USING CALORIMETRY TECHNIQUES FOR MESOPOROSITY CHARACTERIZATION

Korobkov D.A., Nadeev A.N., Safonov S.S.
Schlumberger

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ABSTRACT

Application of the differential scanning calorimetry (DSC) for the characterization of the porous media is considered. Since the phase transition in closed systems (pores) occurs at lower temperatures than in the bulk, measured value of the shift in the temperature of the phase transition can be used for the characterization of the porous media. The shift in the solid-liquid phase transition temperature in the porous media depends on the pore size due to the influence of surface effects, therefore interpretation of the temperature shift measurements can provide information on the pore size distribution. Dependence of the thermal effects of the imbibitions process on the fluid-surface interaction can provide on information on the wettability of the rock sample.

Estimation of the pore size distribution was performed in the set of the experiments on standard samples of controlled pore glass (CPG) and on core plugs with a well-known pore structure. Pore size was estimated from the measured temperature shift using Gibbs-Thomson formula. The wettability of the porous media can be estimated from the measurements of the thermal effect of the liquid intrusion and extrusion. Wetting angle can be estimated from the Young equation that provides relation between variation of the free-energy of the system for these processes and the wetting contact angle. Core fluid intrusion experiments were performed for sandstones and CPG with brine as intruding fluid. Although the process of spontaneous imbibition could not be considered due to the limitations of the experimental setup, the effect of forced injection in mesopores was observed and allows estimation of the contact angle. The estimated value of the contact angle for sandstones was in good agreement with wettability determined on a core plug with Amott-Harvey method.

INTRODUCTION

Wettability plays a significant role in the initial distribution of multiphase, multicomponent fluids, movement of fluids through porous media, as well as the displacement of one fluid by another within the reservoir. To understand properly this displacement behavior and use it to optimize reservoir production, the clear determination of the type of wettability existing within a reservoir is very important. Despite numerous studies of wettability, this phenomena has not yet been well understood [1].

Contact angle is formed by the interface between two fluids at the solid surface. It is defined geometrically as the angle formed by a liquid at the three-phase boundary where a liquid, gas, and solid intersect. Contact angle is an invaluable metric for understanding material surface properties—adhesion, wettability, and free energy of solid surface.

Young's equation is used to describe the interactions between the forces of cohesion and adhesion and measure what is referred to as surface energy:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta, \tag{1}$$

where θ is contact angle, γ_{sv} is solid-vapor interfacial free energy, γ_{sl} is solid-liquid interfacial free energy, and γ_{lv} is liquid-vapor interfacial free energy. Comparison of methods of contact angle measurement [2–4] shows that sessile drop and capillary rise methods are more universal and have significantly high experimental repeatability. The sessile drop method is used for investigation of material surface properties and effects of surface active agents on selective wettability. The capillary rise method is preferred for modeling and investigation of capillary effects. These two methods complement each other and can be helpful in determining features of studied processes. Nevertheless, there are some difficulties in application of contact angle measurement for core wettability analysis: the contact angle cannot describe the roughness, heterogeneity, and complex geometry of pore structure. Contact angle is fixed on a smooth surface, and there is a wide range of possible contact angles on the sharp angles found on a core sample surface. Contact angle is measured on a single mineral crystal while a core contains many different constituents. Finally, presence of permanently attached organic coatings on the core surface can strongly affect wetting properties.

A conventional method of core wettability determination is the Amott method [5, 6]. It combines imbibitions and forced displacement useful for measuring the average wettability of a rock sample. The Amott method is based on the fact that the wetting fluid will generally imbibe spontaneously into the core, displacing the nonwetting one. A number of researchers [7] have used a modification of the Amott wettability method called the Amott-Harvey relative displacement test. The main problem with the Amott wettability method and its modifications is their insensitivity near neutral core sample wettability. Recently another way to study wettability was explored by carrying out calorimetric experiments. Calorimetry has long been used to study the interactions between fluids and surfaces. From calorimetry it is possible to obtain thermodynamic state functions such as internal energy or enthalpy related to the wetting process [8, 9]. The advantage of calorimetric methods is the possibility to carry out experiments in which the initial and final states of the system are really well defined, which is not always the case for contact angle measurements.

DSC monitors heat effects associated with phase transitions, system internal energy change, and chemical reactions as a function of temperature. The difference in heat flow to the sample and a reference at the same temperature in a DSC is recorded as a temperature function. The reference can be an inert material such as alumina, or just an empty calorimetric cell [10, 11]. The heat flow is measured in mJ*sec^{-1}. It can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and therefore heat flow to the sample is higher than that to the reference, so the difference is positive.

It is well known that the temperature shift of materials melting/crystallize inside the pore structure depends on the pore size where the processes occur. Melting temperature of liquid in bulk T_0 and in pore structure T_m can be measured using calorimetry techniques [12]. Phase-transition temperature shift depending on pore sizes can be determined by the Gibbs-Thomson equation:

$$\Delta T_m = T_0 - T_m = \frac{2T_0 \gamma_{sl} \upsilon_l}{R \cdot \Delta H} \quad , \tag{2}$$

where γ_{sl} is solid-liquid free-surface energy (ice water), υ_l is the specific liquid volume, R is the characteristic pore size, and ΔH is the specific heat of phase transition.

The process of liquid intrusion or extrusion into the pore medium where a surface is immersed in a liquid starting from a controlled relative pressure is related to immersional wetting. The free energy variation (per unit area) during the process can be described by equations (3, 4):

$$\Delta F = \gamma_{sl} - \gamma_{sv} \quad , \tag{3}$$

where γ_{sl} is solid/liquid interfacial free energy and γ_{sv} is the solid/vapor interfacial free energy.

Spreading wetting relates to a process in which a solid/vapor interface is progressively replaced by a solid/liquid interface. According to correlation between thermodynamics potentials, change of internal energy of liquid intrusion (immersion) process is expressed from free energy variation:

$$\Delta U = \Delta F - T\frac{\partial \Delta F}{\partial T} = \gamma_{sl} - \gamma_{sv} - T\frac{\partial(\gamma_{sl} - \gamma_{sv})}{\partial T}$$

(4)

Young's formula can be placed in equation (4), so the result is

$$\Delta U = -\gamma_{lv}\cos\theta + T\frac{\partial \gamma_{lv}\cos\theta}{\partial T} \approx \left(-\gamma_{lv} + T\frac{\partial \gamma_{lv}}{\partial T}\right)\cos\theta \quad . \tag{5}$$

The approximation in equation (5) is possible only in the case of constant contact angle irrespective of temperature. This fact for water intrusion in a nanoporous medium was proved in an article by Denoyel et al. [9]. The equation (5) without approximation and its modification can be used for experimental measurement of immersion energy and for following the wetting contact angle in processes of liquid intrusion. In the case of wetting solids, it is very hard to carry out calorimetric experiments corresponding to spreading wetting because it is difficult to efficiently control an initial state of solid.

The calorimeter apparatus

Specifications for the differential scanning calorimeter used for the calorimetric experiments are given in Table 1. For these experiments, a curve in which temperature or time is plotted on the x-axis and heat flux difference is plotted on the y-axis were recorded. The reference specimen was an empty calorimetric cell identical to the one containing the test specimen. The calorimeter is based on the Tian-Calvet calorimetric principle: 3D heat flow sensor. Using the 3D sensor, the sample is almost completely

Table 1. Calorimeter specification.

Temperature	-196°C to 200°C
Scanning rate	0,01 to 1°C*min^{-1}
Cooling (with liquid nitrogen)	1°C*min^{-1}
Limit of (isothermal) power detection	1-2 μW
Limit of (scanning) power detection	2 to 20 μW, depending on sample and scanning rate
Cell size	Diameter 17 mm, height 80 mm

surrounded by rings of thermocouples so that the heat flow emitted from or absorbed by the sample is almost completely measured. The efficiency ratio of the 3D sensor is about 94%. By using two identical 3D sensors for the sample and the reference, the analyzers ensure accurate and reproducible specific heat or heat reaction determinations [13].

RESULTS

Immersion energy measurement using DSC

A special flow unit (FU) was developed to carry out calorimetric experiments of liquid intrusion. Core fluid intrusion experiments were provided for Parker Country sandstone with high porosity (φ = 18.15%) and respectively low permeability (k_{abs} = 16.6 mD). The sample was a cylinder with sizes diameter d = 7.76 mm, and lengths L = 32.14 mm. For the intruded liquid, a brine solution of 20 g of KCl per 1 L of DI-water was used. The calorimeter tank and flow unit pumps were held at 26°C (79°F), which was the temperature of the provided experiments. A sample was placed into one high-pressure calorimetric cell and brine was intruded into cell (flow rate Q = 0.01 mL/min) with the sample. During the whole experiment, differential heat flow between the cell with the sample and the empty one was measured. Two types of experiments were carried out: the first was a blank test with brine intrusion into empty cell and the second was an intrusion into cell with the sample.

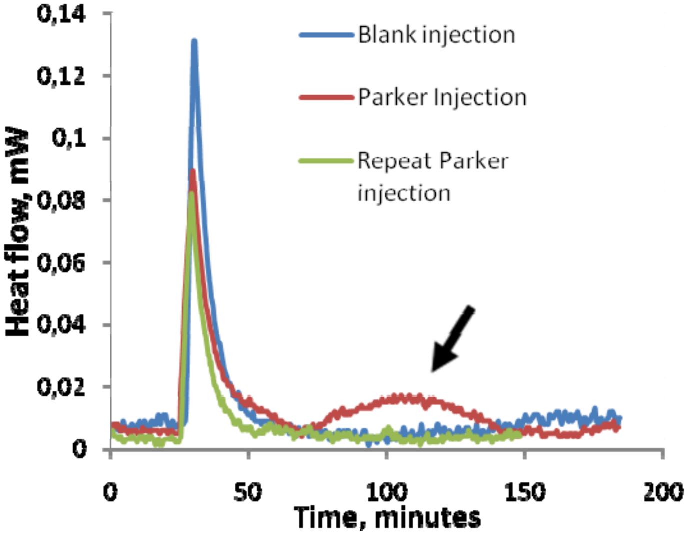

Figure. 1. Heat flow depends on time for brine pressure 1 MPa (10bar) at temperature 26°C (79°F). Addition heat flow peak marked by arrow.

All experiments were carried out using three steps:

1) The cell with sample (or without, for blank experiment) was placed into calorimeter tank and held in average for 3 h at 26°C (79°F) for stabilization of heat flow.
2) Then cell filling started with the flow rate of brine Q = 0.01 mL/min up to pressure of 0.1 MPa (1 bar). To fill the cell with brine, reach adjusted pressure, and stabilize heat flow took about 14 h. Three hours passed for each of the following pressure steps: 0.2

MPa (2 bar), 0.4 MPa (4 bar), 0.8 MPa (8 bar), 1.0 MPa (10 bar), 2.0 MPa (20 bar), and 15 MPa (150 bar). In whole, all the steps took 18 h in aggregate.

3) Brine pressure decreased to pressure of 0.1 MPa (1 bar) and was held for 3 h for stabilization. Then all pressure stages of Stage 2 were repeated during the same time of experiment (18 h).

A detailed view of the results of brine intrusion for pressure of 1 MPa (10 bar) is presented in Figure 1. The main narrow peaks relate to the process of water compressing during increase of pressure; the heat flow effect is increasing with rising pressure. Additional effects related to the appearance of wide heat flow peaks after pressure stabilization can be involved in the process of brine intrusion into pore space. An additional wide peak appeared (Fig. 1, arrow), which compared with the blank experiment and repeated intrusion into Parker sandstone. The main narrow peaks are related to the process of increasing pressure. This additional heat flow peak could be involved in the process of brine intrusion. The same type of wide peak was also observed for a pressure 0.8 MPa (8 bar). The following increase of pressure did not result in the appearance of any additional peak. So, measurable heat flow effects of brine intrusion into Parker sandstone occurred at pressure up to 1 MPa (10 barThe area of heat flow peak is used for calculation of internal energy change (equation 5) and for following estimation of contact angle ($\theta = 43^o$). That is in accordance with the Amott-Harvey test for the sample.

As ideal samples, known sizes of controlled pore glasses (CPG) were used. CPG particles are manufactured from a borosilicate base material that is heated to separate the borates and the silicates. The borates are leached from the material to create a silica glass with uniform and controlled pore sizes with at least 80% of the pores within ±10% of the mean pore diameter. The water fusion temperature in the pores was measured according to international standard ISO 11357-1 for transition temperature measurement with DSC [10]. On the assumption of known parameters v_l, ΔH for water and ice- water interfacial surface tension (equals $\gamma_{sl} = 60.5$ mJ/m^2) CPG pore sizes can be calculated (Figure 2). Effective pore radii for CPG 100 (r_{eff}=120 Å) and CPG 300 (r_{eff}=380 Å) were calculated by formula 2. Radii values are in good agreement with actual values (103 Å and 310 Å correspondingly) given by CPG manufacturer.

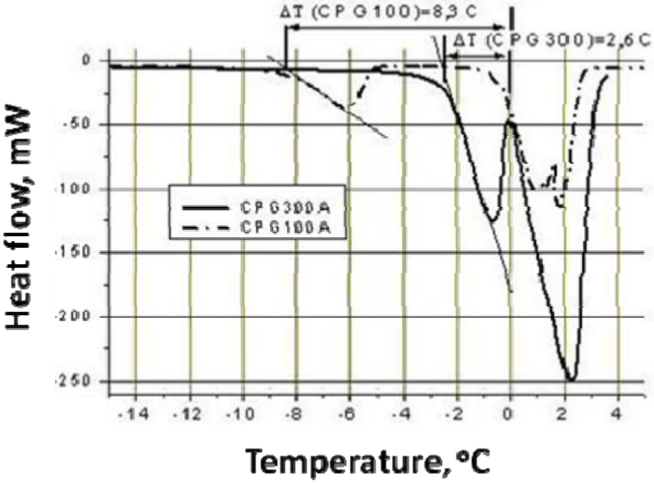

Figure 2. Melting temperature shift for samples CPG 100A and CPG 300A.

CONCLUSIONS

A techniques survey of contact angle measurement shows us that only a few methods for core wettability analysis can be applied due to limits of other methods related to sample preparation, effects of surface contamination, mineralogy heterogeneous, and surface roughness. Calorimetry techniques were used and the experiments are described in the article. We applied calorimetric measurements of brine intrusion into a natural core sample distinguish from those of a modeled pore medium with narrow pore size distribution from 1 to 10 nm [8, 9]. The approach using heat flow measurement can possibly be used for wetting contact angle measurement of natural core samples. Another promising approach of core pore size distribution measurement based on temperature shift of liquid phase transition was applied for CPG characterisation. Limitation of calorimetric methods application and its following development for such processes as phase transition and immiscible liquids displacement will be continued.

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