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CO₂ Capture by Alkaline Carbonation as an Alternative to a Circular Economy

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Abstract: In order to combat global warming and climate change in a sustainable way, it is necessary to capture the anthropogenic CO₂ emitted by different industrial sources and use it as a raw material to obtain a matrix of products for industrial use, such as metal carbonates. Therefore, this work presents the results of CO₂ capture and conversion into carbonates using Sr and Ba alkaline solutions in a semi-continuous batch reactor. The results indicate that the effects of morphological characterization, purity of solids, and reaction time at ambient temperature and atmospheric pressure conditions is an inexpensive alternative process that is easily implemented in small industrial enterprises. The results yielded a 40% conversion of CO₂ at the best reaction conditions with an aqueous solution of Sr(OH)₂.

Keywords: capture CO₂; circular economy; semi-continuous batch reactor; alkaline carbonation

1. Introduction

The CO₂ separation and capture processes are key to combating climate change caused by anthropogenic activities. The separation of CO₂ from various post-combustion or pre-combustion gas streams can be carried out by means of various technologies, one of the most interesting being the membrane separation processes due to its low energy consumption and easy scaling [1–3]. After separation, it is necessary to capture and transform it into useful products such as fuels, chemical compounds, and plastics, among other products that are highly desirable in various sectors of the industry. Net CO₂ emissions can be reduced by various alternatives such as geological sequestration, ocean sequestration, mineral sequestration, and industrial use [4,5]. Today, there is an abundant bibliography on large-scale CO₂ capture in geological sites widely reported in reports and reviews on the subject [6–9]. For actions such as these, there have been funding programs supported by federal entities such as the Ministry of Economy of Japan [10]. However, it is no less important is to abandon the linear economy, (produce–consume–discard) and move to a circular economy (produce–consume–recycle) [9], in which resources are used more sustainably, where that the wastes or emissions generated are transformed into useful products that can be reintroduced into the original process or in other processes, thus reducing their impact on the environment. Under this concept of a circular economy, the anthropogenic CO₂ emitted by different sources can be considered and used as raw material to generate a wide array of products for industrial use, such as carbonated beverages, improved oil recovery, polycarbonate synthesis, extinguisher charges, refrigerants, chemical synthesis, and mineralization to obtain carbonates [5,11]. CO₂ capture by means of mineralization can be carried out either through using a direct process using fine particles of a mineral matrix bearing Ca⁺² or Mg⁺²

ions, such as serpentine, olivine, and wollastonite, which react to form metallic carbonates with CO_2 gas or CO_2 under supercritical conditions as the main reagent, or using an indirect process, where alkali or alkaline earth metals are first extracted from the mineral matrix and then carbonated in a separate stage; the final product of indirect mineral carbonation is usually a pure carbonate [12]. There are few reports on carbonation processes for application in small and micro industries, which are widely dispersed within large and medium cities and use gas or fuel oil in their boilers, generating small volumes of CO_2 compared with large industries. This work aims to explore a CO_2 capture alternative oriented to small and micro industries, through CO_2 capture as carbonates using Sr and Ba solutions in a semi-continuous reactor. In addition, this work addresses morphological characterization, the evaluation of the recovered solids purity, and the effect of reaction time at ambient temperature and atmospheric pressure conditions. This alternative can be considered as a process that is readily implementable and devoid of scaling problems for small industries.

2. Materials and Methods

The precursor salts used are $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ Merck 98% purity and $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ Sigma Aldrich 97% purity. Aqueous solutions were prepared at 25 °C; 0.02 M of $\text{Sr}(\text{OH})_2$, 0.02 M for $\text{Ba}(\text{OH})_2$.

2.1. Reactor/Crystallizer

The carbonation tests were performed in a small-sized semi-continuous batch reactor/crystallizer, adiabatic, wherein the gas phase is fed continuously, the batch is the liquid phase, and the gas phase is dispersed in the liquid phase by a porous glass diffuser coupled to the end of the feed tube. The reaction was carried out at the ambient temperature and atmospheric pressure of Mexico City, 0.7799 Bar; a schematic diagram of the experimental setup is presented in Figure 1. In a typical experiment, the volume of the metal hydroxide solution was 250 mL and the volumetric flow of CO_2 feed was carried out continuously, also at reaction conditions; the solubility of CO_2 is 26 mol m^{-3} [13] the temperature and the pH of the solution were recorded in situ every 5 min until a reaction total of 40 min was recorded, using a portable potentiometer brand WTW model 3110. During all the CO_2 capture tests, the aqueous solution of the metal hydroxide was kept stirred at 300 rpm. In a first test, 250 mL of a 0.02 M solution of $\text{Sr}(\text{OH})_2$ was placed, and three tests were run, each with a different volumetric flow of the CO_2 feed: 1.5, 15.2 and 94.7 mL min^{-1} . At the end of each reaction, the precipitated solid was filtered using Whatman filter paper number 5. Then, the recovered solid was dried at 80 °C in an oven for 24 h and allowed to cool in a desiccator to room temperature; afterwards, its weight was recorded. In addition, studies were conducted on the CO_2 conversion at three reaction times: 20, 30, and 40 min. All tests were performed in triplicate.

Figure 1. Reaction setup system scheme.

2.2. Characterization

The diffraction pattern of the recovered solids was analyzed using a Philips X-ray Diffractometer (XRD), model X-pert, using Cu K α radiation, with a 2 theta scan of 4° to 80°, a step size of 0.03° of 2.5 s. The diffraction pattern of the resulting solid was obtained and compared with the PDF files of the reference standards of the International Diffraction Data Center (ICDD) with the X'pert HighScore Plus software. The morphology, crystal size, and elemental analysis were determined with a Scanning Electron Microscope/Energy Dispersive Spectroscopy (SEM/EDS) Carl Zeiss, Supra 55VP model, using secondary and back-scattered electrons detector. Spectroscopy analysis for Fourier Transform Infrared (FTIR) was performed on a Varian 3600 equipment, Excalibur model. Thermogravimetric Analysis (TGA) was performed in a Perkin Elmer TGA 7 brand TGA thermobalance, in the 25 to 900 °C range for the barium solid, and 25 to 990 °C for strontium solid with a heating ramp of 20 °C min⁻¹.

3. Results

3.1. Trends of Temperature and pH

The maximum amount of SrCO₃ solid precipitated was obtained with a volumetric flow of CO₂ feed of 15.2 mL min⁻¹, which was the flow set as the CO₂ reactor feed in all the carbonation tests. Figure 2a shows the pH and temperature results for the CO₂ reaction system with a 0.02 M Sr(OH)₂ solution. The results exhibit a moderate decrease in pH during the reaction first 10 min, changing the pH decrease rate at higher reaction times until reaching a value of 6.15 after 40 min. This result is consistent with that reported by Ho et al. [14], who stated that the efficiency of the CO₂ carbonation reaction decreases at high volumetric CO₂ feed flows. However, an increase with a slight positive slope of solution temperature is observed. Figure 2b shows that during the CO₂ reaction tests with a 0.02 M solution of Ba(OH)₂, a similar tendency to the Sr(OH)₂ system is present, reaching a minimum pH value of 6.5 in 40 min of reaction. In addition, a similar trend in the temperature increase of the two reaction systems can be observed. In summary, it can be seen in Figure 2 that the pH of the solutions continuously decreased as a function of the reaction time during the capture of CO₂ with the alkaline solutions of the metal precursors investigated. Furthermore, an average temperature increase of approximately 2 °C can also be observed during the 40-min reaction due to the exothermic reaction, which is consistent with that reported by Goldberg et al. [15], indicating the continuous release of heat during the reaction.

(a)

(b)

Figure 2. PH and temperature trend during carbonation reactions: (a) Sr(OH)₂ and (b) Ba(OH)₂.

3.2. Conversion Rate

The results shown in Figure 3 indicate that the maximum conversion percent for the two alkaline solutions was for the 20-min reaction, where the Sr(OH)₂ results were the best.

Figure 3. Conversion percentages obtained in carbonation reactions.

The decrease in the conversion rate at times greater than 20 min can be attributed to the possible dissolution of the carbonates to form the corresponding bicarbonates, which is consistent with the carbonate balance in water [16]. In addition, some authors indicate that the appropriate pH for aqueous carbonation reactions is greater than 10 [12,17]. They also report that below pH = 8.3, there is a solution of carbonates, and we consider that this pH value indicates the end of the carbonation reaction [14,18].

3.3. X-Ray Diffraction

The diffraction pattern of the powder solids, comprising the peaks at 2θ : 25.1, 36.5, 44.1, 47.6 and 49.9 degrees, which correspond to strontianite (strontium carbonate, SrCO₃), is shown in Figure 4.

Figure 4. XRD pattern of solids recovered in reactions with Sr(OH)₂ compared with a reference standard.

Regarding the diffraction pattern of the powder solids after CO₂ reaction with the barium hydroxide solution, the peaks were identified at angles 2θ = 24.0, 34.2, 42.1, 44.8 and 46.9 degrees, as shown in Figure 5, confirming obtaining barium carbonate (BaCO₃), as compared with PDF reference card 00-001-0506, JCPDS, which corroborates barium carbonate (BaCO₃). In addition, as indicated above, a good crystallinity of the barium carbonate yielded was related with well-formed peaks. Both compounds belong to the orthorhombic system.

Figure 5. XRD pattern of the solids recovered after reaction with $\text{Ba}(\text{OH})_2$ compared with a reference standard.

3.4. Scanning Electron Microscopy

The morphology, shape, and size of the solids recovered after the carbonation reactions with $\text{Sr}(\text{OH})_2$ are shown in Figure 6 at 1000X, where a well-defined acicular crystal morphology is readily apparent. The micrometric size strontium carbonates also show the elementary analysis displaying a carbon content (C) of 12.04%, 31.91% oxygen (O), and 56.05% strontium (Sr).

Figure 6. Micrographs and analysis SEM/EDS of solids recovered after carbonation reactions with $\text{Sr}(\text{OH})_2$.

The morphology of the barium solids obtained after reaction with $\text{Ba}(\text{OH})_2$ at 5000X, bearing a micrometric size acicular shape; the elemental analysis indicates the presence of 9.04% carbon, 25.72% oxygen, and barium (Ba) 65.23 wt%, which confirms the presence of the elements that constitute the barium carbonate, as shown in Figure 7.

Figure 7. Micrographs and analysis SEM/EDS of solids recovered after carbonation reactions with Ba(OH)_2 .

In summary, the micrographs of the solids recovered subsequent to reactions with Sr(OH)_2 and Ba(OH)_2 show a well-defined morphology, and the elemental analyses from all samples confirm the presence of carbonate-forming elements (C, O, and the corresponding metal).

3.5. Fourier Transform Infrared Spectroscopy

The FTIR spectrum of solids obtained reacting with Sr(OH)_2 at different reaction times are shown in Figure 8. The typical spectrum associated with carbonates has three absorption bands in the regions $1440\text{--}1452$, 854 , and 705 cm^{-1} . At 20 min of reaction, the presence of these three absorption bands confirms the formation of carbonate during CO_2 capture with the Sr(OH)_2 solution, obtaining strontium carbonate (SrCO_3), which is characteristic of the aragonite group (absorption band at 854 cm^{-1}).

Figure 8. FTIR spectrum of solids formed during carbonation reactions with Sr(OH)_2 in the 1700 to 500 cm^{-1} region.

The FTIR spectrum of solids formed after reaction with Ba(OH)_2 is shown in Figure 9. The spectrum shows the three main absorption bands for carbonates at 1417 , 854 , and 700 cm^{-1} . In this case, the intensity of the absorption bands at 20 and 40 min are very similar. The absorption bands present in the spectrum confirmed obtaining barium carbonate (BaCO_3). In summary, SrCO_3 and BaCO_3 correspond to the aragonite group of carbonates (absorption band at 854 cm^{-1}).

Figure 9. FTIR spectrum of solids recovered in carbonation reactions with $\text{Ba}(\text{OH})_2$ in the 1700 to 500 cm^{-1} region.

Table 1 Presents the wavelengths at which the characteristic absorption frequencies for carbonates occurred; these bands correspond with the characteristic vibrations of the CO_3^{2-} group [18,19].

Table 1. Absorption bands carbonate characteristic by FTIR [19].

Vibration Type	Range (cm^{-1})	Mode
Symmetric stretching	1065	ν_1
Bending out of plane	880–850	ν_2
Bending in-plane	720–680	ν_4
Asymmetric stretching	1450–1410	ν_3

The carbonates of the aragonite group display vibrations within $840\text{--}860\text{ cm}^{-1}$, as observed in the FTIR spectra of strontium and barium carbonates. Some authors have reported the intensity of the absorption bands in the FTIR spectrum at $1429\text{--}1492$, 879 , and 706 cm^{-1} of carbonates obtained after carbonation reactions from CO_2 capture [18,20].

3.6. Thermogravimetric Analysis

The thermogram of strontium carbonate is shown in Figure 10, where a weight loss of 26.51% becomes plain at the maximum decomposition temperature of $943.97\text{ }^\circ\text{C}$.

Figure 10. TGA thermogram of the solids recovered from carbonation reactions with $\text{Sr}(\text{OH})_2$.

This result coincides with the thermal decomposition temperatures of SrCO_3 reported from 959 to 1027 °C in an Ar atmosphere (commercial SrCO_3) [21], beginning at 1000 °C and reaching 1075 °C in an air atmosphere [22], giving SrO and CO_2 as products [23].

4. Discussion

The experimental results showed that the volumetric rate of the CO_2 feed determines the amount of carbonate formed in the reactor; in the first experiment, the CO_2 was fed to the reactor at a rate of 1.5 mL min^{-1} . However, when the volumetric flow rate was increased at 15.2 mL min^{-1} , the mass of the precipitated metal carbonate was increased. In contrast, as the feed rate increased to 94.7 mL min^{-1} , a decrease in precipitated carbonate was found. So, it was determined that the best capture conditions and CO_2 sequestration correspond to a flow of 15.2 mL min^{-1} . In addition, the recommended reaction time corresponds to 20 min, because at higher reaction times, a greater proportion of bicarbonates appears. The capture of CO_2 in aqueous solutions for carbonate formation is a complex gas–liquid reaction system, presenting several series stages of mass transfer and reaction. The analysis of the pH behavior during the first 10 min of reaction shows that the pH of the solution presented a slight decrease, which suggests that at the beginning, the reaction is controlled by CO_2 mass transfer from the gas phase to the liquid phase by solubilization. Then, CO_2 gradually reaches the semi-stationary state, followed by the formation of dissociated carbonic acid in aqueous solution, generating two protons and the carbonate ion that reacts with the cation Ba^{+2} or Sr^{+2} to form the corresponding carbonate. Then, that reaction generates a rapid decrease in the solution pH that is observed as a change in the slope of the pH where carbonate formation exists. Thereafter, the transformation of carbonates to bicarbonates occurs at pH values lower than 8, this behavior is consistent with the stability of chemical species at different pH values according to the carbonate system [16]. Furthermore, if we consider that the reaction is exothermic, the linear increase in temperature suggests that the reaction rate is constant during the first 40 min of the reaction. The highest amount of CO_2 capture was obtained with the solution of $\text{Ba}(\text{OH})_2$, and according to the results of X-ray diffraction, the solid formed is Ba carbonate with a high purity, which was confirmed by comparison with reference card PDF 00-005-0418, JCPDS. In addition, the diffractogram shows narrow, intense peaks that strongly suggest that the (SrCO_3) obtained had formed with good crystallinity. In addition, the scanning electron microscopy results show the shape of the acicular crystals, which are of micrometric size, and the results of the elementary analysis confirm the presence of the elements that make up the carbonates of Sr and Ba. The results of

infrared spectroscopy of the different carbonates present the well-defined signals of the characteristic bands of weak, medium, and strong intensity for the carbonates of Sr and Ba. Dry carbonate samples were analyzed by TGA, and the results show that they are stable up to 900 °C. This agrees with the values reported by some authors, in which the thermal decomposition temperature of BaCO₃ is above 1000 °C; meanwhile, that of the commercial BaCO₃ is from 1140 to 1198 °C in an Ar atmosphere [21], from 1000 °C in an air atmosphere [22], and from 1300 °C, it decomposes into barium oxide and carbon dioxide [24].

The alternative of using minerals such as serpentine, olivine, and wollastonite as a mineral capture matrix is necessary to condition it by means of steps including crushing, sieving, washing, and activation, which is difficult for small companies to implement. So, the use of solutions of metal hydroxides, industrial waste, and metallurgy seems to be viable to obtain these carbonates, thus increasing the storage capacity of CO₂. The range of industrial application of carbonates is wide and diverse; for example, SrCO₃ is used in sugar refining, in military rockets and to prepare other strontium salts and as a low-cost fireworks dye, while BaCO₃ is used to immobilize many water-soluble salts in the manufacture of red bricks. In the glass industry, it is added to improve the refractive index of optical glass and also to decrease the viscosity of molten glass and photographic paper. Many barium salts are prepared from barium carbonate [24].

5. Conclusions

The feasibility of CO₂ sequestration of low volumetric flow rates was verified by carbonation using Sr and Ba alkaline solutions. The CO₂ capture system using a batch semi-continuous reactor is a simple system to implement in small industries. The conversion rate showed the importance of working with a 20-min reaction time to maximize carbonate production with the different alkaline solutions. In addition, the importance of the pH control of the solutions to promote carbonate formation was determined.

The characterization by XRD, SEM/EDS, FTIR, and TGA of these compounds confirmed the capture of CO₂ to synthesize carbonates with the solutions of Sr(OH)₂ and Ba(OH)₂ with high purity, thus fixing the CO₂ in a stable solid material with a possible micrometer particle size.

These carbonates have a commercial value in several sectors, so they represent an alternative to sustainably recycling CO₂, contributing to the mitigation of the greenhouse effect and climate change by reducing CO₂ emissions into the atmosphere.

Author Contributions: D.S.C.-N. carried out the experimental tests of CO₂ capture during her master's thesis, M.G.-A. tested and interpreted the infrared spectroscopy analysis of carbonates, V.M.-Á. conducted the discussion of results, and M.T.-R. participated in the direction and discussion of the results. All authors have read and agreed to the published version of the manuscript.

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