

Precipitation of calcium carbonate in highly alkaline solution through carbonated water

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It is generally recognized that global warming is caused by the accumulation of greenhouse gases in the atmosphere. Particularly, CO₂ has caused most of the warming and its influence is expected to continue. Due to rapid increase of population and energy consumption all over the world, environmental issues have attracted the attention of many researchers in the twenty-first century. CO₂ conversion into precipitated carbonate minerals is considered a promising option for carbon capture and storage (CCS).

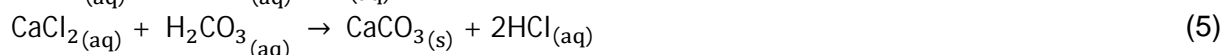
The formation of calcium carbonate is a common crystallization phenomenon based on chemical reaction (reactive crystallization). In precipitation systems, supersaturation, necessary for initiating precipitation, is generated as two highly soluble reactants are mixed to form a sparingly soluble product. Calcium carbonate formation rates are controlled by many factors such as calcium concentration and supersaturation, temperature, pH, etc. At room temperature, solution pH is the most significant factor, and high yield polymorphs are present at different pH values [1]. The main objective of the current study is the lab-scale precipitation process of calcium carbonate by addition of high-pH carbonic acid to calcium chloride (CaCl₂) solution. Throughout this fast-chemical reaction, solid CaCO₃, which at first appears as a cloudiness in the mixture, settle to the bottom of the vessel.

At normal pressures, most gases are only sparingly soluble in typical liquids [2]. The maximum total amount of CO₂ that may dissolve in water is a function of pH. An increase in the alkaline concentration significantly enhances the CO₂ absorption. As shown in Figure 1, at a given constant temperature, CO₂ solubility increases by pH, which also leads to higher calcite production.

Carbonation and precipitation processes can be represented by a sequence of reactions as follows:



H₂CO₃ dissociates in water according to:



Chemical reaction between these components results in calcite precipitation. However, pH control plays a significant role in a successful precipitation process. pH of the carbonated water needs to be increased to a specific limit before addition of carbonic acid for initiating the precipitation process. This pH limit is set according to pH of calcium hydroxide solubility at 20 °C, which is 1.73 g/L or pH of 12.368. This is because of preventing precipitation of any form of calcium hydroxide ($K_{sp}=5.02 \times 10^{-6}$ at 25 °C) during the experiment and at the same time keeping the final solution at higher pH level. As displayed in Figure 2, solubility of calcium carbonate ($K_{sp}=3.36 \times 10^{-9}$ at 25 °C) decreases by increasing the pH value [3]. Han et al. [4] also reported that higher pH value tends to induce calcite crystals. Overall schematic of the experimental set-up is presented in Figure 3. The set-up enables potential pre-treatment of, for instance industrial flue gases, due to separate absorption and precipitation unit operations.

This approach could pave the way toward combining a crystallization process with carbon capture technology. It can provide an appropriate method for proper removal or recycling of the industrial wastes (e.g. flue gases). With this method, CO₂ can be prevented from flowing to the atmosphere, while manufacturing high purity calcium carbonate as a byproduct that also can be used in the wide-range of relevant industries such as paper, cosmetics, construction materials, food and pharmaceuticals.

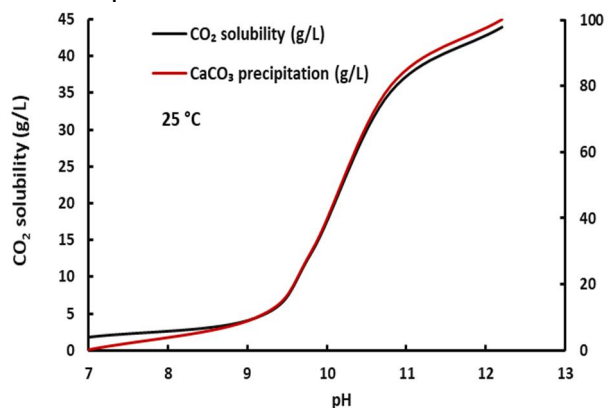


Figure 1: CO₂ solubility dependency to pH at 25 °C and equivalent CaCO₃ precipitation.

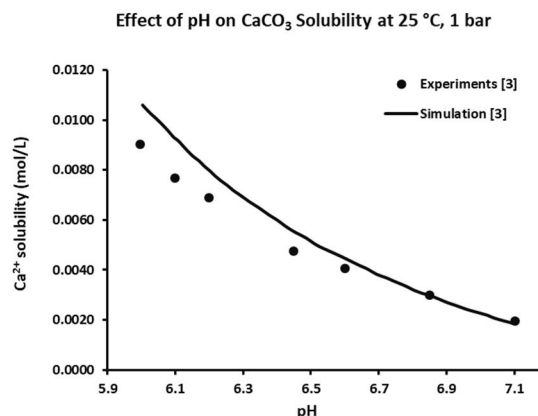


Figure 2: Effect of pH on the CaCO₃ solubility at 25 °C and 1 bar air pressure [3].

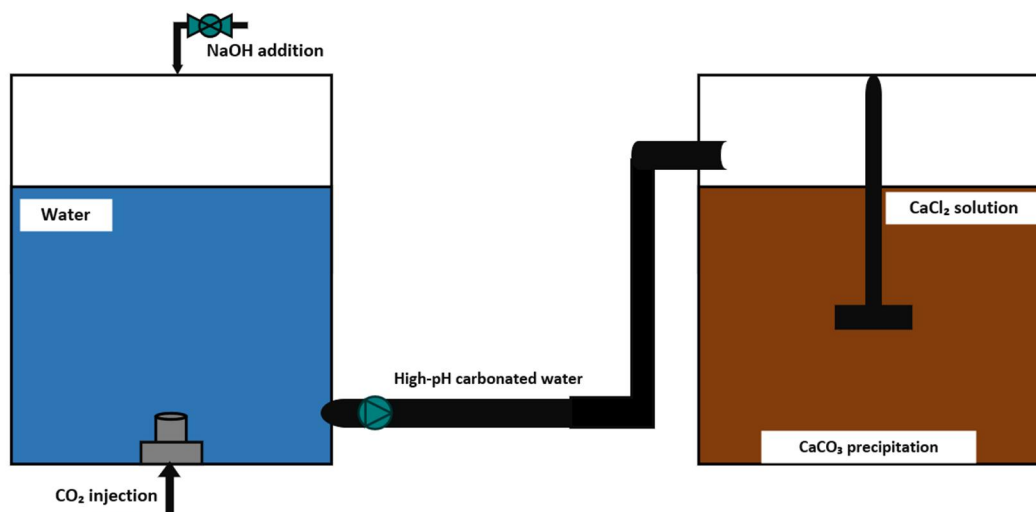


Figure 3: General Schematic of the experimental set-up for calcium carbonate precipitation

Acknowledgements

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References

- [1] C.Y. Tai, F. Chen, Polymorphism of CaCO₃, precipitated in a constant-composition environment, *AIChE J.* 44 (1998) 1790–1798. doi:10.1002/aic.690440810.
- [2] W. Knoche, Chemical Reactions of CO₂ in Water, in: 1980: pp. 3–11. doi:10.1007/978-3-642-67572-0_1.
- [3] B. Coto, C. Martos, J.L. Peña, R. Rodríguez, G. Pastor, Effects in the solubility of CaCO₃: Experimental study and model description, *Fluid Phase Equilib.* 324 (2012) 1–7. doi:10.1016/j.fluid.2012.03.020.
- [4] Y. Sheng Han, G. Hadiko, M. Fuji, M. Takahashi, Crystallization and transformation of vaterite at controlled pH, *J. Cryst. Growth.* 289 (2006) 269–274. doi:10.1016/j.jcrysgro.2005.11.011.