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Process simulation of mineral carbonation of phosphogypsum with ammonia under increased CO_2 pressure

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ABSTRACT

The mineral carbonation of phosphogypsum offers many advantages in sequestering CO_2, solving the pollution problem of phosphogypsum stacking, and manufacturing high value-added chemical products with low energy consumption and cost. Using the Aspen Plus process simulation software, this work simulates a novel process for the mineral carbonation of phosphogypsum with ammonia under increased CO_2 pressure. This process is divided into five sections, namely, pre-carbonation, enhanced carbonation, flash separation, gas phase absorption, and $(NH_4)_2SO_4$ fertilizer production. With its large-scale application, this new process allows the sensitivity analysis of many operation conditions, identifies the optimal conditions for reducing the ammonia and energy consumption of $(NH_4)_2SO_4$ fertilizer production, and achieves a high carbonation conversion with a fast reaction rate. The optimal conditions (6 bar enhanced carbonation pressure, 1 bar flash pressure, 38 °C ammonia absorption solution temperature, 1.05 ammonia excess ratio, 1.024 CO_2 excess ratio, and 0.94 mass ratio of water to gypsum) yield the highest carbonation conversion, ammonia utilization ratio, and enhanced carbonation temperature of 99.9%, 95.2%, and 138.5 °C, respectively, all of which can help achieve a fast carbonation reaction rate.

1. Introduction

Climate change has been widely attributed to global warming, which in turn is driven by increasing CO_2 emissions [35]. These emissions must be reduced by 50%–60% by 2050 to maintain the CO_2 level in the atmosphere below 550 ppm [31]. As a promising approach for CO_2 sequestration, mineral carbonation technology (MCT) captures CO_2 in its mineral form by the reaction of this element with alkaline materials, including calcium and magnesium-rich oxides and silicates, to form environmental friendly solid carbonate products [16,22,28]. Sequestering CO_2 in solid carbonate can improve thermodynamic stability and permanence without leading to long-time environmental monitoring commitments [15,20]. MCT also has a large potential in sequestering CO_2 minerals. Natural minerals and industrial solid residuals can be used as raw materials for CO_2 mineral carbonation [12,30,5]. Solid waste also offers many advantages, such as high reactivity, fast reaction rate, and CO_2 in-situ fixation with low transportation cost or energy consumption [39,10,36].

Phosphogypsum is a main byproduct of the acid treatment of phosphate rocks in the phosphate fertilizer industry [27]. China produces 50 Mt of phosphogypsum every year, and more than 500 Mt of this material are being collected in storage ponds [38]. However, this solid waste only has an average utilization of less than 10% worldwide because of its high water content and impurity [23]. Therefore, the large-scale applications of phosphogypsum must be investigated. Phosphogypsum usually takes the form of calcium sulfate dihydrate ($CaSO_4{\cdot}2H_2O$) with approximately 90% purity and 30% CaO, thereby enhancing its potential for CO_2 sequestration [40]. The mineral carbonation of phosphogypsum for CO_2 sequestration can solve two environmental problems simultaneously (the pollution problem of phosphogypsum stacking and the greenhouse effect of CO_2 emissions) and allow the manufacturing of high value-added chemical products with low energy expenditure and cost.

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Using waste gypsum as a raw material for CO_2 mineral sequestration has recently become a hot research topic. Many laboratory experiments have been conducted to check the feasibility of the mineral carbonation of flue gas desulfurization gypsum [17,32–34,9], red gypsum [26,2–4,24], and phosphogypsum [7,8,19,41] for CO_2 sequestration and pure calcium carbonate production. Around 95% of phosphogypsum carbonation conversion requires a reaction time of more than 1 h under atmospheric conditions. To improve the reaction speed and conversion of phosphogypsum, we performed an experimental study in our laboratory and found that more than 97% of phosphogypsum carbonation conversion can be achieved within 5 min under increased CO_2 pressure conditions [41]. The main reaction for the mineral carbonation of phosphogypsum with ammonia can be expressed as follows:

$$CaSO_4{\cdot}2H_2O(s) + CO_2(g) + 2NH_3(g) \rightarrow CaCO_3(s) + (NH_4)_2SO_4(aq) + H_2O(l) \quad (1)$$

However, under the same conditions, the ammonia may react with CO_2 to form ammonium (bi)carbonate [11,14,18], and the formed ammonium (bi)carbonate in an ammonium sulfate solution must be neutralized by sulfuric acid prior evaporation and crystallization [38]. In this case, $(NH_4)_2SO_4$ fertilizer production consumes a large amount of ammonia, thereby reducing the economic benefits of the entire carbonation process. Given that ammonium (bi)carbonate is usually unstable under high temperature and relatively low pressure conditions, this material can be decomposed into ammonia and CO_2 gas via flash operation. Accordingly, the consumption of ammonia will be reduced with the released ammonia, and CO_2 gas is absorbed and recycled for the mineral carbonation of phosphogypsum.

Considering the large-scale application of this pressured phosphogypsum carbonation technology, this study uses the Aspen Plus process simulation software to simulate a novel process for the mineral carbonation of phosphogypsum. This process allows the sensitivity analysis of many operation conditions, identifies the optimal conditions for lowering the ammonia and energy consumption of $(NH_4)_2SO_4$ fertilizer production, and achieves a high carbonation conversion with a fast reaction rate.

2. Model description

Fig. 1 presents the flowchart of the entire mineral carbonation process of phosphogypsum with ammonia under increased CO_2 pressure. The process is divided into five sections, namely, pre-carbonation, enhanced carbonation, flash separation, gas phase absorption, and $(NH_4)_2SO_4$ fertilizer production. The mineralization reaction begins with pre-carbonation, which involves the mixing of ammonia-absorbed solution with phosphogypsum to form a slurry. The formed phosphogypsum slurry then reacts with pressured CO_2 in the enhanced carbonation section to form calcium carbonate, ammonium sulfate, and ammonium (bi) carbonate. The flash separation section decomposes the ammonium (bi)carbonate into ammonia and CO_2 gas. The separated ammonia and CO_2 gas are absorbed by the diluted ammonia solution in the gas phase absorption section and are further recycled in the pre-carbonation section. The remaining liquid and solid mixture is filtered to obtain calcium carbonate and ammonium sulfate liquor, with the latter being neutralized using sulfuric acid and then treated by evaporation and crystallization for $(NH_4)_2SO_4$ fertilizer production.

The above flowchart is developed using the Aspen Plus process simulation software. Given that $(NH_4)_2SO_4$ fertilizer production, which involves filtration, neutralization, evaporation, and crystallization, usually operates at normal conditions, this section is not considered in this study. Models of the system are then built. These models include a mixer block for modeling the pre-carbonation section; an RGibbs reactor block based on Gibbs free energy minimization for modeling the enhanced carbonation section; a two-outlet flash block for modeling the flash separation section; and a combination of the RGibbs reactor block, a two-outlet flash block, and a heat exchange block for modeling the gas phase absorption section. Fig. 2 shows the simulation process in the Aspen Plus environment. Given that phosphogypsum carbonation with ammonia is strongly exothermic as shown in Eq. (1), all blocks are operated under adiabatic conditions except for the heat exchange block. Given that some blocks for the pre-carbonation and gas phase absorption sections are usually operated under atmospheric conditions, the operated pressure for these sections is set to 1 bar. Tables 1 and 2 show the simulated parameters.

The physicochemical properties of the pure components and mixture are calculated, and the phase-equilibrium parameters are obtained from the Aspen Plus property database. Given the non-ideal behavior of the $CaSO_4{\cdot}2H_2O$-NH_3–CO_2–H_2O electrolyte system, the electrolyte–NRTL property method is used to predict the activity coefficients, enthalpies, and Gibbs energies for liquid phase thermodynamic behavior [42,37,1]. The Redlich–Kwong equation of state calculates the fugacity coefficients for the vapor phase properties based on the recommendations of Qi et al. [25].

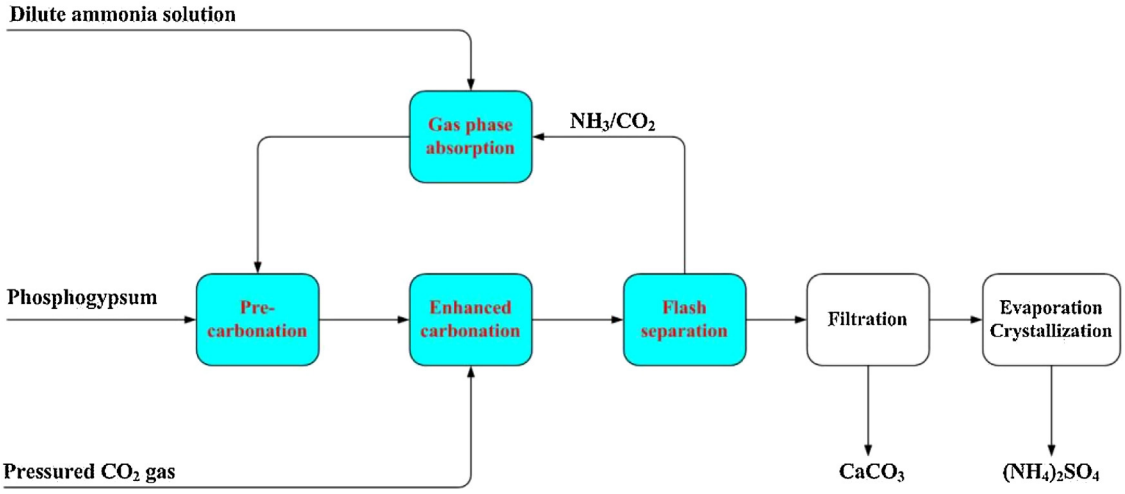

Fig. 1. Flowchart of the mineral carbonation of phosphogypsum with ammonia under increased CO_2 pressure.