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EFFECT OF TEMPERATURE AND SOLUTION COMPOSITION ON THE PERMEABILITY
OF ST. PETERS SANDSTONE: ROLE OF IRON (III)

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INTRODUCTION

Understanding of the permeability of reservoir rocks at elevated temperature is becoming increasingly important both in oil field development and stimulation and in geothermal energy production. Rock properties such as permeability are often measured at ambient conditions with reservoir characteristics then based on these ambient measurements. However, rock and fluid properties may be radically altered at elevated temperatures due to the enhanced rates of mineral dissolution and growth and other geochemical processes.

A number of previous experimental studies have focused on determining the permeability of sandstones at reservoir conditions: Aruna (1976) measured permeability using water, nitrogen, oil, and 2-octanol of quartz sandstones at reservoir conditions as a function of temperature. A strong reversible decrease in permeability was noted when water was used. Rock permeability to the other fluids showed essentially no change with temperature. These results were supported by similar experimental studies of Danesh and others (1978) and Gobran and others (1980). Experiments by Piwinski and Netherton (1977) have shown decreases in permeability during continuous flow of Salton Sea brines through sandstone cores at 90°C. Read (1980) has observed decreases in permeability during dissolution studies of sand packs and cores at temperatures to 260°C.

The purpose of this study was to systematically investigate the effects of temperature and fluid composition on the permeability of quartz sandstones. We have concentrated our initial efforts on the time and flow dependence at 2 elevated temperatures (100°C, 200°C).

EXPERIMENTAL APPARATUS AND PROCEDURE

The equipment used was designed for continuous flow permeability studies to 300°C at confining pressures to 1.5 kbars. Fluid used in the experiments is pumped with a single piston metering pump with a gas-fluid separator in line to dampen pressure pulsations. Fluid is preheated to within 2°C of the experimental temperatures prior to entering the core holder. Metering valves control outflow rate which is simultaneously measured using a ball float gauge. Differential pressure is measured with a differential pressure transducer and readout. The initial system was built using stainless steel tubing and preheater in the flow line system. A second system was later built using titanium tubing and a special teflon liner for the fluid preheater.

Cores 5 cm long by 2.5 cm diameter of St. Peter Sandstone (>99% quartz) were used in these experiments. At room temperature no permeability decrease due to particle migration or clay plugging has been observed in this rock. The fluid used was boiled, distilled, deionized water. Typically the core was placed in the pressure vessel and then evacuated for several hours. The core was saturated at room temperature, and the permeability measured. The core was then reevacuated and the pressure vessel -pressure lines heated to the desired experimental temperature. Permeabilities were measured continuously through the experiment after the core was resaturated at temperature. Viscosity and density of the fluid at experimental conditions were taken from the Handbook of Chemistry and Physics (1969).

RESULTS

The first experiment was run using distilled water and the stainless steel experimental system. The results are shown in Figure 1 (curve a). The relative permeability, normalized to a reference room temperature value K_0 , drops off non-linearly with time. After 400 minutes of flow the pump was shut off. After 5 additional minutes, flow was briefly resumed for an additional measurement. This was repeated several times to determine permeability (K) during the non-flow period. The apparent permeability of the rock increases to a steady level during this period, approximately 73% of the room temperature permeability, and about 8% higher than the value measured during the flow part of the experiment. The core was then reevacuated, resaturated, and the permeability remeasured, at the same temperature. The measured permeability was equivalent to that measured at the start of the first experiment, or 95% of the room temperature permeability. This sequence demonstrates the reversibility of the measured permeability with respect to flow and resaturation. After removal of the core from the permeameter a slight reddish discoloration was noticed on the input end of the core which extended .25 cm into the core.

The results using the stainless steel system suggested that some type of plugging mechanism was responsible for the permeability decreases. The iron derived from corrosion of the steel in the flow system was considered to be a possible fouling material. To test this possibility experiments were repeated at 100°C using an inert flow system equipped with titanium and teflon. Titanium was used because of its inert properties even under extremely corrosive solution conditions (low pH, high Eh). The results of this experiment are shown on Figure 1, (curve b). Essentially no change in permeability was observed even in 400 ml of flow.

To test the system's response at even high temperature, the core was evacuated and heated to 200°C. After resaturating, approximately 400 ml of water was flowed through the core with no observed decrease in permeability. The core was reevacuated and cooled to 100°C with no apparent decrease in permeability. After cooling to 21°C the entire heating and cool-

ing permeability cycle was repeated except that the core was kept saturated the entire time. Only very slight increase (<10%) in permeability was observed during either one of these cycles. The results of these two experiments are shown on Figure 2, where permeability is plotted as a function of temperature.

As a test of the ferric iron fouling hypothesis two experiments were run in the titanium flow system using a dilute FeCl_3 solution (10PPM) at 100°C . The first solution was passed through the core with the pH of the solution (3.5) determined by the hydrolysis of the Fe^{3+} . A second experiment was subsequently run on the same core with the pH of the solution titrated with KOH to 5 prior to entry into the flow system. The permeability of the unbuffered experiment decreased slightly with time, while the permeability of the higher pH experiment decreased more sharply with flow. Figure 1, curve c shows the results of these two experiments. The pH 5 solution became slightly murky with time due to the formation colloidal $\text{Fe}(\text{OH})_3$.

DISCUSSION

The results of our experiments suggest that temperature as such has an insignificant effect on the permeability of quartz sandstones. Non-inert experimental flow through system such as those built with stainless steel will show substantial flow dependent decreases in permeability at elevated temperature due to the precipitation of colloidal ferric oxides or hydroxides in the flow channels. We believe that the ferric ion is produced during the oxidation-corrosion of the steel. Very low concentrations of Fe^{3+} (10PPM or less) can cause measureable decreases in permeability in 30 ml or less of fluid flow at 100°C .

The experiments of Reed (1980) also indicate colloid fouling since he observed strong decreases in permeability with time at elevated temperature even though his solutions (at a pH of 11) dissolved a significant amount of quartz during the experiment. We believe that the results observed by Aruna (1976), Danesh and others (1978), and Gobran and others (1980), all reflect the ferric ion plugging phenomenon which is accentuated at elevated temperature. Our observations of the significant apparent permeability increase during periods of no flow may explain the partial reversibility of previous experimental permeability vs. temperature results. These results are also in agreement with those of Piwinski and Netherton (1977) in which they related sharp decreases in permeability of cores using Salton Sea brines to precipitation of ferric hydroxide and amorphous silica.

There are at least two possible mechanisms for permeability reduction by Fe(III); 1) buildup of colloidal $\text{Fe}(\text{OH})_3$ on surfaces in pore throats (colloid fouling), and 2) formation of large particles of $\text{Fe}(\text{OH})_3$ which collect in pore openings. The equilibrium of pH of a Fe(III) - bearing solution is determined by the hydrolysis of the Fe^{3+} ion. The extent of hydrolysis and nature of the hydrolyzed species depend on the equilibrium solution pH, temperature, and total iron concentration (Baes and Mesmer, 1976). In the experiment in which the solution was

titrated to a pH of 5 before entering the core, nearly all the initial Fe(III) in solution was converted to ferric hydroxide; whereas, in the lower pH solution, more non-colloidal Fe(III) hydrolysis products were present in solution. The magnitudes of the permeability decrease for the different pH solutions shown in Figure 1 indicate that the fouling mechanism is predominantly colloidal fouling. The coagulation rate of ferric hydroxide is probably low in the very low ionic strength solutions used. However, the pH of the solution is clearly the most important factor controlling ferric hydroxide colloid formation, coagulation, and subsequent reduction in permeability. The increase in apparent permeability during static non-flow periods also suggests colloid buildup at surfaces is reversible in these systems. The results suggest a colloid fouling mechanism for permeability reduction may be important in natural systems containing Fe(III)-bearing solutions especially at elevated temperatures.

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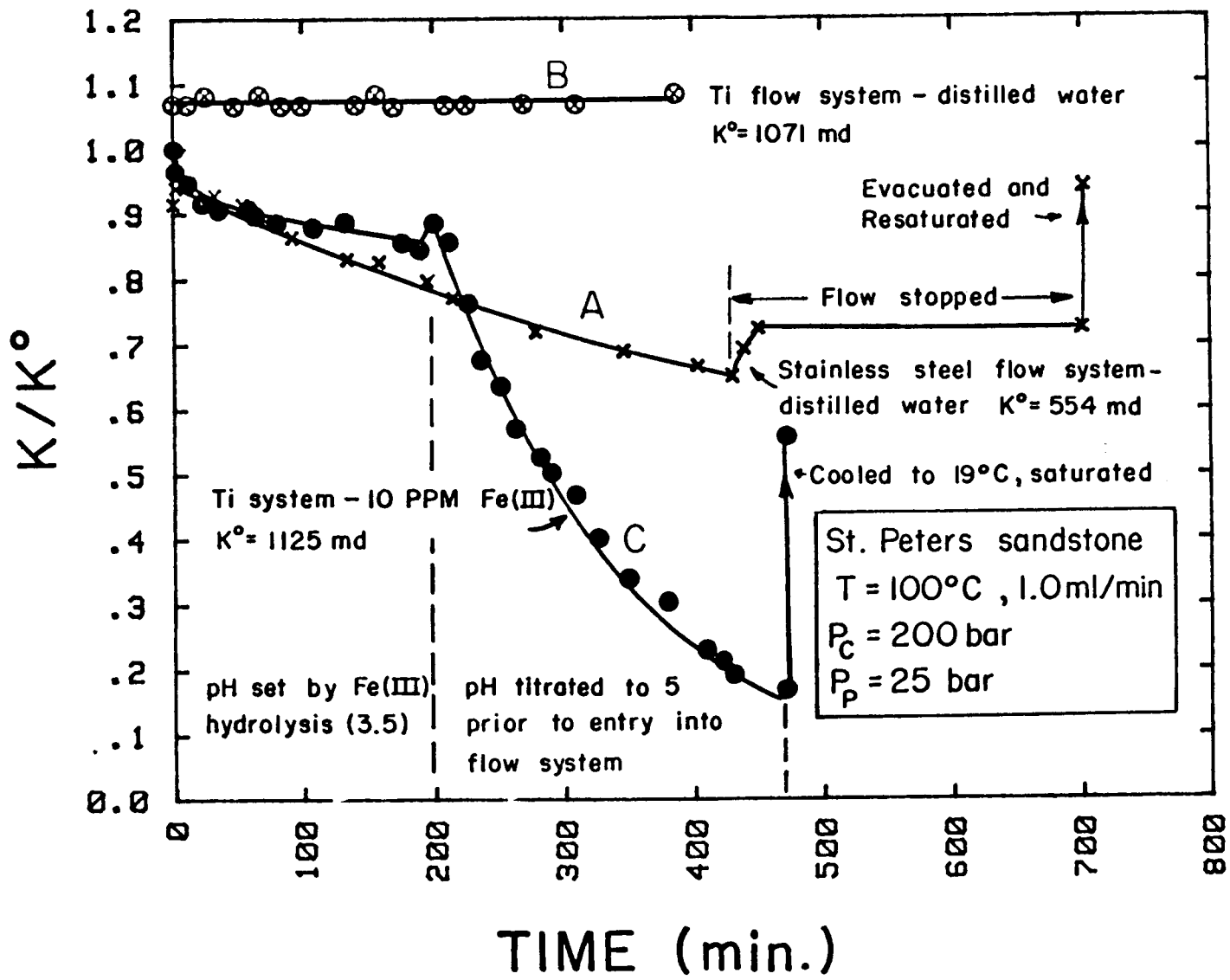


Figure 1. Normalized permeability as a function of time for St. Peters flow experiments at 100°C.

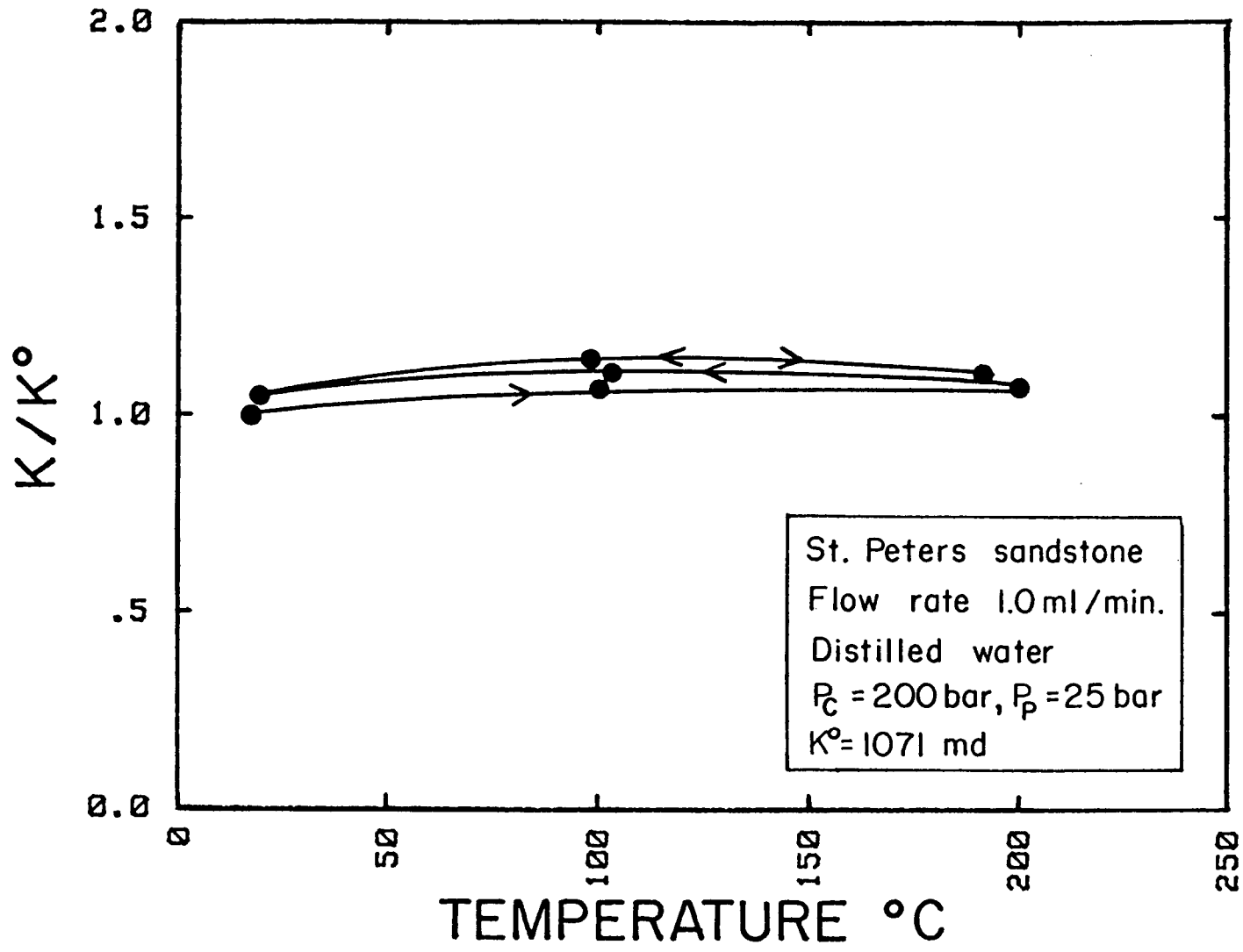


Figure 2. Normalized permeability as a function of temperature, St Peters sandstone.