Dissolution of arkose under conditions relevant to deep reservoirs: the effect of organic acid on the porosity and pore size distribution of arkose

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Abstract. The organic acid is important in forming secondary pores and enhancing total porosity of the clastic rock. But there is little study to investigate the effect of organic acid on the porosity distribution of clastic rock from deep reservoirs. The changes in porosity, permeability, and porosity distribution of the dissolved medium-grained lithic arkose, from Yanchang Formation in Ordos Basin, were examined by nuclear magnetic resonance (NMR). The results show that porosity and permeability of rock increase with the time of exposure of the rock to the organic acid solution and it increases rapidly in the early period, then slightly increases to a saturation level. Besides, organic acid mainly changes the frequency and the shapes of T2 distribution in NMR analysis, and this study suggests that organic acid has more effect on rocks with larger pore throat than those with smaller pore throat.

1. Introduction
With the increase of exploration depth, more deep reservoirs (>4000m, >200°C) were found [1]. The secondary pore is one of the important storage spaces for these reservoirs and it is widely accepted that the organic acids play a key role in the enhancement of total porosity and the formation of secondary porosity [2-3]. Therefore, numerous laboratory experiments have been performed to investigate the interactions of organic acids and rocks [3-7], and most studies mainly focused on the mechanical or chemical aspects of the formation of secondary pores, the kinetics, and reaction of mineral dissolution and the controlling factors on reservoir quality. However, these experiments were carried out under relatively low fluid pressure and most of the experiments did not consider the effect of lithostatic pressure.

Some authors argued that it is unlikely that porosity increased significantly unless large-scale mass transport exist. The dissolution of unstable minerals would lead only a redistribution of porosity rather
than the creation of addition porosity, because new diagenetic minerals precipitated, which are more stable with respect to the pore water environment [8-9].

Nuclear magnetic resonance (NMR) has been used as an effective tool for studying reservoir physical property [10]. The T2 is the transverse relaxation times and used to describe the rate of the NMR signal decay, the T2 spectrum is the distribution of this decay times. The characteristics of effective porosity, porosity distribution, permeability can be directly obtained by interpreting the NMR signals of the hydrogen nucleus in the fluid contained in the pores [11]. In this study, we have conducted a series of laboratory experiments examining the changes in porosity and permeability due to the dissolution of the arkose samples and the effect of acetic acid on porosity distribution of arkose by using NMR technique.

2. Experimental materials and methods

2.1. Materials
In this study, experimental materials include acetic acid solutions and arkose cores (25mm×40mm). Dilute pure acetic acid (analytical reagent) was chosen as the reaction solution. To avoid changes in the original ionic composition, solutions were produced by adding deionized water. The initial concentration of organic acid was 0.16mol/L and the initial pH value was 2.1.

Rock samples DS6, DS8 from Chang 6, and Chang 8 Formations respectively were selected (in Ordos basin), which have similar initial porosity and low permeability but different porosity distributions, and these two samples have similar mineral compositions (Table 1). Samples were first cleaned in a two-step soxhlet extraction procedure using ethanol and toluene, respectively, to remove inorganic and organic residues. After cleaning, the samples were dried at 80°C for 12 h.

2.2. Methods
The experiments were conducted in a semi-closed high-temperature, high-pressure simulation system as introduced by [12]. The experiments were conducted at 200°C and 60MPa water pressure and 60MPa lithostatic pressure. The water-rock mass ratio was 10:1 and the experiment was initiated by injecting a solution of acetic acid into the reaction vessel. Six parallel but independent experiments were conducted for different hours (24 h, 48 h, 72 h, 120 h, 168 h, 240 h, 336 h).

After the experiment, all rock samples were removed from the reaction cells and inserted into a special device to vacuum for 12 h and saturate for 24 h in 30MPa with simulated formation water (CaCl₂ salinity of 25,000 mg/L, according to the salinity of the typical oilfield water in Changqing oilfield). Then, the core samples are tested its T2 spectrum, porosity, and permeability by an NMR apparatus (SPEC, Beijing, China) equipped with a centrifuge (3000 r/min, Huaxing, Jiangsu, China) and a high-pressure saturation device (Huaxing, Jiangsu, China).

| Sample | Mineralogy (wt.%) | Porosity (%) | Permeability (10⁻³ μm²) |
|--------|------------------|--------------|-------------------------|
| DS6    | Quartz 16.3      | Plagioclase 31.3 | K-feldspar 33.1 | Muscovite 6.5 | Kaolinite 3.1 | 10.3 | 4.77 |
| DS8    | 16.9             | 31.3         | 43.5                | 4.6                   | 6.3                   | 9.8 | 1.19 |

3. Results and Discussion

3.1. The changes in porosity and permeability
Figure 1a presents the normalized porosity (ratio between the porosity at an assigned time and the original sample porosity) changes against time. Normalized porosity represents the variation of porosity in the course of the dissolution in relation to the initial porosity. All data points of the two experiments show a similar trend: the changes in porosity are more intense in the early period, especially in the first 72 hours, then slightly increase to a saturation level. The gradually decreasing rates indicate that with the dissolution of feldspar, the clay minerals may precipitate [5]. Besides, the initial porosity for DS8 is lower than DS6, but the lower porosity sample presents higher changes in porosity. After 336 h of
reaction, porosity achieves nearly 1.5 times than the initial porosity for DS6 and DS8.

**Figure 1.** Normalized porosity (a) and permeability (b) versus time of travertine samples.

Figure 1b shows the normalized permeability as a function of the time, and it illustrates a trend for the sample permeabilities increasing and reaching a topline where the permeability has little change. For the DS6 sample (lower permeability), the topline reached faster. On the other hand, although after 120 h of reaction, the permeabilities of two samples change very slightly. While DS6 sample with higher initial permeability exhibits greater changes along the time, about 2.8 times than the initial permeability. The DS8 sample with lower permeability displays smaller changes, about 2.8 times than the initial. This study suggests that the permeability of the samples is not fully controlled by the porosity.

### 3.2. The changes in T2 distribution

The changes in the shape of T2 distributions over time of samples are shown in Figure 2, and four typical NMR test results (72 h, 120 h, 240 h, 336 h) are exhibited because differences among them are more significant. The T2 distribution of two samples ranges between 0.1ms and 1000ms, with two peaks. This indicates that samples mainly have two kinds of pores: T2 distribution in the range of 0.1~11ms represent smaller pores and that in the range of 11~1000ms represent larger pores, and two kinds of pores are connected. The frequency in Figure 2 could reflect the porosity of different pores.

For sample DS6, both two peaks are getting higher with increasing reaction time, indicating an increase of porosity for two kinds of pore after dissolved by organic acid (Figure 2a). Besides, smaller pores have more obvious change than the larger pore through organic acid dissolution. For sample DS8, T2 distribution is similar with sample DS6, but there are more smaller pores in DS8 samples (Figure 2b). The shapes of T2 distribution have small changes before 120 hours, and the right peak shows obvious change after 240 h. After 336 h of reaction, there was a large gap between “336 h distribution” and “0 h distribution” for two peaks, especially the right peak, which indicates that larger pores have more obvious change than the smaller pores through organic acid dissolution for sample DS8. The DS6 and DS8 samples have different shape changes in T2 distribution, which is mainly related to their initial physical properties. Sample DS6 has a larger pore throat and higher permeability and is more easily affected by organic acid. It is concluded that the changes in T2 distribution caused by organic acid was also controlled by the initial porosity distribution and permeability of rock samples.
3.3. Mineral transformation

As shown in Figure 3, the changes in the content percentage of K-feldspar and plagioclase against time suggest the dissolution of two minerals. Due to the higher permeability, the DS6 sample with a high content of K-feldspar and plagioclase shows more obvious changes in porosity and permeability. The dissolution of K-feldspar and plagioclase in acetic acid solutions can be illustrated as follows:

\[
2K\text{AlSi}_3\text{O}_8 + 2H^+ \rightarrow K\text{Al}_3\text{Si}_3\text{O}_{10}(OH)_2 + 2K^+ + 6SiO_2(aq) \tag{1}
\]

\[
2Na\text{AlSi}_3\text{O}_8 + H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4SiO_2(aq) \tag{2}
\]

Therefore, the dissolution of K-feldspar releases muscovite and the precipitated of kaolinite were caused by plagioclase dissolution [5]. The two reactions result in porosity and permeability increased. After 120 hours of reaction, the dissolution tends to balance and more muscovite and kaolinite precipitated and blocked connecting pores. So that the increasing rate of porosity and permeability slow down. The T2 distribution (Figure 2) illustrated the new diagenetic minerals were mainly deposited in the relative larger pore throats for DS6 samples, whereas the clay minerals may precipitate at the original position of feldspar for DS8. This difference is most likely mainly attributed to the different initial permeabilities.

![Figure 2. T2 distribution of DS6 (a) and DS8 samples (b), the numbers in the legends represent hours.](image)

![Figure 3. Mineral content changes of DS6 and DS8.](image)
natural geologic environments in deep reservoirs. The results of experiments do suggest that organic acid has a significant influence on the enhancement of porosity. However, we did not consider pressure and temperature as a variable in this research, in further study, we plan to focus on the effects of high pressure.

4. Conclusions
The porosity and permeability were observed to increase with time of exposure of the rock to the organic acid solution and both of them increased rapidly in the early period, then slightly increased to a saturation level. The gradually decreasing variation rates of porosity and permeability indicated that the new more stable diagenetic minerals may precipitate. Besides, The organic acid changed the distribution range slightly but significantly affected the frequency and the shapes of T2 distribution, therefore the formation of secondary porosity not only makes a net porosity enhancement but a slight redistribution of porosity. The influence of organic acid on T2 distribution was also affected by the initial permeability and porosity distribution of rock samples, the samples with a higher content of larger pore throats (T2: 10–100ms) and higher permeability are more easily affected by organic acid.

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