Mineral CO\textsubscript{2} Sequestration by Carbonation of Glauberite

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Abstract. CO\textsubscript{2} mineral sequestration has significant advantages such as safety and permanence, but its industrial application is limited by high costs. Combining CO\textsubscript{2} mineral sequestration with existing industrial processes can make it economically viable by integrating ore extraction, crushing and grinding, and avoiding the construction of new carbonation plant. In this paper, CO\textsubscript{2} mineral sequestration was combined with the leaching of sodium sulfate from glauberite. The dissolution behavior and carbonation process of glauberite ore were studied in detail. The influences of key parameters such as ammonia dosage, CO\textsubscript{2} pressure and temperature were also investigated. The results showed that under the optimal conditions (ammonia dosage 110%, CO\textsubscript{2} pressure 5 bar, temperature 100\textdegree C), the carbonation rate of glauberite can reach 93.4\%, while the concentrations of sodium ion and sulfate ion were 25.8g/L and 53.8g/L, respectively. The increase of ammonia dosage and CO\textsubscript{2} pressure contributed to the dissolution and carbonation of glauberite. Temperature, however, affected them in two very different ways.

1. Introduction
Since the industrial revolution, the concentration of CO\textsubscript{2} in the atmosphere has risen sharply due to human activities and industrial emissions [1, 2]. With the rapid development of emerging economies such as China and India, energy demand will increase further in the future. In addition, fossil energy is still the main primary energy in the coming decades. Therefore, CO\textsubscript{2} must be captured and stored [3]. Carbon capture and sequestration generally consists of three steps: capture, transport and sequestration. As a core step, carbon sequestration mainly includes geological sequestration, marine sequestration and mineral sequestration [4]. Geologic sequestration is the direct injection of high pressure compressed CO\textsubscript{2} into appropriate geological structures to achieve a long-term CO\textsubscript{2} blockade. However, excessive pressure and chemical reactions between CO\textsubscript{2} and surrounding rocks can upset the original physicochemical balance of the environment. At the same time, the risk of sudden CO\textsubscript{2} leakage requires long-term monitoring after storage. Marine sequestration faces similar problems to geological sequestration. Mineral sequestration is the process of converting CO\textsubscript{2} from gas to solid carbonate by carbonation reaction between CO\textsubscript{2} and minerals. The resulting carbonate is thermodynamically stable and environmentally friendly, so CO\textsubscript{2} can be safely and permanently sequestered [5, 6].
At present, there have been many studies and reports on CO$_2$ mineral sequestration. The feasibility of many types of natural minerals and industrial solid wastes as raw materials for CO$_2$ mineral sequestration has also been verified [7, 8]. However, little consideration has been given to the integration of CO$_2$ mineral sequestration with existing industrial processes. The use of natural minerals as raw materials for carbonation inevitably involves many processes such as ore mining, ore crushing and grinding, mineral separation and processing, and ore transportation and storage. The associated high costs would be unaffordable. Although the use of industrial solid waste does not require the mining and crushing of ores, it still requires the construction of new carbonation plant and material handling. Additional mining and ore crushing processes can be avoided by combining CO$_2$ mineral sequestration with existing mineral processing processes. At the same time, using the existing production system for carbonation reaction can avoid the new construction of carbonation plant. Therefore, this integration approach will be economically promising.

Glauberite is a special compound salt mineral, which is made up of sodium sulfate and calcium sulfate. In China, glauberite is one of the main sources of sodium sulfate, which is widely used in textile, medicine and many other industries. Compared with other sodium sulfate resources, glauberite ore has the advantages of wide spatial distribution and huge deposit, so it has a high development value. At present, the water dissolving technology is widely used in the glauberite mine. Based on the difference in solubility between sodium sulfate and calcium sulfate, the separation of the two is achieved. However, in the water dissolving process, the generated gypsum will cover the surface of the ore, seriously hindering further leaching. The chemical reaction between calcium sulfate and CO$_2$ in the presence of ammonia water can not only fix CO$_2$ permanently, but also avoid the formation of gypsum to promote the leaching of sodium sulfate. The related chemical reaction equation is shown as follows:

$$\text{Na}_2\text{Ca(SO}_4\text{)}_2 (s) + \text{CO}_2 (g) + \text{NH}_4\text{OH (l)} = (\text{NH}_4\text{)}_2\text{SO}_4 (aq) + \text{Na}_2\text{SO}_4 (aq) + \text{CaCO}_3 (s)$$  

The main purpose of this paper is to explore the dissolution behavior and carbonation process of glauberite. In addition, the influences of key parameters such as ammonia dosage, CO$_2$ pressure and temperature were also investigated.

2. Experiment

2.1. Materials

The glauberite ore used in the experiment was taken from a glauberite mine in Tongqing, Sichuan, China. The glauberite ore was broken and ground to obtain the required size range. Element composition of glauberite ore was analyzed by XRF. The mineral composition of glauberite was analyzed by XRD. The major elements were S, Si, Ca and Na, and minor elements were Mg, Al and Fe. Glauberite ore was mainly glauberite, and small amounts of inert impurities.

2.2. Methods

The carbonation experiment was carried out in a high pressure reactor. The reactor comprises a inlet valve and a sampling valve. Firstly, a certain quality of glauberite and the corresponding ammonia water were put into the reactor, and then the reactor was placed in the electric heating jacket of a matching magnetic stirrer. When the reactor was heated to a preset temperature, high-pressure CO$_2$ was injected into the reactor through the inlet valve. When a certain time was reached, the solution was sampled through the sampling valve. The sample solution was filtered by a needle filter. The concentrations of sodium ion and sulfate ion in the solution were determined by ICP-OES and ion chromatograph, respectively.
3. Results and discussion

3.1. Effect of ammonia dosage

Under the conditions of CO$_2$ pressure 5 bar and temperature 100°C, the effect of ammonia dosage on the dissolution behavior and carbonation process of glauberite was studied. Fig. 1 shows the changes of sodium ion concentration, sulfate ion concentration and carbonation rate of glauberite with the ammonia dosage.

As can be seen from Fig. 1, the use of excess ammonia contributes to the dissolution and carbonation of glauberite. When the ammonia dosage is 90%, the concentration of sodium ion is only 20.4g/L, while when the ammonia dosage increases to 100% and 110%, the concentration of sodium ion increases to 23.9g/L and 25.8g/L, respectively. Further increasing the ammonia dosage to 130%, the sodium concentration is essentially the same. The variation trend of sulfate ion concentration and carbonation rate of glauberite is generally consistent with that of sodium ion. When the ammonia dosage increased from 90% to 110%, the concentration of sulfate ions increased from 42.5g/L to 53.8g/L, while the carbonation rate of glauberite increased from 75% to 93.4%. Further increase in ammonia has no effect on either.

3.2. Effect of CO$_2$ pressure

Under the conditions of ammonia dosage 110% and temperature 100°C, the effect of CO$_2$ pressure on the dissolution behavior and carbonation process of glauberite was studied. Fig. 2 shows the changes of sodium ion concentration, sulfate ion concentration and carbonation rate of glauberite with the CO$_2$ pressure.

As can be seen from Fig. 2, the use of excess CO$_2$ pressure contributes to the dissolution and carbonation of glauberite. When the CO$_2$ pressure is 2 bar, the concentration of sodium ion is only 15.4g/L, while when the CO$_2$ pressure increases to 7 bar, the concentration of sodium ion increases to 30.5g/L. Further increasing the CO$_2$ pressure has no effect on either.

Figure 1. Effect of ammonia dosage on the dissolution and carbonation of glauberite.

Figure 2. Effect of CO$_2$ pressure on the dissolution and carbonation of glauberite.
As can be seen from Fig. 2, with the increase of CO$_2$ pressure from 1 bar to 5 bar, the concentration of sodium ions increases continuously and reaches its maximum value at 5 bar. When CO$_2$ pressure exceeds 5 bar, further increase in pressure does not affect the concentration of sodium ions. That means the solution is saturated. The similar situation occurs in the sulfate ion concentration and the carbonate rate of glauberite. At the CO$_2$ pressure of 5 bar, the concentration of sulfate ion and the carbonation rate of glauberite could reach their maximum values 53.8 g/L and 93.4%, respectively.

3.3. Effect of temperature
Under the conditions of CO$_2$ pressure 5 bar and ammonia dosage 110%, the effect of temperature on the dissolution behavior and carbonation process of glauberite was studied. Fig. 3 shows the changes of sodium ion concentration, sulfate ion concentration and carbonation rate of glauberite with the temperature.

![Figure 3. Effect of temperature on the dissolution and carbonation of glauberite.](image)

As can be seen from Fig. 3, temperature has two distinct effects on the dissolution and carbonation of glauberite. When the temperature from 25℃ up to 100℃, the sodium ion concentration, sulfate ion concentration and carbonation rate of glauberite are increasing. While the temperature exceeds 100℃, with the further increase of temperature, the sodium ion concentration, sulfate ion concentration and carbonation rate of glauberite decrease. This is because the rate of chemical reactions increases with temperature, but the solubility of CO$_2$ decreases significantly.

4. Conclusion
The dissolution behavior and carbonation process of glauberite were studied. The influences of key parameters such as ammonia dosage, CO$_2$ pressure and temperature were also investigated. The results showed that under the optimal conditions (ammonia dosage 110%, CO$_2$ pressure 5 bar, temperature 100℃), the carbonation rate of glauberite can reach 93.4%, while the concentrations of sodium ion and sulfate ion were 25.8g/L and 53.8g/L, respectively. The increase of ammonia dosage and CO$_2$ pressure contributed to the dissolution and carbonation of glauberite. Temperature, however, affected them in two very different ways.

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