Experimental study of the hydrothermal reactivity of oxalic acid under high pressure

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Abstract. The thermal stability of organic acids has a close relationship with the formation mechanism of secondary pores in deep reservoirs. Experiments were conducted to investigate the thermal stability of oxalic acid under high pressure and the influence of K-feldspar on oxalic acid decomposition. The experiment temperatures were set in the range of 130-330°C and each experiment was performed for 72h under 60MPa. Results show that both temperature and K-feldspar have significant influence on the decomposition of oxalic acid. The oxalic acid decomposed slowly at temperatures less than 180°C, and most of the oxalic acid decomposed at temperatures between 180°C and 230°C. Besides, the decarboxylation reaction proceeded more slowly in the presence of K-feldspar than the mineral-free experiments, which is most likely attributed to the increasing pH caused by dissolution. In addition, because the decomposition rate of oxalic acid was low, the K-feldspar dissolution was not affected at temperatures lower than 230°C.

1. Introduction

The secondary pore is one of the important storage spaces for deep reservoirs (>4000m), and organic acids play an important role in forming secondary pores in deep reservoirs [1]. Much research has been conducted to study the stability of organic acids in aqueous solutions [2-4]. But most previous experiments were carried out under relatively low fluid pressure and did not consider the effect of lithostatic pressure. More and more research has revealed that high pressure might hinder the decomposition reaction of organic acid [5-6]. Besides, the oxalic acid was considered as a very important organic acid for the formation of secondary pores for the strong acidity and complexation of oxalate by aluminum [2, 5]. Therefore, it is necessary to examine the changes of stability with increasing temperature of oxalic acid under high pressure.

Interactions between organic acids and minerals are the focus of forming the secondary pores, and many of them pay much attention to the feldspar dissolution by oxalic acids [7-8]. The results of these
experiments have shown that feldspar dissolution increases significantly in oxalate solutions. However, these studies are mainly completed under atmospheric pressure and low pressure. Thus, in this study, two series of experiments were designed to address these issues. The first series of experiments was conducted to study the changes of thermal stability of oxalic acid with increasing temperature under high pressure; the purpose of the second series is to study the influence of K-feldspar on the decomposition of oxalic acid.

2. Experimental materials and methods

2.1. Materials
In both two series of experiments (SY1 and SY2), dilute pure oxalic acid (analytical reagent) was chosen as the reaction solution. In order to avoid changes in the original ionic composition, solutions with different fluid composition were produced by adding deionized water. The initial concentrations of oxalic acid were 0.06 mol/L and the initial pH value was 2.1.

K-feldspar was included in SY2 experiment, and this is to simulate actual geologic environments such as sedimentary basins, and because K-feldspar exhibited lower solubility than other kinds of feldspar. The K-feldspar grains were picked up from the fragmentized rocks from a block of pegmatite in the Xingxingxia Beishan Area in Gansu Province. K-feldspar was randomly selected after removing the surface weathering layer, and grain size are about 1mm to avoid the influence of mineral heterogeneity.

2.2. Methods
The experiments were conducted in a semi-closed high-temperature, high-pressure simulation system, as used by [9]. Both two series of experiments include five experiments at different temperatures (130°C, 180°C, 230°C, 280°C, 330°C). All experiments were conducted for 72h under 60MPa water pressure and 90MPa lithostatic pressure. The reaction conditions for each series of experiments are listed in Table 1.

|       | Temperature (°C) | Time (h) | Water Pressure (MPa) | lithostatic pressure (MPa) | Initial pH | Materials           |
|-------|-----------------|----------|----------------------|-----------------------------|------------|---------------------|
| SY1   | 130-330         | 72       | 60                   | 90                          | 2.1        | Oxalic acid         |
| SY2   | 130-330         | 72       | 60                   | 90                          | 2.1        | Oxalic acid + K-    |
|       |                 |          |                      |                             |            | feldspar            |

After experiments, all fluid samples are tested by pH meters three times. The concentrations of ions were measured by Ion Chromatography (ICS3000). The chromatographic conditions for oxalic acid are: IonPac As19 analytical column (250mm × 4.0mm); column temperature is 30°C and the detector temperature is 35°C; the eluent is water (A, 18.2 MΩ·cm⁻³)-18mmol/L NaOH (B), gradient elution (0-3min, 50%B; 3-6min, 50%B→100%B; 6-15min, 100%; 15-17min, 100%B→50%B; 17-25min, 50%B); the flow amount is 1.0mL/min and the sample size is 20μL; the current of suppressor is 50mA. The chromatographic conditions for Na, K, Ca, Mg are: IonPac Cs12 analytical column (250mm × 4.0mm); the eluent is water (A, 18.2 MΩ·cm⁻³, 25°C)-20mmol/L methyl sulfonic acid (B), the current of suppressor is 59mA.

3. Results and Discussion

3.1. The reduction of oxalic acid
3.1.1. The decomposition of oxalic acid
The residuary oxalate concentration decreases with the temperature increasing (Figure 1), which indicates that heating of oxalic acid led to gradual decomposition of the acid. As temperature increases, data points show a slightly decreasing trend at low-temperature stage (<180°C); then the changes in concentrations were more intense at temperatures from 180°C to 230°C, and most of the oxalic acid had
decomposed in this stage; at a temperature above 230°C, the oxalate concentration is very low to zero, and 230°C could be a critical temperature for oxalic acids decomposition in this study. Besides, it is apparent that the decomposition of oxalic acid is hindered under high pressure.

![Figure 1. The concentrations of ∑oxalate in SY1 and SY2.](image)

### Table 2. Measured concentrations of ∑oxalate and ∑formate in SY1 and SY2.

| Temperature (°C) | SY1        |            | SY2        |            |
|------------------|------------|------------|------------|------------|
|                  | ∑oxalate   | ∑formate   | ∑oxalate   | ∑formate   |
| 25               | 61.8       | -          | 61.8       | -          |
| 130              | 54.2       | 0.02       | 45.6       | \          |
| 180              | 48.0       | 6.8        | 39.8       | 0.1        |
| 230              | 18.8       | 0.3        | 9.8        | 0.1        |
| 280              | 7.3        | \          | 2.6        | \          |
| 330              | \          | \          | 0.2        | \          |

“\"” denotes no data, “-” denotes no detection. Because the eluent is NaOH, the oxalic acid will be all converted to oxalate during detection, the “∑oxalate” represents the total concentration of oxalate and oxalic acid.

Some formate was detected in SY1 and its concentration grows with temperature increasing from 130°C to 180°C (Table 2), and then decreased to under detection limit at 230°C. The production of formate at temperatures under 230°C suggests that the decarboxylation of some oxalic acids yield monocarboxylic acids with shorter chains (Eqn.1) in the low-temperature stage. At temperature above 230°C, two reasons should be responsible for the disappearance of formate: (1) the oxalic acid decomposed primarily by Eqn.2 under high pressure [6]; (2) the faster decomposition rate for formate compared to other acid anions.

\[
\begin{align*}
H_2C_2O_4 & \rightarrow HCOOH + CO_2 \\
H_2C_2O_4 & \rightarrow 2CO_2 + H_2
\end{align*}
\]

3.1.2. The influence of K-feldspar

The residiary concentration of oxalate for SY2 at the same temperature in this study are also shown in Table 2 and Figure 1. The data points show a decay behavior for all samples like SY1. The residiary concentration of oxalate for SY2 is significantly lower than the mineral-free experiments (SY1) at the same temperature. This should be attributed to the interactions between oxalic acid and K-feldspar since the complexation of Al³⁺ with oxalate will consume lots of oxalates (Eqn.3).

\[
KAlSi_3O_8 + H_2C_2O_4 + 2H_2O + 2H^+ \rightarrow 3SiO_2 + (AlC_2O_4 \cdot 4H_2O)^+ + K^+
\]

Combining the study above, there are two ways influence the decrease of oxalic acid: one is decomposition and another is complexation, and the experiment SY2 includes these two reactions. So there also might exist the effect of K-feldspar on the decomposition of oxalic acid. To test this hypothesis, an additional dissolution experiment but under atmospheric pressure and the room temperature was
conducted in the presence of K-feldspar. In the additional dissolution experiment, it is assumed that complexation is the main reaction. It is found that after 72 hours, the oxalate concentration decreased 14.1mmol/kg in the additional experiment, whereas the concentration decreased 16.2mmol/kg in SY2 and 7.6mmol/kg in SY1 at 130°C. The decrease of oxalate concentration was caused by decomposition and complexation in SY2, by decomposition in SY1 and by complexation in the additional experiment. The reduction of oxalate concentration in SY2 is smaller than the sum of the other two, which may suggest that the decomposition proceeded slowly in the presence of K-feldspar. A previous study has shown that the decarboxylation of oxalic acid was found to slow with increasing pH [10] and the dissolution of feldspar increased the pH value of the solution, therefore the K-feldspar did not promote the decomposition but lead a slower decarboxylation rate of the acid. In addition, different from SY1, less formate was detected in SY2 (Table 2) also suggest that the decarboxylation reaction proceeded more slowly in SY2.

3.2. The K-feldspar dissolution by oxalic acid

Table 3 and Figure 2 show changes of typical ion concentration (Na⁺, K⁺, Ca²⁺, and Mg²⁺) in SY2. The changes in K⁺, Na⁺, Ca²⁺, and Mg²⁺ indicate that the K-feldspar was dissolved by oxalic acid and the solubility of feldspar increased with temperature, the dissolution of minerals consumed large numbers of hydrogen ions and oxalic acids (Eqn.3). The concentration of Na⁺ and K⁺ increased markedly at low-temperatures (<230°C). With the gradual increase in the ion concentrations in the system, the change gradually stabilized at higher temperature experiments and the dissolution rate slowed down with the increasing temperature. The decomposition of oxalic acid is the reason why dissolution proceeded slowly at temperatures above 230°C, even though the concentrations of K⁺ and Na⁺ reach the maximum at 330°C. The concentration of Mg²⁺ and Ca²⁺ are much lower than Na⁺ and K⁺ and exhibit a slightly growing tendency. Almost all the concentrations of ions illustrate that 230°C is a critical temperature: at the temperature above 230°C, the increasing tendency grows very gentle.

| Temperature (°C) | Concentration (mmol/kg) | pH |
|------------------|--------------------------|----|
|                  | Na⁺ | k⁺ | Ca²⁺ | Mg²⁺ |    |
| Additional experiment | 0.61 | 0.54 | 0.20 | 0.28 | 3.1 |
| SY2              | 0.66 | 0.65 | 0.22 | 0.32 | 4.3 |
| 180              | 0.74 | 0.86 | 0.23 | 0.42 | 4.5 |
| 230              | 0.97 | 1.19 | 0.27 | 0.40 | 5.4 |
| 280              | 0.90 | 1.23 | 0.35 | 0.41 | 5.7 |
| 330              | 1.05 | 1.24 | 0.36 | 0.44 | 6.3 |

“\" denotes no data, “-” denotes no detection.
The initial pH value of the oxalic acid solutions was 2.1 since the dissolution of minerals consumed large numbers of hydrogen ions, the pH value increased rapidly. In SY2, the pH value was controlled by the decomposition of acid and the dissolution of K-feldspar. The pH values in SY1 were 2.7, 3.1, 3.8, 4.6, 5.6, respectively. A comparison of these pH values in SY1 and SY2 (include the room temperature experiment) suggests that the main factor was dissolution at low-temperature stage (<230°C) and then the pH values were controlled by the decomposition of aciD.

However, the increasing concentrations of these typical ions with increasing temperature indicate that there are lots of dissolutions that occurred in the SY2 and it seems that the dissolution was not affected by the decomposition of oxalic acid at temperatures lower than 230°C. Figure 2 also shows the changes with the decarboxylation of oxalic acid (C/C₀) in typical ion concentration. The concentration of these four ions increased with the decomposition of oxalate and then the changes stabilized when the acid reduced to 37% of the initial concentration. Therefore, when the temperature is up to 230°C, the decarboxylation of most acids leads to the decrease of solubility of K-feldspar and since the decomposition rate was low at a low-temperature stage the K-feldspar dissolution was not affected temporarily.

4. Conclusions
(1) Under high pressure, as temperature increases, concentrations of oxalate show a slightly decreasing trend at temperatures less than 180°C, and have a rapid decrease at temperatures between 180°C and 230°C, and then decrease very slowly at temperatures above 230°C.

(2) The decarboxylation reaction proceeded more slowly in the presence of K-feldspar, this should be attributed to the increasing pH values and concentration of oxalate produced by dissolution. Besides, because the decomposition rate of oxalic acid was low at low-temperature stage (<230°C) the K-feldspar dissolution was not affected temporarily.

Acknowledgments
This research was jointly supported by the National Science and Technology Major Projects of Ministry of Science and Technology of China (Grant No. 2016ZX05003002-004, 2016B-0502), National Nature Science Foundation of China (Grant No. 41072105, 41872147) and Shaanxi Provincial Postdoctoral Science Foundation (Grant No. 2018BSHGZZHQQYXMZZ07).

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