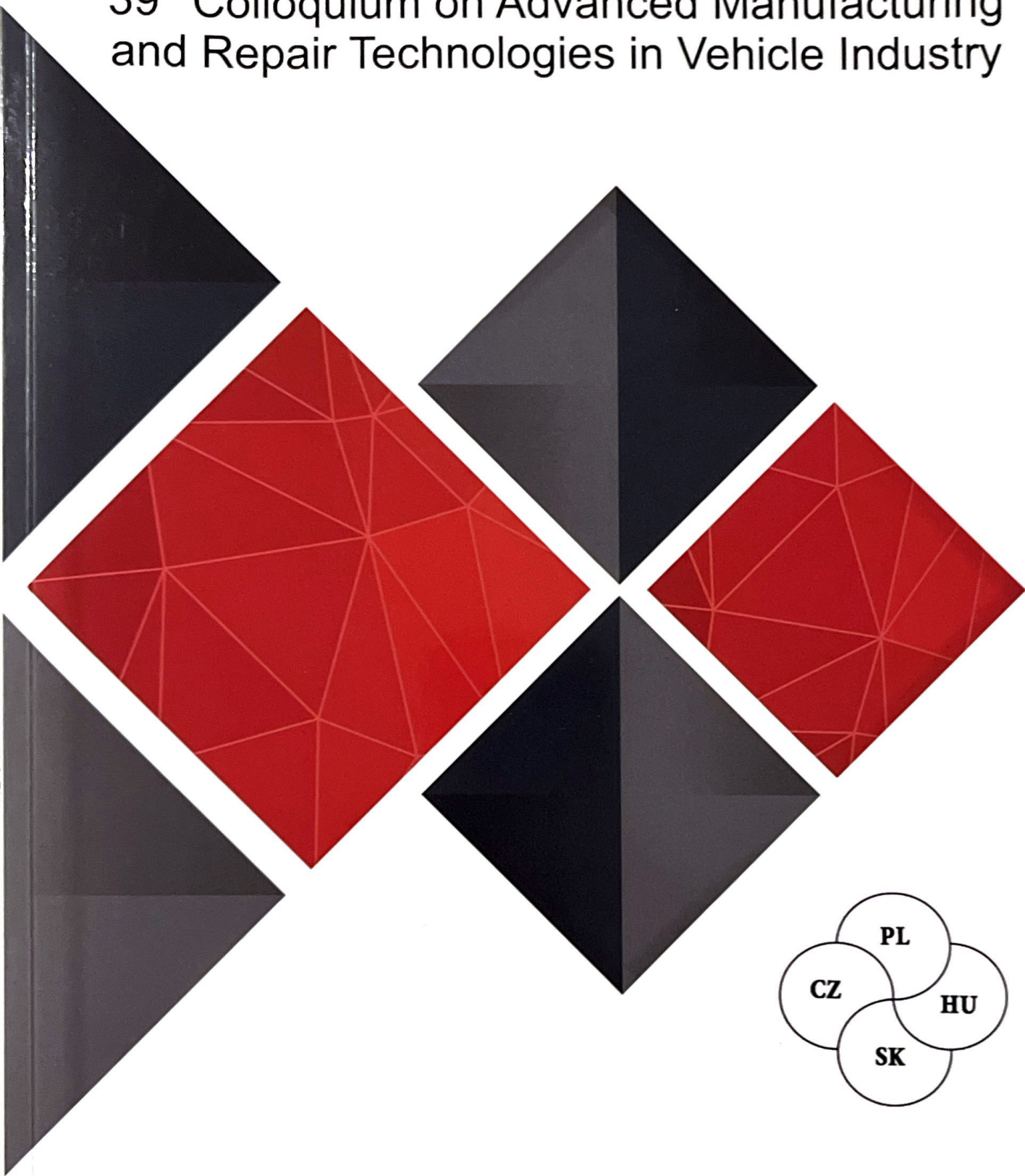


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POLAND 2024

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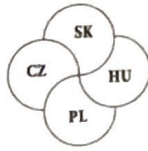
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A Review of Micro-wetting Phenomena: Recent Advances, Applications and Characterization Techniques

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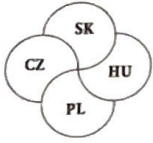
Abstract

The targeted modifications of surface properties, such as improved wettability, are crucial in various fields including aerospace, nanotechnology, nuclear science, electronics, and industrial manufacturing. The wettability of most materials is determined based on traditional macroscopic contact angle measurements (sessile drop, captive bubble techniques). However, these measurement techniques can yield significantly different results depending on the surfaces heterogeneity, droplet (bubble) size, anisotropic wetting behavior (in nature on rice leaves, spider silk, cactus spines etc.) and environmental vibrations. Furthermore, macroscopic contact angle measurements are limited to characterizing the average wettability of the surface-liquid system and along one direction only. In microscale wetting analysis, however, the examination of droplet shapes from different angles provides additional insights into surface properties, chemical, and physical heterogeneities. Research in this field highlights significant differences between macro- and micro-scale contact angles. Moreover, micro-scale surface wetting takes into account the material's physical and chemical properties, including surface roughness, pore size and distribution, as well as chemical composition. In this work, we describe and discuss the state of the art of micro-wetting science and the measurement methods, characteristics and results of micro-wetting itself.

Keywords: Contact angle, Wettability, Measurement, Imaging, Macro-/micro-scale

1. Introduction

Micro-level wetting measurement can be a highly innovative, accurate and reliable measurement technique after appropriate experiments, research and development. The current state of the science is that the uptake of this type of wetting method is still in its infancy, but there is one area of industry where it is already being used in research, trials and testing. Carbonate reservoirs, in particular dolomitic and calcite limestones, contain more than half of the world's oil and gas reserves. The efficient exploitation of such carbonate hydrocarbon reservoirs by conventional methods, such as flooding with water or gas, depends to a large extent on the wetting properties of the rock, especially in fractured, low permeability reservoirs where spontaneous water absorption is the main oil-producing mechanism. The contact angle represents a quantitative measure of wetting of a solid by a liquid. For characterisation of the liquid phase, knowledge of the surface tension is required. The aim of micro-scale research is to gain deeper insights into the wettability properties of rocks and the effect of organic acids on wettability, which will allow accurate prediction of CO₂ storage, H₂ storage or oil production regimes. In addition, microscale imaging (SEM) can be used to analyse the microstructure of the material with microscale resolution images, allowing the measurement of microscale contact angles with high accuracy. International studies have investigated the magnitude of the differences between the two methods, with some reporting a 40° difference in contact angle and others as small as 8°. It is assumed that the differences vary with the texture of the materials, mineralogy, surface roughness and ageing of the rocks (Zimmer et al., 2016; Al-Naimi et al., 2023; Deglint et al., 2017; Ivanova et al., 2022; Hlinka et al., 2020; Weltsch, 2020; Weltsch et al., 2013; Hlinka et al., 2013; Weltsch et al., 2010).



2. Applied micro-wetting measurement methods

2.1. Ionic liquids

F. Zimmer and his colleagues used an ionic liquid on polyethylene to determine the contact angle and the differences between micro wetting and conventional wetting methods. The use of smaller droplet sizes and different orientations of the droplet shape may provide additional information on surface properties. Since ionic liquids have very low vapour pressures, micrometer or even smaller droplets can be investigated. The measurement method was carried out by (1.) Droplet deposition (Sessile drop method) of the ionic liquid on the polyethylene surface (2.) Image acquisition of the droplet shape using a 3D laser scanning confocal microscope. (3.) Generation of the side view of the droplet shape in MatLab Tool. (4.) Determination of the edge angles at different points of the 3- dimensional image of the droplet. (5.) Plotting of the quantitative results in a polar diagram, which allows the identification of the preferred wetting directions. In addition, scanning electron microscopy (SEM) was used to analyse the wetting behaviour on a nanometer scale. This method can be used in a number of applications to help improve the understanding of inhomogeneous surface properties (e.g.: amorphous and crystalline areas). Their research results were investigated as a function of boundary angles and droplet diameter. Using the conventional method, they found no change in the value of the contact angle as the drop diameter increased (assumption: the drop diameter is the same everywhere). They also found contact angle differences of 10-15° when looking at the diameter of smaller drop sizes from a top view compared to the conventional method (drop is not regular, diameters are not the same). They also noted that as the drop diameter increases, the difference in contact angle values between the two methods increases (Zimmer et al., 2016).

2.2. Water condensation and evaporation

Khaloud Al-Naimi et al. investigated the wettability of carbonate rocks for subsurface applications. In the experiment, they used a distilled water condensation method to determine the wettability at the micro level. In their research, they tested the wettability of four types of rocks, which are (A) 100 wt% calcite, (B) 100 wt% dolomite, (C) 61 wt% calcite and 39 wt% dolomite, (D) 100 wt% calcite (samples (A) and (B) from the Arab-D formation, samples (C) and (D) from the Sulay formation). Furthermore, the rock samples were subjected to three different types of treatments before the tests were performed. The first type was the control, natural surface, the second type was subjected to aging with surfactant (24 h, 323 K, toluene cleaning, vacuum drying for 2 h), and the third type was aged in crude oil (4 days, 323 K). After measuring the macro- and micro-level wetting, the results showed a significant difference between the measured macro- and micro-contact angles (Table 1). Samples (A), (C) and (D) were wet with oil at the macro level (>110°) and slightly wet at the micro level (<70°). However, sample (B) showed the same wetting behaviour at both macro and micro scales, i.e., it was moderately wet. Samples (A) and (D) were pure calcites but showed slight differences in wettability due to their different surface roughness. It is also important to note that larger, denser populations of micro-droplets were observed on the less rough surfaces. In addition, it was observed that several wetting states can occur within a single rock, which is in contrast to the macro-level wetting state (Al-Naimi et al., 2023).

Table 1. Average micro-scale contact angles measured on carbonate rocks using ESEM. (Major θ : predominant and minor θ : less frequent, wettability states) (Al-Naimi et al., 2023).

	Sample A		Sample B		Sample C		Sample D	
	major θ	minor θ	major θ	minor θ	major θ	minor θ	major θ	minor θ
Natural	79.46 ± 8.33°	57.06 ± 10.28° 132.03 ± 22.55°	76.38 ± 6.89°	66.19 ± 5.53°	51.02 ± 14.65°	83.14° 150.25°	83.40 ± 8.26°	59.63 ± 8.54°
Surfactant-aged	≥5°	62.27 ± 5.18° 97.23 ± 8.42° 115.90 ± 3.89°	≥5°	58.39 ± 14.91° 89.86 ± 10.18°	≥5°		≥5°	56.83 ± 12.60°
Oil-aged	89.95 ±10°	60.27 ± 6.79°	85.58 ± 11.21°	58.61 ± 5.91° 132.05	55.92 ± 11.94°	78.55 ± 6.05° 111.62°	94.68 ± 10.86°	51.55 ± 25.75° 147.33

Hanford J. Deglint et al. investigated the micro wetting properties of samples from the Bakken reservoir (Viewfield Saskatchewan, Canada), an active, low-permeability oil-producing area. The aim of their research is to characterise the reservoirs, thereby building field-scale models to evaluate the efficiency of hydrocarbon extraction and CO₂ storage potential. The Cardium samples were subjected to water condensation, cryogenic cooling and micro-injection based micro-wetting tests. In the water condensation test, Peltier heating/cooling was used to heat/cool the samples in order to control the condensation and evaporation of distilled water. In the electron microscope study, time lapse images of droplet formation were taken to define the ideal moment for the acquisition and measurement (micro-droplet growth followed by evaporation cycle). Following the recording, a parameterized version of the Young-Laplace equation was fitted to the drop profile to determine the contact angles. The resulting extracted microdroplet sizes are 17.1 μm (height) and 48.4 μm (width) with an average (left and right) contact angle of 69°. Further droplet profiles were then investigated and changes in micro-scale wetting behaviour were observed (Fig. 1). Using X-ray element mapping, it was clearly demonstrated that the variability in droplet contact angles is caused by the presence of different mineral grains. This gives the possibility to investigate the wettability of different mineral grains as a function of the contact angle values (Deglint et al., 2017).

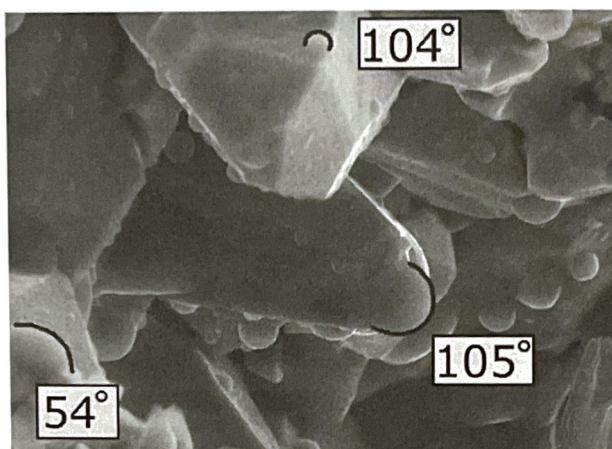


Fig. 1. Image (using E-FeSEM) of micro-droplet formation on a Cardium sample during a condensation/evaporation experiment illustrating water contact angle variability at the grain- (micron) scale (Deglint et al., 2017).

A. Ivanova et al. investigated the macro- and micro-wetting properties of carbonates as a function of microscale changes caused by the adsorption of carboxylic acids (palmitic, stearic and naphthenic acids). As a first step of the experiment, the macro contact angles of the carbonate samples before and after ageing in acids were determined. A part of the carbonate samples was immersed in palmitic acid and another part in stearic and naphthenic acids (0,01 M solution). The calcite exhibited a water-wet behaviour with an average contact angle of $34.7^\circ \pm 4.06^\circ$ before ageing, but the contact angle increased drastically after ageing with organic acids. The drastic increase was especially observed for palmitic and stearic acids, which made the sample surface more hydrophilic. This phenomenon was caused by the adsorption of acid on the calcite surface through covalent bonding between Ca^{2+} and COO^- acid groups. The different effects of different acids on the contact angle are due to the different molecular structure of the acids. Subsequently, measurements of the micro-level contact angles were carried out using the water condensation evaporation method. As a first step, the time distribution of droplet formation was determined using electron microscopy and the most suitable water condensation time (appearance of droplets on the surface ($t=1:20$ min)) for the recording and measurement was defined. As a result of the measurement performed in this way, droplet values of 1.7 μm (height), 4.07 μm (left radius) and 4.5 μm (right radius) and average contact angle of $40.59^\circ \pm 3.47^\circ$ were reported (Fig. 2). They also carried out energy dispersive X-ray (EDX) analysis (after acid ageing of the samples), which identified the areas of the samples where the acid layers had adsorbed. EDX analysis of the palmitic acid treated sample showed the presence of high levels of carbon (presence of adsorbed acidic layer) at some points, while at other points the presence of pure calcite was observed. Furthermore, EDX analysis was used to measure the elemental composition of areas with different contact angle values, with the hydrophobic zones having a higher carbon content than the hydrophilic areas. Furthermore, EDX analysis of the cross-section

of the sample allowed the thickness of the acid layers to be determined, the measured thicknesses were 85 ± 5 nm, 70 ± 8 nm and 50 ± 5 nm for palmitic, stearic and naphthenic acids, respectively (Ivanova et al., 2022).

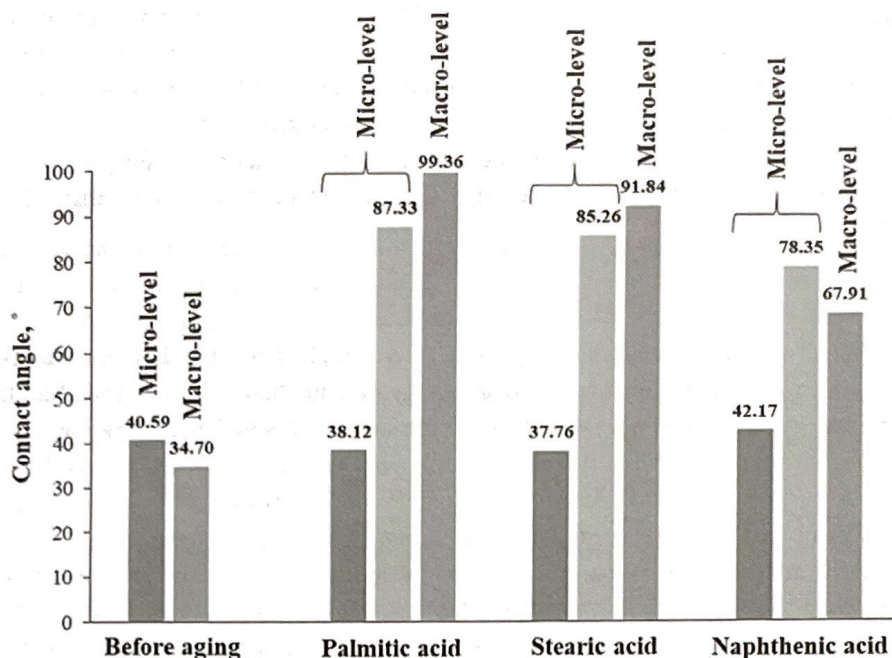


Fig. 2. Comparison of contact angle data obtained at micro and macro scales before and after aging palmitic, stearic and naphthenic acids (Ivanova et al., 2022).

2.3. Cryogenic freezing

Hanford J. Deglint et al. also investigated micro wetting in a sample from the Bakken Reservoir (Viewfield Saskatchewan, Canada) using cryogenic freezing. Imaging and X-ray imaging of the sample after cryogenic freezing allows the determination of the sample distribution and contact angles of native fluids on the preserved sample. As a first step, the sample was immersed in formation oil for six weeks (to allow the oil to soak into the sample), then cryopreserved and cracked. Two oil microdroplets were then analysed, one droplet measuring $0.67 \mu\text{m}$ (height) and $0.87 \mu\text{m}$ (width) and having an average contact angle of 111° . For the other droplet, $1.3 \mu\text{m}$ (height) and $1.2 \mu\text{m}$ (width) and an average contact angle of 129° were measured (Fig. 3).

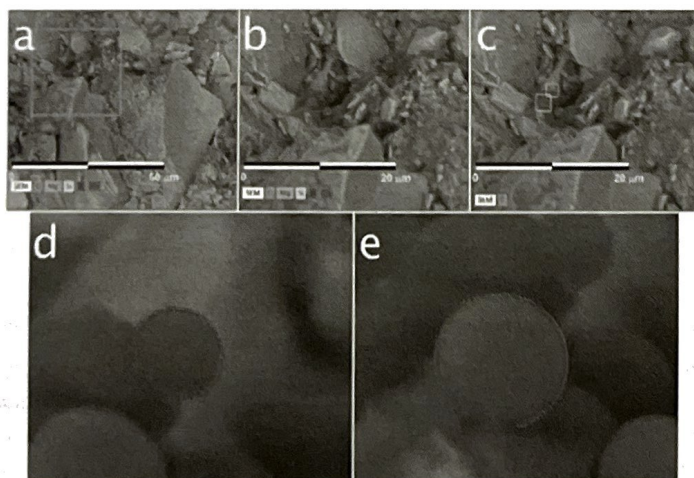


Fig. 3. (a-c) Elemental maps superimposed on a back-scatter electron image of the cryogenically-frozen middle Bakken sample after it had been submersed in formation oil. The elemental map in (a) is zoomed in (b) (green box, $30 \mu\text{m}$ wide) to reveal oil micro-droplets (green) in the intergranular space. In (c), only the element carbon is shown, emphasizing the location of the oil droplets in the intergranular space. The micro-droplets in (d-e) has a measured drop height and width and calculated right and left contact angles (Deglint et al., 2017).

Due to the irregularity and heterogeneity of the sample surface, it is difficult to judge on which mineral(s) the oil droplets adhered to, but the immediate region surrounding the micro-droplets appears to be rich in quartz, consistent with the non-oil wettability of the surface (Fig. 3). Subsequently, the same sample was immersed in synthetic brine for three and a half weeks and the measurement procedure was repeated. Their results confirmed that the saturation of the synthetic brine was limited to locations close to the edge of the sample. Elemental mapping again showed mineralogical heterogeneity. As the magnification was increased, the distribution of the synthetic brine and oil in the intergranular spaces was observed, although the contact micro-droplets were not in contact. Sodium and chlorine elemental analysis confirmed that the influent medium was synthetic hydrochloric acid (Deglint et al., 2017).

2.4. Micro-injection

Hanford J. Deglint et al. also tested microinjection of a sample from the Bakken Reservoir (Viewfield Saskatchewan, Canada), which is the most accurate and innovative method currently available. In this case, two samples were examined, one sample (1A) oriented so that the surface on which the droplet was placed was nearly perpendicular to the imaging plane. While the other sample was less ideally oriented (1B). Nanoliters of liquid were injected onto the surface of the samples and the forward and backward contact angles were first measured (the liquid droplet was moved back and forth across the sample surface). The contact angle of the droplets was then determined and the microcapillary tube was lifted off the surface (at rest, time lapse recording) (Fig. 4). For each image, the droplet profiles were first defined and then the parameterized Young-Laplace equation was fitted to the top surface of the microdroplet. Differences between the profiles as a function of time were then examined, which can be used to estimate the imbibition velocity, which in turn can be used to understand the time scale of fluid infiltration from hydraulic fractures into unconventional reservoirs (Deglint et al., 2017).

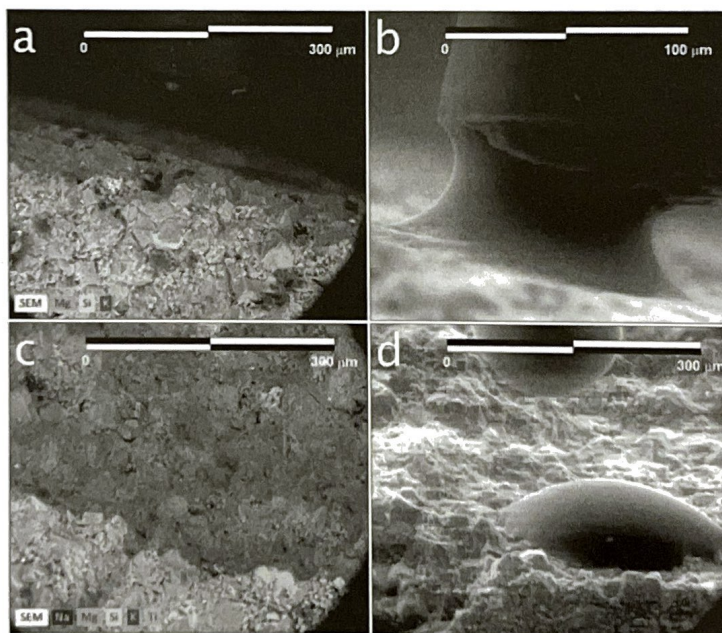
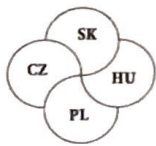


Fig. 4. (a) Elemental map of the edge of a middle Bakken sample (Sample 1A) used for micro-injection analysis. This sample orientation is nearly orthogonal to the imaging plane, offering an ideal view of micro-droplet formation. (b) A secondary-electron image of water injected out of the silica tube (10 μm ID, 150 μm OD) onto Sample 1A during a micro-injection experiment. (c) Elemental map taken of a less-ideally oriented Bakken sample (Sample 1B) used for micro-injection analysis. (d) A secondary electron image of sessile droplet formation on Sample 1B during a micro-injection experiment (Deglint et al., 2017).



3. Conclusion

In this work, we have described micro-wetting as a possible measurement and research method. Furthermore, we analysed and described the research and publications on this topic available in the literature. The vast majority of the literature reviewed focused on the wettability of different rocks, from the point of view of subsurface applications, and on the improvement of hydrocarbon extraction efficiency and CO₂ storage potential. Of the four techniques used to quantify micro-wettability, the microinjection method is considered the most reliable and accurate, as it allows to control the placement of the fluid on the sample, the observation of the receding and advancing contact angles, and the absorption rate.

In our literature review, we found a clear scientific and research gap in the science of micro-wetting. Therefore, our future goals are to continue experimental, research and publication activities on micro-wetting phenomena. Our further objectives include the dissemination of micro-wetting to various sectors of industry.

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