

THE MEASUREMENT OF CORE SAMPLE SURFACE WETTABILITY HETEROGENEITY BY ADSORPTION CALORIMETRY

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ABSTRACT

Adsorption calorimetry is one of the methods that allow assessing surface wettability heterogeneity. The comparison of water vapor adsorption enthalpy on the surface of the rock sample to water liquefaction enthalpy at different water vapor partial pressures allows one to determine the surface wettability state and the spatial heterogeneity of the wettability state of a rock surface. The described measurements were done on low-permeability dolomite core samples prior to and after the extraction of the cores.

INTRODUCTION

Reservoir formation surface wettability is a major factor controlling the location, flow, and distribution of fluids in a reservoir [1; 2]. Being a major factor controlling fluids behavior, wettability affects all types of reservoir analysis – electrical properties, capillary pressure, relative phase permeabilities, etc. Reservoir wettability strongly affects oil recovery, particularly in secondary and tertiary methods of oil recovery.

Wettability can be vaguely described as a tendency of one fluid to spread on or adhere to the solid surface in the presence of another immiscible fluid. Reservoir wettability is often classified by the average affinity of the liquids to the surface: water, neutral, or oil wet; and by the spatial distribution of wettability: uniform, fractional (heterogeneous surfaces with random distribution of differently wet formation particles), and mixed wet (smaller pores are more water wet, while bigger pores are more oil wet).

Wettability is determined by the physicochemical interactions of fluids with each other and with the heterogeneous surface of the solid media. Because investigation of surface interactions is quite complex, no universal in-situ method for wettability measurements currently exists, which drives continuing research on this theme.

The wettability of strongly water-wet or strongly oil-wet reservoirs may, in some cases, be inferred from log analysis, but core analysis methods are implemented for a more accurate wettability characterization. The US Bureau of Mines (USBM) and Amott-Harvey method, or a combination of the two, are considered as industry standards for wettability estimation in core analysis. Both methods simulate reservoir processes during oil recovery and are based on the measurements of the displacement efficiency of oil by water and water by oil during spontaneous imbibition and/or forced fluid displacements in the centrifuge. As the outcome of these tests as a rule, just one number is retrieved:

between -1 and 1 for the Amott test and between $-\infty$ and $+\infty$ for the USBM test. A single parameter does not allow one to understand the average wettability of the surface, nor does it give any information on the spatial distribution of wettability on the surface of the rock.

Complex spatial distribution of wettability over the surface of a rock is a well-known fact and is one of the major concerns in the oil industry. At the same time, surface wettability heterogeneity is rarely addressed because of the lack of characterization methods. Adsorption calorimetry is one of the methods that can be used to quantify surface wettability heterogeneity of the core samples.

EXPERIMENT DESCRIPTION AND RESULTS

Adsorption can be described as the enrichment of the adsorbed material in the vicinity of the interface. Adsorption occurs when a solid surface is exposed to liquid or gas [3]. Gas adsorption isotherm measurements (mass of the gas/vapor adsorbed versus gas partial pressure) can, in some cases, be used for surface wettability characterization. Thus, for a limited number of kinds of adsorption isotherms, this method can be used to quantify average surface wettability [4] or, sometimes, can be used to quantify hydrophobicity coefficient, i.e., the ratio of hydrophobic surface area (covered by adsorbed oil components) before core cleaning to the pure solid surface area after core cleaning [5].

Adsorption calorimetry measurements (heat of adsorption versus partial pressure) give information on the energetics of surface interactions. The evolved heat is related to the energy of bonds formed between the adsorbed species and the adsorbent and can be used, for example, to discriminate chemical adsorption from physical adsorption.

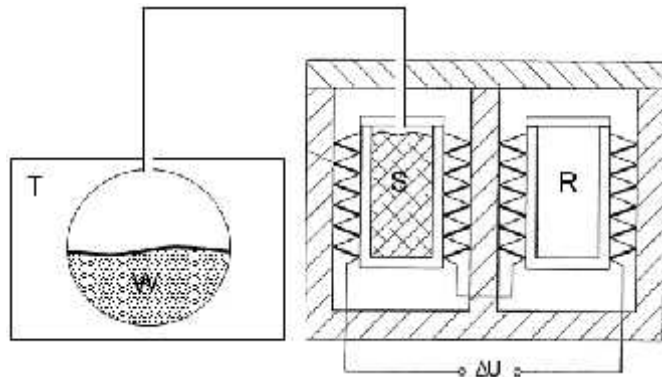
Even richer information on surface properties is obtained if one combines the adsorption isotherm measurements and the adsorption calorimetry measurements. Thus, the measurements were used to quantify the wettability variation due to the modification of calcite, kaolinite, and quartz powders by different long-chain fatty acids [6]. In this method, integral specific enthalpy of adsorption (total enthalpy divided by the total adsorbed vapor mass) at each vapor pressure is compared to the enthalpy of water liquefaction (2444 kJ/kg at 25 °C). The most energetic surface sites are occupied first by the adsorbed species with a bigger release of energy followed by the adsorption of the less energetic sites, which allows monitoring surface heterogeneity.

In the present work, the adsorption isotherms were determined by the measurements of the variation of the mass of core samples that were placed under different humidity conditions, and a differential scanning calorimeter was used to measure the heat of adsorption in separate experiments.

The differential scanning calorimetry (DSC) technique allows one to measure transient differential heat flows between the two cells of a differential scanning calorimeter [7]. The measurements can be done either at constant temperature (isothermal mode) or during the controlled variation of the temperature (scanning mode) of the calorimeter furnace. In the isothermal mode of measurements (the mode used in this work), the second cell allows compensating external temperature fluctuations providing high signal-

to-noise ratio of the measurements. High accuracy and versatility of the DSC devices leads to a broad use of this technique in many modern industries. The application of the DSC technique to laboratory core analysis can provide a lot of valuable information; in particular it can help to accurately measure core sample specific heat capacity, pore size distribution, surface area, and average wettability state [8].

A Calvet-type DSC was used for the experiments. All measurements were made in the isothermal mode at 25 °C. The calorimeter measurement cell was hermetically connected to an external glass bulb, filled with distilled water (Figure 1). Water temperature was controlled by a high-precision (0.01 °C) thermo-circulator. The variation of the temperature in the glass bulb allowed controlling the vapor partial pressure in the cell. Prior to the calorimetry experiment, the sample cell with a sample is evacuated under temperature (85 °C). Each step in pressure lasted several hours (5 to 12 h.), and the complete calorimeter adsorption isotherm lasted about 4 days for each of the samples.



Water, W, temperature is controlled by a thermocirculator, T. Sample cell with a sample S is connected to the water tank. R – is an empty reference cell.

Figure 1. Experimental setup photo and scheme.

Adsorption isotherm (mass variation versus partial vapor pressure) measurements were done by the use of a microbalance (~ 0.5 mg accuracy). Each of the core samples was put in a beaker, and all the beakers were put into a hermetically closed desiccator at 25 °C (Figure 2). Another tank with saturated solution of NaOH for $P = 0.07 P_{\text{sat}}$; LiCl 0.11 P_{sat} ; $\text{C}_2\text{H}_3\text{K}_0_2$ 0.22 P_{sat} ; MgCl_2 0.33 P_{sat} ; K_2CO_3 0.43 P_{sat} ; $\text{Mg}(\text{NO}_3)_2$ 0.53 P_{sat} , etc., was put in the desiccator to control the vapor pressure [9]. The variation of the mass of the beakers was controlled until the weight was constant. Each step in vapor pressure took approximately 7 days. Distilled water and



Figure 2. Adsorption isotherm measurement setup.

chemically pure (99.5%) chemicals were used for the preparation of the solutions.

Five pairs (prior to and after the extraction) of low-permeability (~3 mD) dolomite core samples were studied by the proposed method. The extraction of core samples was done by benzol in a Soxhlet apparatus. Three companion groups of core plugs were prepared. The first group of samples was used for routine core analysis and special core analysis measurements. The second group was used for carbonate analysis and residue X-ray diffraction (XRD). A third group was small plugs cut for micro-computed tomography analysis (micro-CT), and adsorption calorimetry. Cores in each triplet were drilled from the same full-size core and had similar properties. XRD analysis of studied samples demonstrated that they consist mostly of dolomite (~85 %) (Table 1). Analysis of insoluble residue showed that it consists of quartz (60 – 84%), microcline (8 – 37%), albite (up to 15%), and gypsum (1 – 3%). Joint analysis of mercury capillary pressure micro-CT showed us that most pores (more than 70% of porous space) have a pore radius of 2 to 20 μm . These relatively big pores are connected with a network of capillaries with a radius of less than 1 μm .

Table 1. Carbonate and residue XRD analysis.

Sample #	Calcite %	Dolomite %	Insoluble residue, %	SiO ₂	Fe ₂ O ₃
1	0.0	82.4	17.6	1.7	2.2
2	5.6	88.0	6.4	1.3	2.0
3	0.0	82.9	17.1	3.6	1.2
4	0.0	91.4	8.6	5.6	5.3
5	0.0	82.5	17.5	1.6	2.3

Miniplug core samples photographs and designations are shown in Figure 3. Figure 4 and 5 contain core sample weight loss after extraction versus oil saturation from nuclear magnetic resonance measurements (S_o) (notice the corresponding color variation in Figure 3). Figure 6 and 7 show the adsorption isotherms and calorimetry heat isotherms respectively. All curves are drawn with a corresponding color; the curves for the extracted cores are plotted by the dashed lines. Figure 8 and 9 show the final calculated integral specific heat isotherms and differential specific heat isotherms (adsorption enthalpy divided by the adsorbed vapor mass at each step) for the studied core samples.

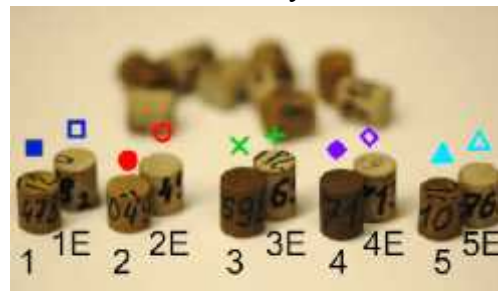


Figure 3. Core samples designations.
Miniplug sizes: 8 mm X 8 mm

The obtained results look very interesting for analysis. The adsorption isotherms on the extracted cores lie below the isotherms for the non-extracted cores. One of possible reasons for this is a diminishing of the surface area during the extraction. BET measurements of the core surface areas disprove this idea. The surface area of the samples after the extraction has grown by ~ 1.7 times. So, the adsorption isotherms for oil-containing samples do lie above the ones for clean dolomitic surfaces of rocks. Erroneous interpretation on wettability state would be obtained if the regular procedure for hydrophobicity coefficient calculation [5], which works well for clastic formations, would be implemented in this case. The adsorption calorimetry measurements, in reverse, show the anticipated results on the wettability state of the cores (dashed lines lie above).

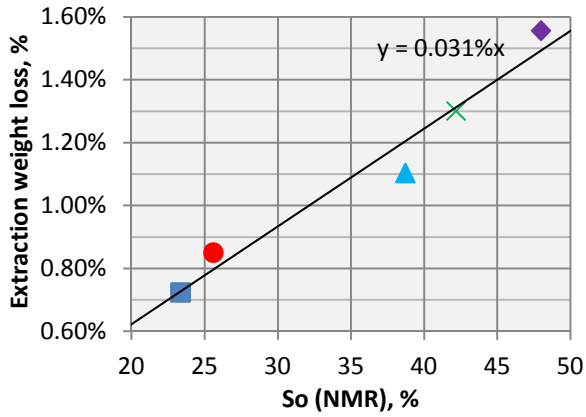


Figure 4. Core weight loss versus S_0 .

Sample designations: 1 ■; 1E □; 2 ●; 2E ○; 3 ×; 3E +; 4 ◆; 4E ◇; 5 ▲; 5E Δ.

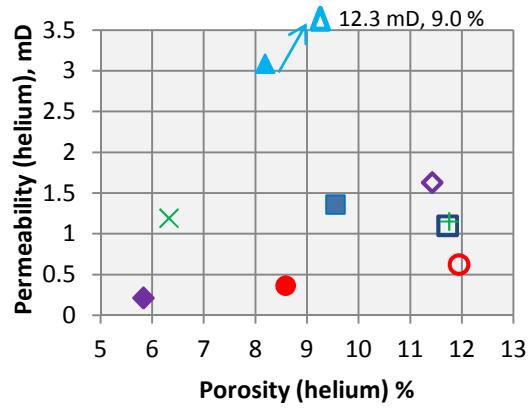


Figure 5. Porosity and permeability.

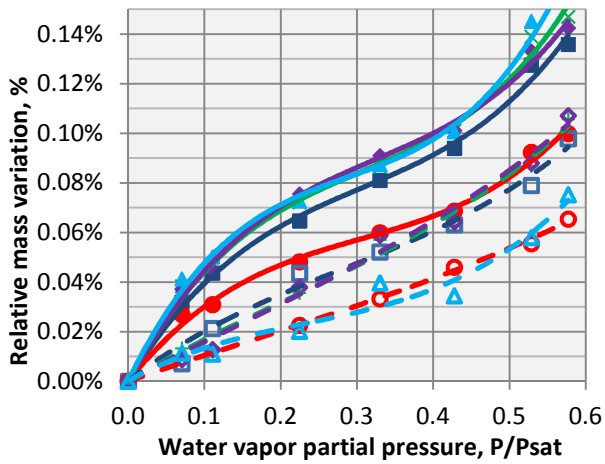


Figure 6. Adsorption isotherms.

Solid and dashed lines are for samples prior to and after the extraction accordingly

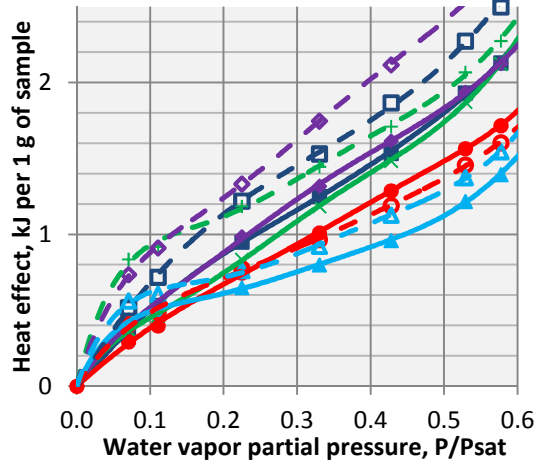


Figure 7. Calorimetry isotherms.

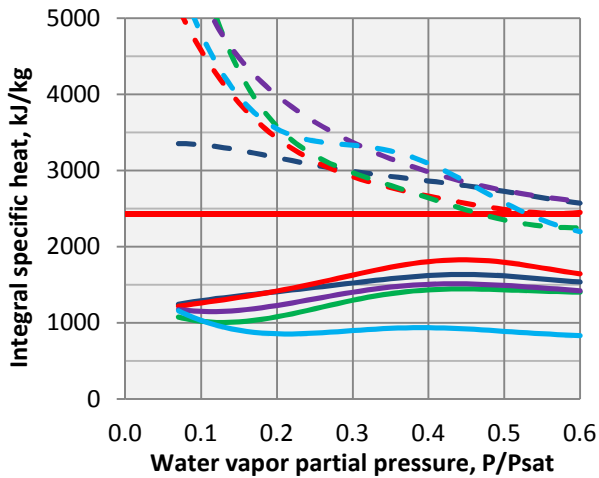


Figure 8. Integral specific heat.

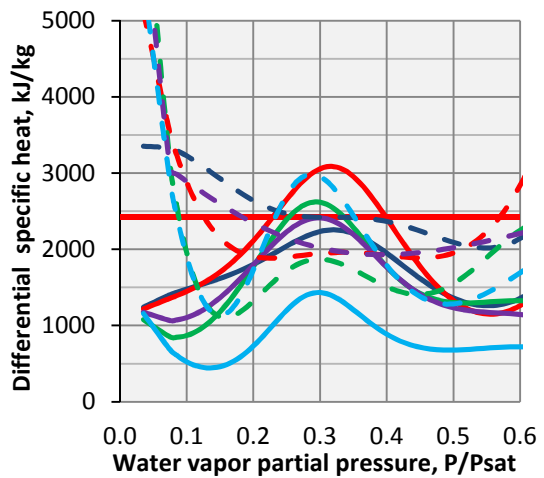


Figure 9. Differential specific heat.

A combination of the measurements gives even better understanding of the wettability state. Thus, the integral specific heat curves (Figure 8) clearly show that the oil-containing cores have much lower affinity for water than the extracted cores. The solid lines for non-extracted cores lie below the water liquefaction heat (shown by a flat red line) whereas the dashed lines, which correspond to extracted cores, lie above this threshold. The differential specific heat curves, although with a bigger spread compared to integral curves (due to the differentiation procedure), show that extracted cores are clearly heterogeneous surfaces (initial part of the curve corresponding to a first monolayer formation is quite steep) whereas the non-extracted cores are rather homogeneous with curves very similar to the curves obtained for vapor adsorption on pure carbon surfaces [10]. This allows us to make a conclusion on the wettability state of the non-extracted cores as being completely modified by adsorbed oil components to oil-wet state without much signature for smaller pores to be water wet in the studied cores.

CONCLUSION

A known approach for characterization of surface media by adsorption calorimetry was implemented for low-permeability carbonate core samples. The obtained results allowed understanding of the wettability state of the cores prior to and after the extraction. Further development of the experimental procedure would allow for more quantitative results.

REFERENCES

1. *Fundamentals of Wettability*. **Abdallah, W., et al.** 2, 2007, Oilfield Review, Vol. 19, pp. 44-61.
2. **Donaldson, E. and Alam, W.** *Wettability*. Houston : Gulf Publishing Company, 2008. ISBN 1-933762-29-2.
3. **Rouquerol, F., Rouquerol, J. and Sing, K.** *Adsorption by Powders and Porous Solids*. s.l. : Academic Press, 2009.
4. *Wettability: Thermodynamic Relationships between Vapour Adsorption and Wetting*. **Schlangen, L., et al.** 1994, Colloids and Surfaces A: Physicochemical and Engineering Aspects, pp. 157-167.
5. **Gudok, N., Bogdanovich, N. and Martynov, V.** *Measurements of Physical Properties of Oil Reservoir Formation (Opredelenie Neftefizicheskikh Svoistv Gornykh Porod - in Russian)*. Moscow : Nedra, 2007. ISBN 978-5-8365-0298-0.
6. *Wettability of Calcite and Mica Modified by Different Long-Chain Fatty Acids (C18 Acids)*. **Rezaei Gomari, K., Denoyel, R. and Hamouda, A.** 2006, Journal of Colloid and Interface Science, Vol. 297, pp. 470-479.
7. **Hohne, G., Hemminger, W. and Flammersheim, H.** *Differential Scanning Calorimetry*. 2nd. Berlin : Springer, 2010. pp. 38-40. ISBN 978-3-642-05593-5.
8. *Application of Differential Scanning Calorimetry to Core Analysis*. **Dyshlyuk, E.** Napa Valley, California, USA : Society of Core Analysts 2013. SCA2013-055.
9. *Standard Solutions for Humidity Control at 25 deg C*. **Stokes, R.** 9, 1949, Ind. Eng. Chem., Vol. 41, pp. 2013-2013.
10. *Water Adsorption on Carbons - Critical Review of the Most Popular Approaches*. **Furmaniak, S., et al.** 2008, Advances in Colloid and Interface Science, Vol. 137, pp. 82-143.