Technical viability and exergy analysis of membrane crystallization: Closing the loop of CO_2 sequestration

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ABSTRACT

The potential of membrane crystallization has been studied for the recovery of Na_2CO_3 from aqueous streams, as a tool that can be used in CO_2 sequestration. The influence of various crystallization conditions (i.e., concentration and flowrate of the Na_2CO_3 solution, concentration and flowrate of the osmotic solution and kind of osmotic solution: NaCl or $MgCl_2$) on the process performance has been determined. The concentration of the osmotic solution was found to be the key parameter that may condition the applicability of the system. The flowrate of the Na_2CO_3 solution has also an important influence on the mass transfer through the membrane. Thus, concentration polarization may occur since the transmembrane flux increases with the flowrate. In addition, the characterization of crystals demonstrated that $Na_2CO_3 \cdot 10H_2O$ crystals were obtained. An exergy analysis was made for the membrane contactor. The higher the concentration of NaCl, the higher the exergy of the outlet streams. It yields a positive variation of exergy, reaching a maximum value at a specific Na_2CO_3 concentration. In addition, a range of concentrations can be established in order to operate under conditions of positive exergy variation. Increasing the flowrates of the feed or osmotic solutions has also an effect on the exergy variation, reaching an asymptotic value.

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1. Introduction

Carbon dioxide is the most critical greenhouse gas and its capture and recovery for further reuse or storage is being intensively researched to develop most efficient and modern methods (Luis et al., 2012). Several technologies and strategies are considered, depending on the application (Aaron and Tsouris, 2005; Kuramochi et al., 2012; Luis et al., 2011; Merkel et al., 2010). Both pre-combustion and post-combustion oriented technologies involve the separation of CO_2 from a gas mixture, composed of CO_2 and H_2 in the first approach and CO_2 diluted in air and other combustion gases, such as sulphur dioxide or nitrogen oxides, in post-combustion. Absorption using amines (e.g., using monoethylamine, MEA) is the reference technology to separate CO_2 from flue gases in a post-combustion scenario, where an absorber removes CO_2 and a regenerator (or stripper) releases the CO_2 in a concentrated form and the original solvent is recovered (Aaron and Tsouris, 2005; Ebner and Ritter, 2009; Olajire, 2010). For the pre-combustion capture approach, due to the high concentration of CO_2 in the high pressure gas, physical solvents (mixture of dimethyl ethers of polyethylene glycol in Selexol process or refrigerated

methanol in Rectisol process) are used to take advantage of the high pressure of the gas stream (Figueroa et al., 2008). Both processes are very intensive from the point of view of energy and material consumption (Luis et al., 2012). Changing the organic solvent for other more environmentally friendly solutions, such as water-based solutions, are proposed in the recent literature (El-Naas et al., 2010; Mansourizadeh et al., 2010; Zhang et al., 2010). For example, sodium hydroxide has shown high CO_2 removal efficiency but its further reuse is still subject of research. When an aqueous alkaline solution is used as the liquid absorbent, CO_2 reacts with the hydroxyl ions within the liquid film as follows (Mansourizadeh et al., 2010):

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (R1)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} \qquad (R2)$$
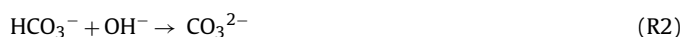
where reaction (R1) is the second order in the forward direction and the carbonization reaction (R2) is much faster than reaction (R1). Thus, the carbonate is formed in solution and its reuse is conditioned by the further purification steps. Alkaline absorption has also achieved much attention in the direct capture of CO_2 from ambient air, "air capture", in order to manage dispersed emissions, such as transportation (Mahmoudkhani and Keith, 2009). But the main challenge that has to be solved to close the loop by reusing the carbonate (e.g., $NaCO_3$) or recovering the reagent (e.g., NaOH) and the pure CO_2 is the development of a process that allows

obtaining the dried carbonate (e.g., Na_2CO_3). It may be reused directly as reagent in the industry (e.g., in the ceramic industry) or it can be converted back to sodium hydroxide and pure CO_2 by means of, for example, a causticization process with $Ca(OH)_2$ (Mahmoudkhani and Keith, 2009).

This work is focused on developing a process in which the carbonate, Na_2CO_3, can be obtained in optimal conditions for further reuse. Membrane crystallization is proposed as the technology to crystallize Na_2CO_3 since it has demonstrated a high potential for the recovery of salts from concentrates (Curcio et al., 2010; Drioli et al., 2004, 2005; Ji et al., 2010; Kim, 2011). Crystallization of ionic salts (Kieffer et al., 2009a,b; Watanabe and Akashi, 2009), metal ions (Tang et al., 2010), low molecular organic acids (Curcio et al., 2003; Kuhn et al., 2009), proteins and pharmaceutical compounds (Di Profio et al., 2005, 2007, 2009; Zarkadas and Sirkar, 2006; Zhang et al., 2008) are examples of the applicability of this technology. In addition, the main advantages of membrane crystallization have been already demonstrated: (1) it is possible to control the maximum level of supersaturation due to a defined mass transfer through the membrane (Charcosset, 2009); (2) the membrane induces heterogeneous nucleation; (3) size, shape and purity of crystals can be controlled; (4) there is a significant reduction of energy consumption compared to conventional crystallization by means of cooling or evaporation (Drioli et al., 2006); and (5) comparable or slightly higher nucleation rates with respect to batch crystallizers or tubular precipitators have been obtained (Zarkadas and Sirkar, 2006). Furthermore, the use of membranes has been already considered to satisfy the requirements established by the "process intensification" strategy (Criscuoli and Drioli, 2007; Drioli and Curcio, 2007; Van Gerven and Stankiewicz, 2009).

The basic concept of membrane crystallization consists of a technique in which crystal nucleation and growth is carried out across a well-controlled pathway, starting from an undersaturated solution, by adjusting solution composition (supersaturation) by means of a membrane (Di Profio et al., 2010). The membrane acts as a barrier that separates the feed stream (with the compound to crystallize) and the stripping stream, which consists of a hypertonic solution of inert salts (NaCl, $CaCl_2$, etc.) that enhances mass transfer of water in the vapor phase from the feed to the stripping side, resulting in the supersaturation of the feed stream under isothermal conditions. Thus, the membrane is not selective and the separation is based on the phase equilibrium (Curcio and Drioli, 2005). Examples of hypertonic solutions can be the brines obtained from integrated membrane desalination systems, reaching concentrations higher than 250 g/L of salt (Criscuoli and Drioli, 1999), of which the recovery and/or reuse is subject of further study (Charcosset et al., 2010; Rodríguez-DeLaNuez et al., 2012; Van der Bruggen et al., 2003; Van der Bruggen and Braeken, 2006). In addition, the porous surface of the membrane induces heterogeneous nucleation (formation of nuclei locally close to the surface) while the crystal growth can be produced in a separate place. The driving force for the isothermal transport of volatile compounds through the membrane is given by a partial pressure gradient due to an activity difference between the solutions contacting the membrane (Curcio and Drioli, 2005). This gradient induces evaporation of the solvent at the liquid/membrane interface on the feed side, the migration of the solvent in vapor phase through the porous of the membrane and its recondensation at the membrane/liquid interface on the stripping side. The continuous removal or solvent from the feed solution increases the solute concentration and generates supersaturation (Di Profio et al., 2010). The main requirement is the use of hydrophobic membranes in order to ensure the non-wettability of the membrane. If membrane wetting occurs, the resistance to mass transfer that the membrane itself produces will increase significantly, reducing the flux of the volatile compound through the membrane and decreasing, thus, the process efficiency increasing the operation or investment costs

Table 1
Characteristics of the membrane contactor and hollow fibers.

Contactor type	Liqui-Cel® 1 × 5.5 Minimodule™
Module configuration	Hollow fibers
Housing/potting	Polycarbonate/polyurethane
Membrane type	Celgard® X50-215 Microporous Fiber
Membrane material	PP (hydrophobic)
Porosity	40%
Effective pore size	0.04 μm
Inner diameter/outer diameter	300 μm/220 μm
Active surface area	0.18 m²
Number of fibers	2300
Burst strength	27 bar
Contact angle (θ)	112° (Azoury et al., 1986)

(more time or larger membranes should be required to obtain the same production of crystals).

The nucleation rate, i.e., the rate at which the nuclei are formed, in a membrane crystallizer depends on the concentration of crystals in the magma, hydrodynamics (e.g., stirrer speed, pump impeller, rotation rate) and the difference of concentration between the mother liquor (feed solution) and the value at equilibrium (solubility) (Curcio and Drioli, 2005). Different conditions lead to different supersaturation dynamics, affecting the quantity and quality of the crystals produced (Zhang et al., 2008). Thus, their evaluation and control of supersaturation are crucial to adjust the working conditions to a specific membrane.

In this work, the crystallization of $NaCO_3$ is studied systematically in order to evaluate the effect of the following variables on the process performance and crystal characteristics: (i) concentration of $NaCO_3$ in the feed solution; (ii) concentration of salt in the stripping solution; (iii) flow rate of the feed and osmotic solution; (iv) kind of stripping agent (NaCl, $MgCl_2$); (v) stirring velocity of the feed solution. The crystal structure is evaluated and an exergy analysis of the membrane contactor is made, aiming at establishing the reference conditions and the technical viability of the crystallization process using a membrane contactor.

2. Experimental

2.1. Materials and experimental procedure

Deionized water (18.2 MΩ cm⁻¹) was used to prepare the feed and stripping solutions. $NaCO_3$ (anhydrous, Riedel-de Haën, purity >99.5%) was used to prepare the feed solution, and NaCl (AnalaR NORMAPUR, purity >99.7%) and $MgCl_2$·6H_2O (Applichem, purity >99%) were used for the osmotic solutions. The equivalent $MgCl_2$ concentration in g/L was considered in the calculations.

A hollow fiber membrane contactor (1 × 5,5 MiniModule™ Liqui-Cel®, Membrana GmbH, Germany) was used as membrane crystallizer. Details are given in Table 1. Two peristaltic pumps (Watson Marlow 503S-Belgium and Gilson Minipuls III-The Netherlands) recirculated the feed stream and the stripping stream from the cylindrical glasses to the membrane contactor in a counter-current mode with flow rates ranging from 500 to 2500 μm/s. The feed consisted of Na_2CO_3 solutions with concentrations 150 and 200 g/L. Aqueous solutions of NaCl or $MgCl_2$ with concentrations ranging between 35 and 300 g/L were used as stripping agent. The feed and stripping solutions were introduced in the lumen and shell sides of the contactor, respectively. The experiments were performed at room temperature (20 ±1 °C).

A balance was placed below the feed stream glass cylinder in order to measure the weight of the solution over time. Fig. 1 shows the setup of the process. The stripping solution was stirred with a magnetic mixer (Fisher Scientific, Belgium) at 300 rpm. A similar