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Simultaneous carbon dioxide capture and utilization using thermal desalination reject brine

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HIGHLIGHTS

- The simultaneous capture and utilization of CO_2 with reject brine is feasible.
- The use of 2 amino 2 methyl propanol (AMP) resulted in high precipitation yield.
- The proposed amine process is a good replacement for ammonia in the Solvay process.
- Higher brine concentration improved the CO_2 absorption capacity.

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ABSTRACT

This study evaluated the feasibility of a chemical process which uses desalination brine to convert CO_2 into useful sodium bicarbonate. The process is based on the integration of a modified Solvay process with conventional amine based post-combustion carbon dioxide capture for the simultaneous capture and conversion of CO_2 into solid bicarbonates. A range of amine solvents were evaluated to select the most suitable solvent for the process. Then the effects of parameters such as temperature, brine concentration and amine concentration on the carbonation step of the process were evaluated. Moreover, different techniques for recovering the amine from the chloride rich solution were proposed and investigated.

The sterically hindered amine, 2-amino, 2-methyl propanol (AMP), was found to be the best alcohol amine for the process and the CO_2 absorption step was found to be significantly improved at lower temperatures, high brine concentrations and moderate amine concentration. For AMP, the optimum concentration was found to be 30 wt%. Finally, the amine recovery technique tested showed promise and could be optimized further to give better results.

1. Introduction

Carbon Capture and Storage (CCS) has been recognized as a technology capable of playing a vital role in mitigating the risks associated with climate change [1]. However its implementation on a large scale by sources of CO_2, like power plants and cement factories, has been slow due to a number of issues. The most important among these issues include the high capital and operating costs required and the general lack of understanding of the technology which has inspired fear and opposition among members of the public [2,3]. Also, the vagueness on the part of authorities and policy makers regarding how CCS will be implemented and how liabilities will be distributed among the stakeholders has been cited as a major barrier to the deployment of CCS [4]. In the absence of a strong policy commitment which will minimize the economic risks of CCS, many investors have shied away from undertaking CCS projects, causing the technology to grow at a much slower rate than what is required to meet the 2050 target of reducing global CO_2 emissions to 15 Gtpa [5].

Recently, there has been an emerging consensus in the CCS community that one of the strategies for encouraging investment in CCS is to show a successful business case for it [6]. To enable investors see CCS projects not just as a noble activity to save the planet but also as something which can have a positive impact on the balance sheet. The only way CCS can fulfill this business mandate is through the sale of captured CO_2 to third parties who would utilize it for the manufacture of other useful products like chemicals and synthetic fuels thereby providing a moderate revenue stream to offset some of the costs of CCS.

As a matter fact, CO_2 utilization has been a major driver of large scale CCS projects in the past few years. The Global CCS Institute

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reported that 70% of all projects in operation, construction, or financial investment decision phase of their asset life are all related with enhanced oil recovery (EOR) [7], strengthening the notion that CO_2 utilization can support CCS deployment in its early stages of development.

It is therefore important to seek out existing technologies, or develop new ones which will consume CO_2 at a scale which is large enough to generate revenue that can offset some of the cost of CCS. A host of technologies both existing and emerging are available for utilizing CO_2. They include but are not limited to Enhanced oil recovery (EOR), food processing, packaging and preservation, urea yield boosting, supercritical CO_2 as a solvent, algal bio-fixation, and baking soda manufacture (sodium bicarbonate) [8,9].

In the Arabian Gulf countries like the UAE, water supply is a big problem due to the low rainfalls and depleting levels of underground water resources [10,11]. Meanwhile rising population [12], urbanization, and wasteful consumption patterns [13] continue to fuel water demand. The challenge now is to meet a rising water demand with a dwindling supply of fresh water. It is estimated that by 2015, the renewable water resources (annual amount of water available to recharge groundwater and streams through precipitation and inflow of water outside the country) of the region will be able to satisfy only 67% of the demand [14].

For this reason, desalination is heavily relied upon for the production of potable water. At present there are more than 199 plants and there are plans to add 38 more in the future [15]. The total seawater desalination capacity of the Gulf countries is about 5 billion m^3/year translating to about 45% of the global desalination capacity [15]. Since the desalination processes are generally energy intensive, desalination plants are usually integrated with Power plants in the Gulf region [16].

A major drawback of the desalination process is the highly concentrated brine waste which is usually deposited into the sea. It is estimated that for every 1 m^3 of desalinated water, 2 m^3 is generated as reject brine [15] containing, alongside high salt concentrations, residues of pretreatment chemicals and heavy metals due to corrosion. The reject brine has the potential to destabilize local seawater conditions, such as temperature and salinity, and constitute significant threat to marine life [17]. Increased temperature can affect water quality processes and result in lower dissolved oxygen concentrations which are vital for the survival of aquatic life and the increased level of salt concentration in the Gulf sea would make desalination processes more difficult and expensive [18]. Therefore, it is necessary to find a way to de-concentrate reject brines before disposal in order to mitigate their harmful impact on the environment.

Today, as Gulf countries begin to embrace CCS in the bid to reduce their high per capita CO_2 emissions, it is important to consider CO_2 utilization opportunities offered by another environmental problem which is the highly concentrated brine waste coming from desalination plants [19]. The idea is to simultaneously capture, sequester and utilize CO_2 from power plants with the reject brines from desalination plants to produce saleable solid carbonates while reducing the salinity of the brine in the process. Na^+ ions from the brine can be carbonated via the Solvay process [20] to give sodium bicarbonate and soda ash which are essential precursors for various industrial processes. These products can then be sold to generate revenue which would lower the cost burden of CCS and encourage its deployment in the region [21].

The Solvay process uses ammonia as a catalyst to aid the reaction of CO_2 with sodium chloride for the production of sodium carbonate. This reaction is performed by first saturating brine with ammonia, and then with carbon dioxide. Following the reaction, sodium bicarbonate, which is fairly insoluble, is separated by filtration and the ammonia is recovered from the solution by reacting it with CaO.

While the Solvay process has been successfully applied for the commercial manufacture of Soda ash, its use for purposes such as CO_2 capture and brine treatment gives rise to some new challenges. The classical Solvay process has a low percentage conversion of sodium [22] which makes it inadequate for processes such as reject-brine treatment where sodium conversion (or removal) is a main process objective. Furthermore, unlike the Solvay process where a pure CO_2 stream is used to carbonate brine, for our purposes, the brine will be used to extract CO_2 from a dilute, low pressure stream of flue gas. And this raises important questions about the suitability of ammonia for our proposed process.

Although ammonia has been shown to be suitable for the absorption of CO_2 from flue gases, its use is problematic due to its high volatility at the operating temperatures of CO_2 capture processes [23,24]. For this reason, it is desirable to find other amines which can take the place of ammonia in the Solvay process.

Alkanolamines which are already being used in amine-based post combustion carbon capture processes are very good options considering their relatively higher thermal stability and CO_2 capacity [25]. Huang and coworkers showed a modified Solvay process which uses a sterically hindered amine, Methylaminoethanol (MAE), in the place of ammonia with good result. However, they were unable to recover the amine from its chloride salt so that it can be recycled and to also prevent its discharge into the environment [26].

The aim of the current work is to address the aforementioned problems which have been previously encountered during the modification of the Solvay process for CO_2 capture applications. This will be done by evaluating the potential of different alcohol amines, other than MAE, as replacements for ammonia in the Solvay process. Optimum carbonation conditions such as temperature, and amine/NaCl ratios which have been previously obtained for ammonia will be determined for the most suitable amine. While earlier work on the adaptation of Solvay process for carbon capture have focused only on the carbonation step, this work goes beyond that to address the problems of the subsequent stage involving chloride removal by developing and evaluating a technique for recovering amine from their chloride salts and by characterizing the solid precipitates obtained from the carbonation of the amine/brine solvent mixture.

1.1. Proposed process description and evaluation

The proposed process scheme is shown in Fig. 1. It consists of three major units namely carbonation, filtration, and the chloride and amine recovery units. In the carbonation unit, power plant flue gas is brought in contact with reject brine from desalination plants pre- mixed with alcohol amine. During the carbonation, CO_2 from flue gas dissolves in the solvent and reacts with Na^+ present in the brine to give a sodium bicarbonate precipitate while the gas exits as a CO_2 free gas. The precipitated $NaHCO_3$ is separated in the filtration unit and the liquid portion containing dissolved CO_2 and amine chloride is sent to the recovery unit. The main aim of the recovery unit is to free up amines from their chloride salts so that they can absorb CO_2 when returned to the carbonation step and to also control the build-up of chloride in the system which promotes corrosion and, ultimately, causes damage to plant equipment.

Two ideas were considered for recovering the amine from its chloride salt. The first technique is based on conventional lime method used in the Classical Solvay process. In the Solvay process, ammonia is recovered from ammonium chloride by the reaction with lime water and then sending the reaction mixture to a distillation column from where ammonia is recovered as distillate and the bottom sludge evaporated and dried to give calcium chloride.