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A new process for the capture of CO_2 and reduction of water salinity

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HIGHLIGHTS

- A new process for CO_2 capture and water desalination has been developed.
- It is based on a Modified Solvay process without using ammonia.
- It is more efficient in CO_2 capture and Sodium reduction than the Solvay process.
- The new process can achieve 99% CO_2 capture efficiency and 35% Sodium removal.
- The energy requirements are much lower than that of the Solvay process.

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ABSTRACT

The present work evaluates a new process for the capture of CO_2 and the reduction of water salinity. It is based on the Solvay process without the use of ammonia and involves the reaction of CO_2 with saline water such as reject brine in the presence of calcium hydroxide. The effects of operating parameters such as reaction temperature, water pH and reaction stoichiometry on CO_2 capture efficiency and sodium removal were examined for both traditional and modified Solvay process. The optimum conditions for maximum CO_2 capture efficiency and sodium removal were determined using response surface methodology and were found to be at temperature of 20 °C and a pH of greater than 10 for both processes. At the optimum conditions, CO_2 capture of 86% and 99% and sodium removal of 29% and 35% were achieved for the traditional Solvay and the Modified process, respectively. The water pH was found to be a key parameter in the effectiveness of the reaction process; higher pH leads to better process performance in both CO_2 capture efficiency and sodium removal. The experimental results clearly illustrated that the Modified Solvay process is superior in terms of CO_2 capture efficiency, sodium removal and energy consumption.

1. Introduction

Climate change and variability is an evident phenomena around the world and can be attributed to global warming. Most of the observed increase in global average temperatures is very likely due to the observed increase in the concentrations of greenhouse gases such as CO_2 in atmosphere. CO_2 is a major contributor to global warming, and it is often emitted by various activities associated with industrial processes and the burning of various types of carbonaceous fuels [1]; it is believed to cause approximately 55% of global warming [2]. Relying on fossil fuels as the main source of energy in many parts of the world has contributed to the rise of CO_2 emissions to unprecedented levels [3]. Many industries such as natural gas sweetening, hydrogen production for ammonia and ethylene oxide, oil refineries, iron and steel production facilities, desalination and power plants, cement and limestone manufacturing plants represent major sources of CO_2 emissions. In recent years, there has been an increased interest in carbon capture and storage (CCS) as an option to reduce the CO_2 emissions. CCS is based on the separation and capture of carbon dioxide produced by fossil fuel power plants or other sources either before or after combustion [1]. A number of CO_2 capture technologies have been used in many processes such as oxy-fuel combustion, post-combustion, pre-combustion and chemical looping combustion. Among the post-combustion capture techniques, the most promising and most effective are adsorption using solid sorbents [4], solvent absorption [5], cryogenic fractionation technology [6] and membrane separation [7]. CO_2 capture using chemical solvent is one of the most promising technologies for decreasing the rising emissions of greenhouse gases [8]. Key parameters for selecting an effective solvent for CO_2 absorption include high absorption, fast reaction

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kinetics, low degradation rate, and low regeneration energy [9] as well as the ability to handle large amounts of exhaust streams [10]. The most common solvents used for CO_2 capture are amines (either in aqueous solution or immobilized on solid support) [11] and aqueous ammonia [12]. Aqueous ammonia is considered to be a competitive option for CO_2 capture due to low chemical cost, corrosiveness and relatively low regeneration temperature [13].

The ammonia-based Solvay process has recently been considered for the capture of CO_2 and the production of useful and reusable carbonate products, as well as the desalination of saline water [14]. The Solvay process is used for sodium carbonate (soda ash) manufacturing, where carbon dioxide and ammonia gas are passed through a saturated sodium chloride solution to form soluble ammonium chloride and a precipitate of sodium bicarbonate according to Reaction (1) below. The sodium bicarbonate is heated to form the washing soda; whereas the ammonium chloride solution is mixed with calcium hydroxide and heated to recover the ammonia according to Reactions (2) and (3), respectively.

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl \quad (1)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad (2)$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \quad (3)$$

Several studies and patent applications have described Solvay-based approaches for the capture of CO_2 and desalination of high salinity water [14–17]. One of the major drawbacks of the Solvay process is the presence of ammonia, which is considered an environmental and health hazard. Exposure to high concentrations of ammonia can cause severe injuries such as skin, nose, throat and respiratory tract burning, which can be a reason of alveolar and bronchiolar edema and airway annihilation, leading to respiratory failure [18]. Ammonia is not involved in the overall Solvay reaction, but it plays a key role in buffering the solution at a basic pH; without ammonia, the acidic nature of the water solution will hinder the reaction and hence prevent the precipitation of sodium bicarbonate [14]. In addition to the safety concerns, the ammonia recovery process through Reaction (3) is an energy intensive step that adds to the overall cost of the process. The aim of the current study, therefore, is to modify the Solvay process to reduce or eliminate the drawbacks associated with the presence of ammonia and then use the modified process for the capture of CO_2 and reduction of water salinity. In addition, carry out a comparative evaluation of the Solvay (S) and the Modified Solvay (MS) processes in terms of CO_2 capture efficiency, sodium ion removal and energy demand.

2. Modification of Solvay process

In the original Solvay process, concentrated brine is ammoniated through direct contact with ammonia gas and then contacted with CO_2 in a bubble column reactor. The product which contains soluble ammonium chloride and precipitate of sodium bicarbonate is sent to a filter to remove the sodium bicarbonate. The remaining solution is reacted with calcium hydroxide to recover the ammonia, which is then sent again to the ammonization step. The proposed modification of the Solvay process does not involve the use of ammonia. Instead, calcium oxide is added directly to the bubble column reactor, which converts to calcium hydroxide as soon as it contacts the brine, raises the pH and captures CO_2 by reacting with sodium chloride according to the reaction given below:

$$2NaCl + 2CO_2 + Ca(OH)_2 \rightarrow CaCl_2 + 2NaHCO_3 \quad (4)$$

Calcium oxide or calcium hydroxide could be obtained from any alkaline solid waste products to avoid the need of calcination to produce CaO according to the following reaction at high temperature [19].

$$CaCO_3 \rightarrow CaO + CO_2 \quad (5)$$

However, according to this reaction, the production of one mole of CaO results in the generation of one mole of CO_2, while in the Modified Solvay process, each mole of $Ca(OH)_2$ can be used to capture two moles of CO_2. The process has the dual benefit of brine desalination and carbon dioxide capture. In addition, the process eliminates the need for ammonia recovery (Reaction (3)) which is an energy intensive step in the Solvay process.

3. Thermodynamic analysis

HSC Chemistry 6.1 software [20] was used to perform a thermodynamic analysis based on sodium chloride as the main reactant in the reject brine. The software was used to define the equilibrium composition for Reactions (1) and (4) at different temperatures and to evaluate the heat of reaction as a function of temperature. Gibbs free energy minimization method was used to determine the number of moles present at equilibrium for any species at a fixed temperature and pressure [21]. Tables 1 and 2 present the calculated thermodynamic properties for Reaction (1) and (4), respectively. The analysis indicates that both reactions are spontaneous for the whole temperature range (0 to 90 °C) as indicated by the negative ΔG. The changes in the heat of reaction from (0 to 100 °C) for both reactions are negative, which indicates that the reactions are exothermic (at 20 °C, ΔH is −129 kJ/kmol for Reaction (1) and −208 kJ/kmol for Reaction (4)). Since a more negative ΔG indicates more spontaneous reactions [22], the Modified Solvay process is more spontaneous than the traditional Solvay process at 20 °C with ΔG of −56 kJ/kmol and −26 kJ/kmol, respectively. It is also worth noting that calcium carbonate formation (Reaction (6)) may take place and compete with the formation of sodium bicarbonate.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (6)$$

However, thermodynamic analysis indicated that Reaction (6) is only competitive when calcium oxide is present at amounts greater than or equal to the stoichiometric ratio. The formation of sodium bicarbonate can be favored by controlling the amount of $Ca(OH)_2$ in the reaction [23].

4. Experimental evaluation

4.1. Experimental apparatus

Both Solvay and the Modified Solvay processes were evaluated experimentally using desalination reject brine in a bubble column reactor. Experiments were carried out in a stainless steel jacketed, bubble column reactor with an internal diameter of 78 mm and an overall height of 700 mm. The reactor was operated in a semi-batch mode, where the

Table 1
Thermodynamics data of Reaction (1).

Temperature (°C)	ΔH (kJ/mol)	ΔS (J/mol·°C)	ΔG (kJ/mol)
0	−124	−332	−33
10	−129	−353	−29
20	−129	−352	−26
30	−129	−352	−22
40	−129	−351	−19
50	−128	−350	−15
60	−128	−349	−12
70	−128	−348	−8
80	−127	−347	−5
90	−127	−346	−1
100	−127	−346	2