Mechanism of karst formation in sulfate rocks

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Abstract

For understanding the effects of ambient temperature, water flow rate, and pH of water on the dissolution of sulfate rocks, the present work aims at studying the mechanism of sulfate rock dissolution through laboratory experiments. The results suggest that each experimental factor has a different effect on the dissolution of sulfate rock. High temperature caused the transformation of the sulfate minerals, resulting in the dissolution of sulfate rocks. At high water flow rate solutions remain under-saturated with respect to sulfate mineral phases resulting in an increase of dissolution rates. The sulfate karst formation is different from carbonate karst, i.e. the water is corrosive with regards to the sulfate rock system even in the absence of CO₂ in the system. The results will give an insight into the mechanism of karst with respect to the coexistence of sulfate and carbonate rocks.

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1. Introduction

Karst research is principally focused on the dissolution of carbonate rocks, since the carbonate karst is widely spread. However, the development of caves in deep oil reservoir in the Tarim Basin, China, and some geohazards associated with karst, such as collapses, land subsidence as well as karst water invasion, cannot be well explained without considering the sulfate rock dissolution. Previous studies on gypsum dissolution in sulfate rocks were carried out by in-situ test. Dissolution rates obtained from the tests were different depending on the samples and the environment. Some studies on the mechanism of geohazards and the genesis of oil reservoirs noticed the role of sulfate rock dissolution on karst development [1]-[4]. But they did not give a reasonable explanation on the mechanism of the dissolution of sulfate rocks in buried environment. The purpose of this study is to reveal the mechanisms of sulfate rock dissolution.
under the different conditions through laboratory experiment, and to discuss the effects of controlling factors on the dissolution of sulfate rocks.

2. Materials and Methods

2.1. Samples

The sulfate rocks within the carbonate rocks formation are widely distributed in China. Samples of sulfate rocks both from marine and lacustrine sedimentary deposits were collected from the Ordovician formation in the North China and the Paleogene formation in the South China (Table 1). The chemical compositions of the samples were measured in the Laboratory of Beijing Institute of Geology. The results are presented in Table 1. The mineral assembly in the sulfate rocks was calculated on the basis of chemical compositions. The dominant mineral is gypsum and accounts for 88% (Sx5) and 87% (Gx5) of the rock.

Table 1. Chemical compositions of samples.

| Sample No | Site            | Sedimentary type | CaO (%) | MgO (%) | SO₃ (%) | Ignition loss (%) | Acid insoluble (%) | H₂O⁺ (%) | H₂O⁻ (%) |
|-----------|-----------------|------------------|---------|---------|---------|------------------|-------------------|-----------|-----------|
| Sx5       | Taiyuan, China  | Marine           | 32.17   | 0.37    | 45.1    | 21.36            | 1.27              | 18.23     | 0.04      |
| Gx5       | Guangxi, China  | Lacustrine       | 32.61   | 0.02    | 46.58   | 20.98            | 0.23              | 18.66     | 0.05      |

2.2. Experiments on sulfate rock dissolution

The samples were cut into 2 × 2 × 4 cm³ cubes. Each of them was rinsed with deionized water and then placed in a constant temperature drying oven at 45 °C for 48 hours. The solutions for experiments were prepared with deionized water and dissolved carbonic acid. The dissolution experiments were carried out by using samples in contact with solution at different controlled factors (temperature, water flow rate, pH) for one week. The experimental device is shown in Figure 1. Study of temperature effects on sulfate rock dissolution was done with Sx5 sample and deionized water using a 1 ml/min flow rate at different temperatures 25 °C, 50 °C and 75 °C, respectively. The hydrodynamic effect was conducted at 50 °C with Sx5 sample and deionized water using different flow rates 0.5 ml/min and 1 ml/min, respectively. The pH effect on sulfate rock dissolution was performed with Gx5 sample at pH 5.9 in deionized water and pH 4.1 in deionized water with carbonic acid under the condition of 1.0 ml/min flow rate and at 25 °C. Solution of interaction was daily sampled during the experiment and measured for chemical compositions. The Ca²⁺ concentration was determined by EDTA titration method. SO₄²⁻ concentration was measured by barium sulfate turbidity.

3. Results and Discussions

3.1. Temperature effects on sulfate rock dissolution

The dissolution amount of sulfate rock increased with temperature at the different rates. The dissolution amount increased from 31.39 mg/cm² at temperature 25°C to 94.92 mg/cm² at 50°C and 274.81 mg/cm² at 75°C. The difference of dissolution rate between 50°C and 75°C is about 3 times that observed between 25°C and 50°C. This is in agreement with the temperature-dependence of sulfate
minerals crystallography and their solubility. Zanbak [5] and Klimchouk [6] suggested that the dependence of the gypsum solubility is a nonlinear relationship. At temperature below 43°C, gypsum solubility increases with increasing temperature, reaching a maximum at 43°C. When the temperature is higher than 43°C, gypsum solubility decreases with increasing temperature. In particular, gypsum will be transformed to bassanite when it is heated at 66°C. Note that the solubility of gypsum is lower than that of bassanite at this temperature. Sx5 is composed of about 88% gypsum and 12% bassanite. The gypsum dissolution was predominant when temperature increases from 25°C to 50°C, while bassanite dissolution prevailed when temperature increases from 50°C to 75°C. This difference led to an uneven increase in the dissolution amount.

3.2. Hydrodynamic effects on sulfate rock dissolution

The dissolution amount of sulfate rocks increased with water flow rate. The dissolution rate at 0.5ml/min flow rate and 1ml/min one was 10.41 mg/cm²•d and 15.82 mg/cm²•d, respectively. It showed that the dissolution amount of sulfate rocks was not directly proportional to the flow rate. This indicates that solutions of interaction after one-day reaction tend to reach saturation with respect sulfate mineral phases leading to the decrease of dissolution rate.

3.3. pH effects on the dissolution of sulfate rocks

The pH of water plays an important role in water-rock interaction. The molar ratios of SO₄²⁻/Ca²⁺ in solutions sampled daily at different pH are close to 1:1. The dissolution rates of sulfate rocks are nearly same, 7.45 mg/(cm²•d) and 7.54 mg/(cm²•d) for pH 4.1 and 5.9, respectively.

Fig. 1. Schematic view of the experimental dissolution apparatus used in laboratory. Numbers represent: 1. N₂ gas cylinder; 2. CO₂ gas cylinder; 3. Gas regulator; 4. Buffer vessel; 5. Reaction solution; 6. Blow-off pipe; 7. Preheating chamber; 8. Peristaltic pump; 9. Rock sample; 10. Reactor; 11. Thermostat caloristat; 12. Thermostat control; 13. vessel.
Theoretically, the dissolution of gypsum will produce 1 mol SO$_4^{2-}$ and 1 mol Ca$^{2+}$, according to the molar ratio of S/Ca of 1.0. The measured SO$_4^{2-}$/Ca$^{2+}$ molar ratios in the solutions of interaction are indicative that dissolution of gypsum is the only involved process.

Study of pH effect indicates that the pH of solution has a minimum effect on the dissolution of sulfate rocks. This is not surprising as the sulfate mineral dissolution process does not consume protons.

4. Conclusions

The dissolution of sulfate rocks was significantly affected by the ambient conditions, such as temperature, water flow rate. Increasing temperature transforms gypsum into bassanite or anhydrite, resulting in the further dissolution of sulfate rocks. The high flow rate of water in the experiments led to an increase in the amount of sulfate rock dissolved by reducing the state of saturation of solution with respect to sulfate minerals.

In natural geological environments, the temperature (25-75°C) in deep buried sulfate rocks, and the chemical conditions prevailing, even in absence of CO$_2$ are as many factors aggressive for sulfate minerals resulting in the occurrence of sulfate karst in carbonate-sulfate rock formation.

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