Title: Use of infrared nano-spectroscopy to study the existence and thickness of the wetting film in oil-wet carbonates

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In recovery of hydrocarbons from the subsurface wettability plays a key role. Wettability is a property controlled by the crude oil-brine-rock (COBR) interactions. It is known that wetting properties of a rock contributes to the microscopic oil displacement efficiency and the ultimate achievable recovery factor. Rocks (or rather minerals composing them) are water-wet at their initial (clean) state. It is commonly observed that long-term exposure of rock surfaces to heavy components of crude oil under high pressure and temperature conditions of subsurface hydrocarbon reservoirs causes the wetting to change towards more oil-wet. Heavy and polar organic compounds within crude oil (e.g. asphaltenes and resins) have the tendency to interact with the rock (mineral) surfaces resulting in adsorption of these compound onto the surface to form an oil film.

Understanding the scale of the oil film thickness as well as the main functional groups contributing to formation of these films are the underlying questions we address in this work. We present the outcome of a series of experiments using the infrared nano-spectroscopy beamline at the Brazilian synchrotron to study the COBR interaction at nano-scale. The IR1 beamline of the Brazilian synchrotron is equipped with a scattering Near-Field Optical Microscope (s-SNOM). Using this facility broadband infrared (IR) imaging and atomic force microscopy (AFM) topography can be performed with a lateral resolution of approximately 25 nm. It enabled us to perform an investigation on the surface of rock grains at clean and aged conditions.

The experiment was designed to investigate the interactions of a carbonate rock (Ketton limestone from England) with a crude oil (from Brazil) in presence of a brine (containing divalent ions). The crude oil was known to have significant levels of heavy components (e.g. asphaltenes and resins). Prior to the synchrotron session we prepared the samples by exposing several grains of this limestone to the crude oil

following the aging procedure explained in Pak (2015)[1]. After the aging process the grains where sliced using an ultra-cryo microtome device to prepare ultrathin slices for use at the IR1 beamline. We focused on identifying the functional groups adsorbed to the grain surface by measuring line IR profiles starting from inside of a grain (where the IR signal detected pure calcium carbonate) moving towards the grain surface where the adsorbed organic compounds were expected. The measurements were repeated many times to overcome issues faced as a result of contamination of the cantilever tip which occurred as the tip approached the grain interface. We will also discuss the challenges we faced in cutting the samples and the impacts this has had on the observed signals.

The infrared spectrum of absorption of the crude oil used in this study was recorded using a bench-top Fourier-transform infrared spectroscopy (FTIR) equipment. This spectrum is considered as the background IR signature of this crude oil as a whole. Collecting the broadband point spectra at different locations near the grain surface of the ultrathin sections reveals the chemical composition of the grain surface and the compounds adsorbed to it.

References

1. Pak, T. Saturation tracking and identification of residual oil saturation. (The University of Edinburgh, 2015).