

Investigation of CO₂ mineralization of alkaline brine in continuous tubular reactor.

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Highlights

- CO₂ mineralization of gas-liquid-solid flow system in tubular reactor was investigated.
- Brine and BF slag, which are industrial wastes, have been applied to obtain carbonates.
- Flow rate of gas and liquid and basicity of solution are the main influencing factors.

1. Introduction

Carbon dioxide (CO₂) has drawn increasing attention due to its greenhouse effect on the change of the Earth's temperature and climate. Carbon capture, utilization and storage (CCUS) ^[1] is a portfolio of technologies aimed at reducing the adverse effects of anthropogenic CO₂ emissions, for example by concentrating, transporting and storing it in geological formations or in the deep oceans, or by converting it into mineral carbonates. Mineralization ^[2,3] is a more attractive type of carbon sequestration process, as it will form solid products that can store CO₂ permanently. A source of alkaline earth metals for CO₂ mineralization are desalination brines, which is a kind of concentrated seawater containing sodium, magnesium, calcium, chloride, iron, among other ions. The alkaline cations can be applied to form carbonates ^[4] by injecting CO₂ directly into the brine.

The traditional reaction system for most CO₂ mineralization research consists of continuously-stirred batch reactors, whereby CO₂ is contacted with a mechanically mixed slurry. In this study, we investigate CO₂ mineralization with a continuous plug-flow tubular reactor, which is a reaction system more appropriate for industrial applications given its ability to be easily scaled-up, and enabling better process control, optimization and integration. In order to obtain saturation and precipitation of carbonates, it is necessary to control the pH value, as the continuous injection of CO₂ into the system leads to solution acidification. The approach used in this research to counter this effect was to contact the brine with blast furnace (BF) slag, to transfer alkalinity to the brine, with sodium hydroxide solution being used as an additional alkali substance.

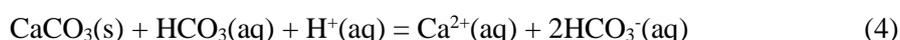
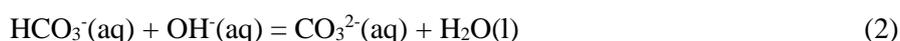
2. Methods

Artificial brine was prepared with CaCl₂·2H₂O (0.02 M) and NaCl (0.8 M) in DI water. Pelletized BF slag was crushed and sieved to obtain different size fractions. NaOH was prepared to act as an additional alkali additive. The tubular reactor (Armfield CETMkII) consists of a helically-coiled tube immersed within a temperature-controlled bath; the reactor length is 20.9 m, with internal diameter of 5.0 mm, and total volume of 410 cm³. Two lines feed the reactor and are mixed in a T-junction: one is for CO₂, coming from a compressed gas cylinder (industrial-grade), with flowrate controlled by a needle valve, and the other is for the alkaline brine, pumped by a peristaltic pump from a feed tank where brine and slag are gently mechanically agitated to avoid slag particles from entering the half-immersed feed line. Liquid and gas flowrates were determined by gravimetric and volumetric determination, respectively, of the reactor outlet discharge.

Different particle sizes of slag, gas and liquid flow rates, reaction temperature, and various amount of NaOH solution were adjusted to investigate the optimal conditions and kinetics of carbonation reaction. Solid precipitates were characterized by TGA, FTIR-ATR, SEM and XRD; changes in concentration of metal ions were measured by ICP-OES, and inlet and outlet brine pH was measured.

3. Results and discussion

Influence of flow rate of gas and liquid on the conversion was investigated. Different CO₂ and brine feeding solution flow rates (L:40-80 mL/min, G: 20-60 mL/min) were selected. The reactions were conducted at 50 °C, it showed that the outlet Ca²⁺ concentration decreased more significantly with the lower gas flow rate under a fixed liquid flow rate. This means that the conversion of calcium to carbonates is greater. Additionally, outlet pH value was lower when the CO₂ flow rate was higher. The reactions that occur when the pH is higher are proceed according to equations (1)-(3), while when the pH is below 7, CaCO₃ will remain dissolved in the form of Ca(HCO₃)₂ according to equation (4).



Effect of residence time, temperature and different initial pH values were also studied. The results showed that the precipitates were easily formed at higher temperature, 50 °C, comparing to 30 °C under a certain pH value range. The calcium utilization efficiency was high with increasing residence time. More alkaline solution introduced improved CO₂ capture at the pH range from 10.5 to 12.5. Figure 1 shows the thermogravimetric analysis of collected product, and it is characterized to be high-purity CaCO₃.

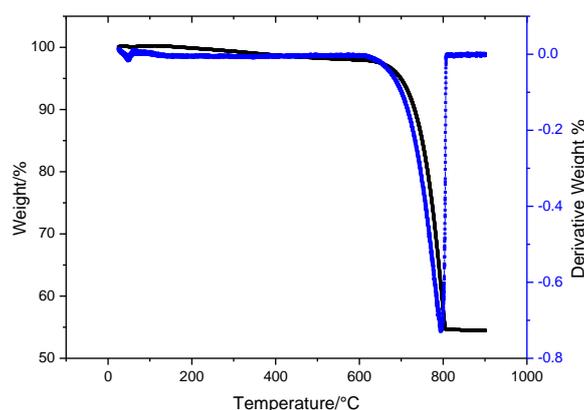


Figure 1. TGA/DTG of the product.

4. Conclusions

In this research, various experimental reaction conditions were explored and the results showed that higher pH value, higher temperature and lower gas/liquid ratio are beneficial to the calcium utilization from brine for CO₂ mineralization. The shape and size of precipitates varied with the gas/liquid ratio, calcium concentration and temperature.

References

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Keywords

CO₂ mineralization; tubular reactor; desalination brine; blast furnace slag