



## Experimental study of the decomposition of acetic acid under conditions relevant to deep reservoirs



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### ABSTRACT

The thermal stability of organic acids is critical in studying the formation mechanism of secondary pores in deep reservoirs (>4000 m). However, the thermal stability of organic acids in geochemical systems is strongly dependent on temperature, minerals and pressure (fluid pressure and lithostatic pressure). To investigate the activity of organic acids and the influence of these factors (temperature, pressure and K-feldspar), four series of experiments were conducted over a wide range of reaction conditions. Pure acetic acid solutions were selected for this study. The temperatures ranged from 130 °C to 380 °C, and each experiment was performed for 72 h in steps of 50 °C. The results indicate that the decomposition reaction rate was slow but accelerated with increasing temperature. At temperatures higher than 230 °C, the decomposition of acetic acid proceeded to a much more significant extent than at low temperatures. The results of experiments also show that the decomposition rates were faster at lower lithostatic pressure, and the lithostatic pressure played a larger role than water pressure in affecting the decomposition of acetic acid. Additionally, the presence of K-feldspar influenced the reaction rates of acetic acid, especially the oxidation rates. This was attributed to the increasing concentration of acetate produced by dissolution.

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## 1. Introduction

With the increase of exploration depth, more deep reservoirs (>4000 m) have been found, such as the Dongying depression in the Bohai Bay Basin, NE China (Yuan et al., 2007). Secondary pores are an important storage space for these reservoirs. Previous studies have shown that organic acids play a key role in mineral dissolution and the formation of secondary porosity (Surdam et al., 1984, 1989; Barth et al., 1990). Therefore, understanding the thermal stability of organic acids is critical in studying the formation mechanism of secondary pores in these deep reservoirs.

Numerous laboratory experiments have been performed to investigate the thermal stability of organic acids in aqueous solutions (Kharaka et al., 1983; Palmer and Drummond, 1986; Drummond and Palmer, 1986; Crossey, 1991; Bell and Palmer,

1994; Bell et al., 1994; Fein et al., 1994; Shock, 1994; McCollom and Seewald, 2003a, b; Ong et al., 2013). These previous studies have shown the possible reaction pathways for the decomposition of organic acids in geologic systems and the factors that influence the thermal stability of organic acids. These observations, however, had only been reported for experiments under relative low fluid pressure, and most of the experiments did not consider the effect of lithostatic pressure. In fact, pressure may play an important role in regulating the reaction process, because the decomposition reaction of organic acids generates lots of gaseous products, which will significantly change the molar volume of the reaction, and because the fluid and lithostatic pressures are distinctly different in natural systems, and their effects need to be assessed individually. What's more, the temperatures of deep reservoirs in different basins vary tremendously. For example, the temperature of the reservoirs at depths of 4000 m is lower than 100 °C in the Kela Gas Field, Kuqua Depression, Tarim Basin, China, whereas there are still liquid hydrocarbon accumulations at a depth of 7550 m and 295 °C in the

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Pre-Caspian Basin, Russia (Sun et al., 2013). However, most previous experiments have been conducted in a very narrow temperature range (Palmer and Drummond, 1986; Bell et al., 1994; McCollom and Seewald, 2003a, b; Ong et al., 2013). Without more detailed knowledge about the changes in stability of organic acids with increasing temperature, it is difficult to use these experimental results to accurately predict the distribution and reactivity of organic acids in deep reservoirs.

On the other hand, numerous experiments have been conducted to study the interactions of organic acids and minerals (Palmer and Drummond, 1986; Barth and Riis, 1992; Bell et al., 1994; White and Brantley, 1995; McCollom and Seewald, 2003a, b; Ganor et al., 2009; Shao et al., 2011; Declercq et al., 2013). A wide range of minerals (including stainless steel, quartz, pyrite, calcium montmorillonite, calcite, hematite and magnetite) were chosen to study the catalytic decomposition of acetic acid (Pittman and Lewan, 1994). However, feldspar is far more common than most of the minerals selected in previous studies of sedimentary rock and volcanic rock, but most studies have only focused on feldspar dissolution by water-soluble organic acids (Bevan and Savage, 1989; Welch and Ullman, 1996; Blake and Walter, 1999; Ma et al., 2012; Crundwell, 2015; Yang et al., 2015). If feldspar significantly promotes the decomposition of organic acid, the dissolution reaction might be affected, leading to some changes in the formation of secondary pores. Here, we select K-feldspar to simulate a clastic reservoir, since K-feldspar is more stable than other feldspars, such as albite and anorthite, especially in an acid aqueous solution (Zhang et al., 2009).

Above all, due to the abundance of acetic acid in oil field water (Barth and Riis, 1992), we have conducted a series of laboratory experiments examining the reactivity of acetic acid under 45–60 MPa lithostatic pressure and 45–60 MPa water pressure at elevated temperatures (130–380 °C). The degradation rate, activation energies and pre-exponential factors were obtained by analyzing the reaction dynamics. In this study, pressure and K-feldspar were selected to simulate actual geologic environments, such as deep clastic reservoirs in sedimentary basins. Changes in the total concentration of acetate over time were measured to assess the degradation rate under different conditions to address three issues in particular: (1) the influence of water and lithostatic pressure on the thermal stability of acetic acid; (2) the changes in the thermal stability of acetic acid and acetate over a wide temperature range; and (3) the role of K-feldspar in affecting decomposition pathways and rates.

## 2. Experimental materials and methods

### 2.1. Materials

Dilute pure acetic acid (analytical grade) was chosen as the reaction solution. To avoid changes in the original ionic composition, all solutions were made in degassed deionized water. In Experiment 1 (Ext. 1) to Experiment 4 (Ext. 4), the solute was pure acetic acid (155.4 mmol/kg), and because acetic acid is a weak acid, the main species in these samples was acetic acid (>90%). K-feldspar was included in Ext. 4. A block of pegmatite was obtained from an outcrop in the Xingxingxia Beishan area. After removal of the surface weathered layer, all rocks were fragmentized to screen out the K-feldspar grains. Randomly selected parts of the K-feldspar grains were used for experiments to avoid the effect of mineral heterogeneity.

### 2.2. Methods

The experiments were conducted in a semi-closed high-

temperature, high-pressure simulation system (WYMN3 HTHP, Fig. 1), as used by Sun et al. (2015) and Wu et al. (2016). The instrument consists of a software control system (computer) and a hardware performance system (apparatus). The software control system was used to set experimental conditions and collect data. The hardware performance system included the following systems: reaction cell, heating system, pressure system and collecting systems. The reaction cell was made of titanium alloy and contained within an autoclave (stainless-steel), and the advantages of the reaction cell are the resistance to acid and alkali corrosion with a maximum tolerable temperature of 550 °C and pressure of 100 MPa. The accuracy of heating system is  $\pm 0.1$  °C. The pressure system contains a hydraulic control system for lithostatic pressure and confining pressure and a turbocharger for hydrodynamic pressure. The lithostatic pressure accuracy is  $\pm 0.1$  MPa, water pressure accuracy is  $\pm 0.05$  MPa. With the aid of pressure system, this instrument can simulate the lithostatic pressure and hydrostatic pressure achieved in reservoir rock.

It is widely accepted that high temperatures can be used to model reactions that occur at lower temperatures and over a long period of time in geologic systems, and the experiments in this study investigated six different temperatures: 130 °C, 180 °C, 230 °C, 280 °C, 330 °C and 380 °C. Every experiment at a different temperature was conducted for 72 h. The reaction conditions for each series of experiments are listed in Table 1.

The experimental procedure was as follows:

- (1) loading of K-feldspar (Ext.4) or skeleton (titanium alloy, Ext1-3);
- (2) vacuuming;
- (3) equal lithostatic pressure was applied to the top and bottom of the skeleton or mineral;
- (4) injecting solutions through high pressure liquid pump into the reaction cell until the water press reaches the target pressure. When the water pressure displayed by the pressure gauge exceeds 10% of the initial water pressure, the magnetic valve B is opened to discharge the gas production into the gas-liquid separator until the water press decreases to the initial water pressure;
- (5) After the separation of the gas and liquid, the gas was extracted using a standard purge-and-trap device and the liquid was injected into the reaction cell again by the liquid pump;
- (6) The experimental conditions (including temperature, time, lithostatic pressure, and water pressure) were recorded by a computer every minute.

Once the experiment was over, the reaction cell was put into a cold trap to separate the gas and liquid. Hydrochloric acid was added into the cell to convert carbonate and bicarbonate to carbon dioxide. Then, all gas samples were extracted using a standard purge-and-trap device. Gases were analyzed on an Agilent 6890 gas chromatograph (Agilent USA) fitted with a flame ionization detector operating at 200 °C for gaseous hydrocarbons. One milliliter gas samples were injected at 100 °C, with separation performed on a HP-PLOT-Q fused silica 30 m  $\times$  0.32 mm  $\times$  20  $\mu$ m column, with helium as the carrier gas. The oven temperature was programmed to increase from 35 °C (5 min hold) to 150 °C (3 min hold) at 5 °C/min, then to 270 °C (2 min hold) at 10 °C/min.

Liquid samples collected from the reaction cell were divided into four aliquots. One aliquot was used to determine the abundance of dissolved CO<sub>2</sub> (aq) and CH<sub>4</sub> (aq) by GC (Agilent 6890). The remaining three aliquots were used to determine the concentrations of Na, K, and acetate by ion chromatography. A Dionex ICS 3000 Ion Chromatography system (Dionex USA) equipped with

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