On-line monitoring of clay mineral precipitation in sandstone porespace under flow conditions

J.S. Small
D.A.C. Manning
Department of Geology, University of Manchester, Manchester M13 9PL, UK.

Introduction

Knowledge of the mechanism and rate of precipitation of clay minerals formed in sandstone reservoirs is important to predicting the permeability of petroleum reservoirs as they respond to chemical changes during diagenesis, and over the much shorter time scale associated with petroleum engineering. Here we describe a high PT flow cell apparatus in which clay minerals can be precipitated in sandstone porespace. On-line monitoring of Si and Al concentration enables precipitation to be monitored and permits the measurement of reaction kinetics. To illustrate the technique we present some preliminary results of clay precipitation as a consequence the decomposition of a solution Al-malonate. Malonic acid is a dicarboxylate, present in oil field waters, which strongly complexes Al, but which is unstable at temperatures above ~110°C. These properties make malonic acid a potentially important transient species which may be significant to the redistribution of aluminosilicate species during diagenesis in organic-bearing pore waters (Surdam *et al*, 1989).

Methodology

Figure 1 provides a schematic illustration of the flow cell apparatus and on-line analysis system. The high pressure flow cell is a once-through system supplied by Coretest Systems, Mountain View California (model FT-21-C). The supplied software has been rewritten so that the analytical system can be integrated with flow cell control and PT data collection routines. The analytical technique is based upon colourimetry and uses a Dionex UV-visible chromatography detector.

The pore fluid is contained in an 800ml flexible bladder made from Viton rubber with titanium closures which is pressurised at 25°C in a stainless steel pressure vessel. Fluid can be released at a precise rate from the fluid bladder into the core holder by a metering pump which displaces pressurised water into the pressure vessel around the bladder.

The sandstone core is 1 inch diameter and is contained within a tight fitting gold tube (0.02inch wall thickness). The tube is sealed by two titanium closures which clamp the gold between a cone-on-cone seal (Potter *et al*, 1987). By annealing the gold

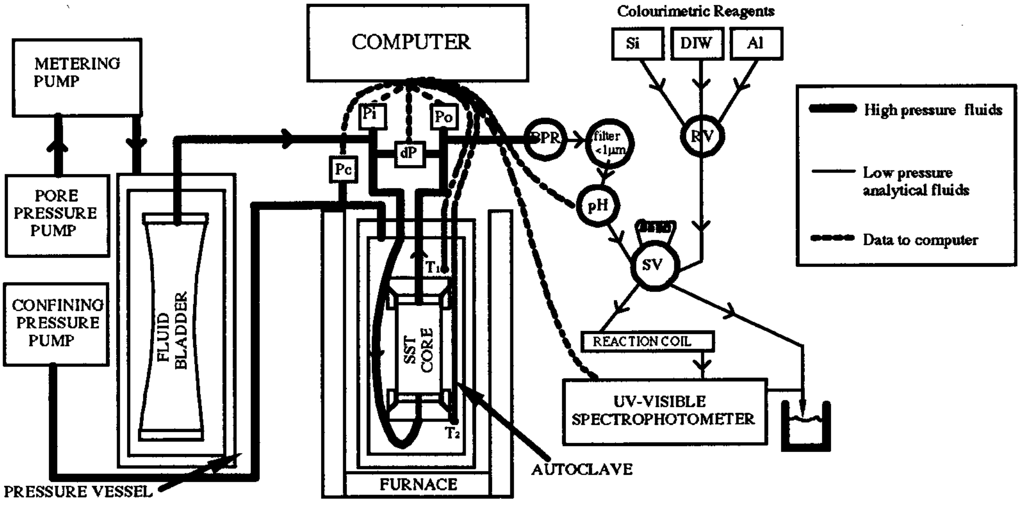

FIG. 1. Schematic of flow cell apparatus.

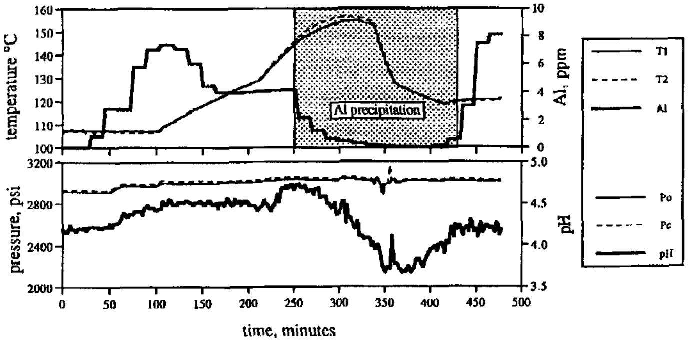

FIG. 2. Example data showing Al precipitation during Al-malonate decomposition.

tube and applying an external pressure of 100 psi the gold forms an effective seal around the outside of the sandstone core. The core holder is contained within a stainless steel autoclave which is held within a furnace. The confining pressure in the autoclave (Pc) is controlled by a separate pump. The lower inlet end of the core holder is connected to the fluid bladder and the outlet end is connected to a back pressure regulator (BPR) which allows fluid to be released to low pressure. High pressure titanium tubing with titanium isolating valves is used to connect the core holder. Temperature is measured at both ends of the core (T_1, T_2) by type K thermocouples. The confining pressure, inlet pore fluid pressure (Pi) and outlet pore fluid pressure (Po) are measured with 0-5000 psi transducers. Differential pressure (dP) across the core can also be measured by a 0-20 psi transducer, from which permeability can be calculated.

Cool fluid exiting the BPR at low pressure ($\sim$5 psi) passes through a 1mm in-line filter and through a flow pH electrode. The fluid then enters a six port sampling valve (SV) where either sample fluid, or colouring reagent can be directed through a 1 ml sample loop. Normally SV is in the 'load' position where sample fluid flows through the loop and then exits; in this position colouring reagent passes directly to the spectrometer. Periodically, under the control of the computer, the valve position switches to 'inject' and colouring reagent then flushes the sample loop; complete reaction is ensured by passing the reagent and sample through a 1m long knitted mixing coil. The absorbance measured by the spectrometer records a series of peaks corresponding to each sample injected by SV. The area of each peak is recorded, correcting for any drift in baseline absorbance. The peak area can be calibrated using standard solutions. The colouring reagent flows through the analytical system under a pressure of 5 psi of nitrogen. The reagent can be changed through valve (RV) which can select either Si sensitive reagent (Na molybdate, 410nm), Al sensitive reagent (pyrocatchecol violet, 570nm) or deionised water. The spectrometer wavelength and position of valve RV are controlled by the computer.

Results and discussion

Figure 2 shows example data output during the precipitation of clay minerals in a 5 cm long core of Fontainebleau sandstone. In this experiment a solution of 0.01M malonic acid containing pre dissolved Al (3 ppm) and Si (10 ppm) was passed through the core at a flow rate of 0.02ml/min. Al concentration was measured at 900 second intervals. The experiment was initially stabilised at 108°C and 2900 psi for several days before flow was started (time 0 in Fig. 2 represents start of flowing). Initially the fluid is enriched in Al relative to the starting concentration, this is probably a consequence of the dissolution of aluminosilicate on standing at 108°C, which was precipitated in an earlier test. Al concentration subsequently stabilises at 4 ppm between 150 and 250 min. At 100 min. temperature was increased, and at 260 min., when T = 145°C Al concentration started to decrease as a result of the decomposition of Al-malonate and the precipitation of Al. After 300 min. the autoclave was cooled, associated with a subsequent rise in Al concentration at 400 min. as the temperature falls below the threshold of Al-malonate decomposition ($\sim$130°C) The variation in Al concentration lags, by $\sim$50 min, behind the changes in temperature which induce malonate decomposition; a consequence of dead volume in the tubing exiting the core. A decrease in pH correlates with the decomposition of Al-malonate to acetic acid, CO2 and precipitated Al. These data illustrate how the on-line analysis of Al monitors Al precipitation and dissolution in response to temperature. Similar correlation between precipitation rate and flow rate has also been obtained. On going work involves quantification of the rate of malonate decomposition and Al precipitation reactions and mineral characterisation of the precipitates.