the environment. Weathering of alkaline rocks is a natural method of CO₂ sequestration. To enhance the rate of the natural process, Kojima et al. suggested that alkaline minerals could be pulverized, dissolved, and reacted with power plant CO₂ to form magnesium and calcium carbonates. Lackner et al. has extensively investigated the thermodynamics and processes of using chlorides to accelerate the carbonate formation from various minerals, including Serpentinite and Peridotites.

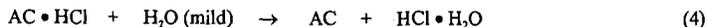
With previous research on the conversion of CO₂ to benign carbonate in mind, a new method is addressed, a dual alkaline approach. The approach involves the use of a salt in an alkaline solution, such as ammonia, to capture CO₂, leading to the formation of a bicarbonate salt.



We have found that an activated carbon (AC), a secondary alkaline in solid form, can then be employed to regenerate the first alkaline at ambient temperature (25°C).



The AC can then be regenerated by the extraction of the adsorbed hydrochloric acid with water washing at a mild temperature (<100°C).



The hydrochloric acid extracted by the water may then be injected into the ground where it would react with calcium silicate minerals to produce calcium chloride.



The aqueous solutions of calcium chloride produced underground can either be safely stored in the ground or provide a source of salts for the first step as shown in Eq. (2). In addition to the man-made salts produced by Eq. 5, another source of salt is brine (NaCl), which can be obtained from the ocean.

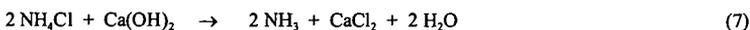
The dual alkaline approach requires low temperatures and little heat input in the regeneration of bases. The approach is self-sustaining, the needed chloride salt is supplied by the ground (Eq. 5) or can be obtained at low costs from the ocean (about \$5/ton sodium chloride based on Encyclopedia of Chemical Technology, Kirk-Othmer, Vol 21), which is especially suitable for power plants located near the coast.

Proven Process

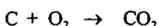
Ammonia has been demonstrated to be an effective catalyst for the reaction of CO₂ with sodium chloride in the production of sodium carbonate (the Solvay process). The reaction was performed by first saturating brine with ammonia, and then with carbon dioxide.



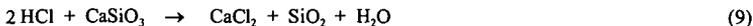
Following the reaction, sodium bicarbonate, which is fairly insoluble, was separated by filtration. Sodium carbonate is subsequently obtained by heating sodium bicarbonate. The ammonia was recovered by the reaction of ammonium chloride with lime, Ca(OH)₂ where limestone served as the source of lime



However, this scheme poses several drawbacks when applied to coal-fired power plants. Among others, the use of limestone for the regeneration of ammonia renders the process ineffective mainly because for every mole of CO₂ captured and transformed, two moles of NaCl are consumed, wasting a mole of NaCl that is needed to react with CO₂ produced during the calcination of limestone to lime:



To circumvent these drawbacks, activated carbon is used as a base to replace lime for the regeneration of ammonia. The HCl subsequently produced may be disposed of by reacting it with silicate minerals to produce benign CaCl₂ and SiO₂. This reaction is performed in subsurface areas by injecting HCl underground, where silicates are abundant in the Earth's crust. Plagioclase (NaAlSi₃O₈ or CaAl₂Si₂O₈), Feldspar (KAlSi₃O₈), and Amphibole [(Ca, Mg, Fe),Si₈O₂₂(OH)₂] constitute about 42%, 22%, and 5% in vol, respectively.



The soluble CaCl₂ salt may be pumped out of the ground for use in the fixation of additional CO₂ according to Eq. (2).

2. Experimental Approaches and Results

The use of an aqueous solution of ammonia and sodium chloride for the reaction with CO₂ to produce sodium bicarbonate precipitate is a proven process as mentioned previously. After the reaction and the separation of a sodium bicarbonate precipitate, the remaining solution contains ammonium chloride.

We have discovered that ammonium chloride can be separated into hydrochloric acid and ammonia. Experiments were performed by passing an aqueous solution of ammonium chloride ($\text{pH} = 4.7$) through a column of activated carbon. The resultant liquid was analyzed by ion chromatography. Results indicated that the liquid after the column contained more ammonium ions than chloride ions (Figure 1). The pH of the liquid also increased from 4.7 to as high as 9.5, indicating that the ammonia is regenerated from the ammonium chloride solution.

The kinetics of the decomposition of ammonium chloride and subsequent adsorption of hydrochloric acid by the acid adsorbent was studied. It was found that the reaction order was first order and 0.617 order with respect to the concentration of the adsorbent and ammonium chloride, respectively (Figure 2). The temperature dependence on the adsorption of hydrochloric acid from an ammonium chloride solution was investigated. The Van't Hoff plot indicates that the adsorption is exothermic (-2.48 kcal/mol).

The regeneration of the activated carbon with water as a function of temperature was also investigated. The kinetics of the desorption of hydrochloric acid from the adsorbent was studied at 298, 313, 333, 353, and 373°K (Figure 4). The desorption rate increased with an increase in temperature. The Van't Hoff plot showed that the enthalpy of the desorption of hydrochloric acid was 6.25 kcal. This energy was substantially less than that (47.85 kcal) required in the regeneration of MEA from an MEA-carbamate.

The capability of repeated use of the activated carbon was also demonstrated. Several cycles were performed (Figure 5). The results show that the cyclic process can sustain itself.

3. Conclusion

The research performed has demonstrated that: 1. It is feasible to capture CO_2 and directly transform it into a bicarbonate precipitate using an aqueous mixture of an alkaline and a chloride, 2. It is possible to regenerate ammonia from an ammonium chloride solution using an activated carbon. Future work includes the study of the effectiveness of different types of activated carbon and adsorbents for the regeneration of ammonia from ammonium chloride solutions.

Acknowledgments

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Reference

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Fig. 1 Production of NH₃ from NH₄Cl using Carbon

Conditions: 10 g AC, 100 ml 10 mM NH₄Cl solution was pumped at 1 ml/min flow rate at room temp.

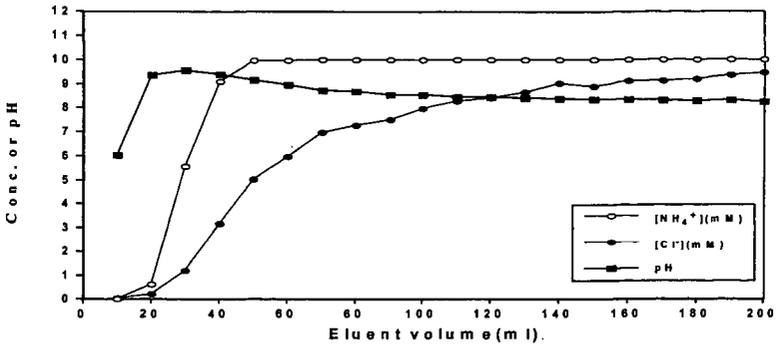


Fig. 2 Reaction order for the adsorption of HCl from NH₄Cl by Carbon

Conditions: 2g AC, 100ml L NH₄Cl solution, room temp., stirring speed: 800 rpm

Forward reaction rate expression: Rate = 0.0028 [AC][NH₄Cl]^{2.517}

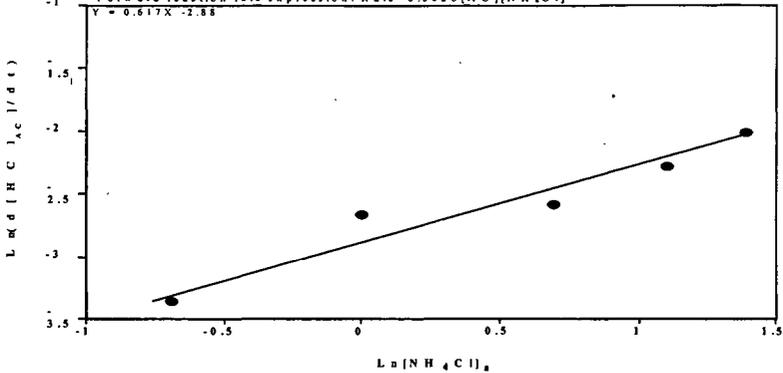


Fig. 3 Van't Hoff plot for adsorption of HCl on Carbon from NH₄Cl solution

Conditions: 10 g AC, 500 ml 2M NH₄Cl solution, stirring speed: 800 rpm at 293, 313, 333, 353 K, respectively

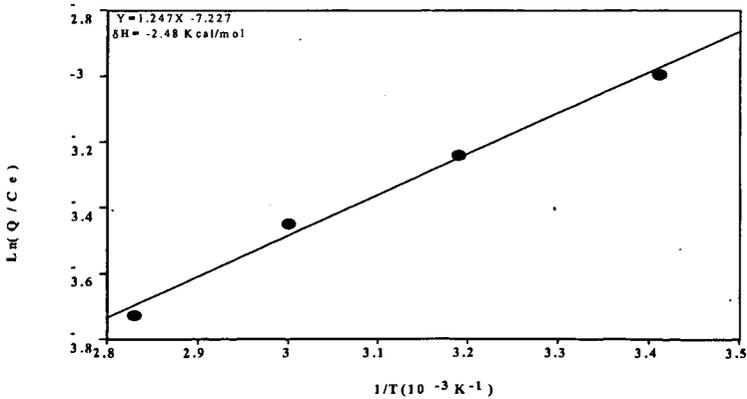


Fig. 4 Van't Hoff plot for desorption of HCl from Carbon in water

Conditions: 10 g AC, 500 ml, 2mM NH₄Cl solution, stirring speed: 800 rpm at 298, 313, 333, 353, 373 K, respectively

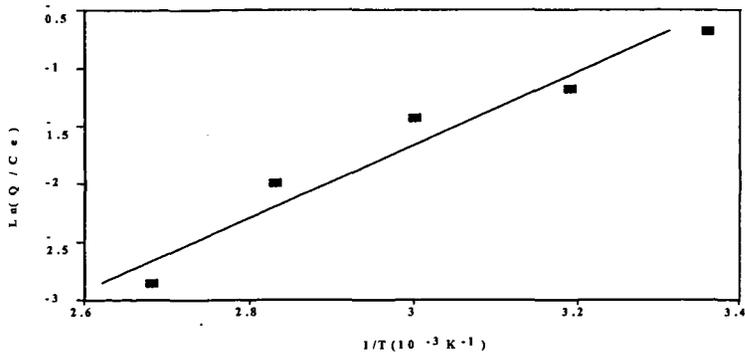


Fig. 5 Regenerability of Carbon for HCl adsorption

Conditions: 2 g AC adsorbed 1.225 mM HCl from 100ml 1.3 mM HCl solution at room temp. The desorption was run at 100 ml boiling water, and adsorption was run at the same solution after cooling overnight.

