CRYO ESEM STUDIES OF EMULSIONS AND FLUID DISTRIBUTION AT PORE SCALE

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ABSTRACT

In this work we illustrate the potential of using Cryo ESEM (Cryogenic Environmental Scanning Electron Microscope) and X-ray energy dispersive system (EDS) in studies of emulsions and fluid distribution at pore scale. Sample preparation is simplified to involve only freezing in liquid nitrogen followed by fracturing in frozen condition. The sample can be studied without any conducting material on the sample surface or dopant added to the fluids. The method can be used to verify hypotheses of fluid distribution gained from other SCAL analyses and NMR spectroscopy. In addition, samples from seal peel preserved cores can be studied in their original state before cleaning and wettability restoration. The method can also be used to study particles on the oil/water interface.

INTRODUCTION

The wetting properties are fundamental for the understanding of multiphase flow in all aspects of oil production, and can affect the production characteristics greatly during water flooding as described in several reviews (Anderson 1987, Morrow 1990). Fluid distribution in the pore space is to large extent determined by the wetting properties, hence by examining the fluid distribution at pore level it is possible to analyze the wettability of the porous media. These analyses can be performed by using Cryo SEM as reported by several authors (Sutanto *et al*. 1990, Rueslåtten *et al.* 1994, Robin *et al*., 1995, Durand *et al.* 1998). However, this technique requires a coating layer (i.e. carbon, chromium or gold) on the sample surface to obtain electric conductivity.

Wettability studies using ESEM are normally associated with dynamic experiments like condensing water wapor on the mineral surface or introducing fluid into the microscope by a microinjector (Robin *et al*. 1999). Common for these ESEM studies are that they require some portion of subjective interpretation.

By combining the cryo technique with ESEM there is no need for this surface coating, which simplifies both sample preparation and the interpretation of the results. The elemental distribution is examined by EDS X-ray analyses. There is no interference from additional X-ray lines generated by the coating material. Lighter elements, like carbon in the oil phase, can be detected by the present generation X-ray spectrometers.

Backscattered electron images (BSE) images and X-ray elemental images can be analysed by image analysis, giving the possibility to quantify the observations. The development of the Cryo ESEM technique has been shown to give very promising results and valuable information about the pore level fluid distribution in different recovery mechanisms (Kowalewski *et al*. 2005).

The technique can also be used to characterize emulsions. It is well known that particles can stabilize emulsions, both oil-in-water and water-in-oil (Binks, 2002). A number of factors control the formation and stability of emulsions: particle wettabillity, particle size and shape, interparticle interaction and particle concentration. The particle wettability control the type of emulsion, as water-wet (hydrophilic) particles tend to stabilize oil-in-water emulsions, while oil-wet (hydrophobic) particles tend to stabilize oil continuous emulsions (Hannisdal et al., 2006). Earlier work on characterization of emulsions with Cryo SEM includes the studies of Mikula *et al.* (2000) and Binks *et al.* (2002).

EXPERIMENTAL

The electron microscope used in this study is a FEI Quanta 400 equipped with a Thermonoran Vantage EDS system. The ESEM is operated in low vacuum mode with nitrogen inlet gas. The accelerating voltage was 15kV and the working distance 10mm. The cryo system is a modified version of Oxford instruments cryo transfer system CT1500. The modification involves a newly constructed robust fracturing device and sample holders designed for larger samples.

Both siliclastic and carbonate rock samples were studied. An end cut from a calcite carbonate core plug was saturated with paraffin oil (small n-alkane molecules). The sample was then studied after spontaneous imbibition, after centrifugation at 500 rpm and after centrifugation at 3000 rpm in brine. North Sea sandstone core plug material used in other flooding experiments and seal peals are also studied. The fluid saturated sample is rapidly frozen in liquid nitrogen. For instant freezing the sample size should be held as small as possible to minimize ice crystal growth. A typical sample sizes is 2-4 cm of a core plug. The sample is then trimmed by a chisel and hammer in frozen condition to approximately $1cm^3$ to fit the sample holder. The sample is then glued to the sample holder by fresh water immersed in liquid nitrogen and rapidly transferred to the cryo system. The cryo chamber is evacuated and the sample is freeze-fractured under vacuum conditions to avoid ice crystal growth on the surface. The freeze-fractured sample is transferred with the transfer rod to the ESEM cold stage, held at a temperature of below -100^oC.

Samples of oil in water emulsions are stabilized by barium sulfate particles made by mixing solutions of 1M $BaCl_2$ and 1M Na_2SO_4. The resulting particles were recovered by centrifugation. A solution of 1 wt% $BaSO_4$ in water (with 3.5 wt% NaCl) was prepared and the particles were dispersed by ultra sonication. Crude oil from a North Sea reservoir (10 vol%) was mixed into the aqueous solution with an Ultra Turrax (IKA, T18 with 10 mm head) at 22,000 rpm for 2 min. 2-3 ml of the oil-in-water emulsion was sampled into a 5 mm plastic pipette. Similar emulsions were also made using silica, kaolin and

bentonite particles. The pipette was immediately immersed in liquid nitrogen, in order to freeze the emulsion. The pipette was broken to yield a 2 cm long cylinder, which was attached to a metal sample holder and transferred to the cryo system for fracturing.
When the sample is transferred to the cold stage, the ESEM is operated in normal manner with the cold stage constantly held at low temperature. Areas of interest are located by live scan BSE images. From these located areas X-ray images and spectra are acquired for later processing and analysis.

RESULTS AND DISCUSSION

A combination of BSE images and X-elemental images/X-ray spectra are used for fluids and mineral identification. BSE images give mean atomic number contrast. Oil will appear darker than water, while the minerals will have different degrees of brightness depending on the mineral chemistry. X-ray images of carbon (C) are used for oil identification, while the elements oxygen (O) and chlorine (Cl) can be used to identify the water phase.

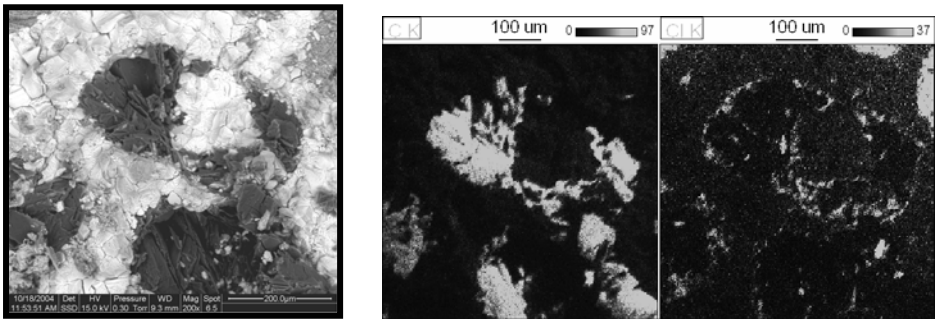

Figure 1. BSE image left and X-ray images of carbon (C) and chloride (Cl).

Figure 1 illustrates moldic pores in a calcite carbonate. BSE image gives good contrast between calcite and the fluid phases. However, the X-ray images of C and Cl clearly visualize the oil and brine distribution. The brine is mainly found on the mineral surface, indicating a water wet situation.

Fluid saturations can be quantified by image analyses of BSE and X-ray images. From BSE images (Figure 2, left) the oil and brine can be discriminated by the difference in grey level values. A grey value histogram with threshold settings for the fluid discrimination is shown in Figure 3, left. In this case the area representing the oil phase is measured to 30,6% (Figure 2, middle) and the measured area for the brine (Figure 2, right) is 17,2%. This gives a value for the oil saturation (So) of 0,64. Several areas, depending on the pore structure and the pore connectivity, have to be analysed to get representative saturation values.
X- ray elemental images can also be used for saturation measurements. The resolution of the X-ray images was 256x256 pixels. The quality of the X-ray images is dependant of the primary beam current, the acquiring time and sample topography. The X-ray images are “dot images” and have to be processed, in this case by a gaussian filter prior to discrimination. X-ray images of elements C, O, Cl and Ca are shown in Figure 4. An

example of the difference in intensity of a processed oxygen X-ray image is shown in the histogram in Figure 3, right. The brine has higher concentration of oxygen than the carbonate, and can be used to identify the brine. In the same manner, oil has higher concentration of carbon than the carbonate (both dolomite and calcite), and can be used for identifying the oil phase (Figure 4).

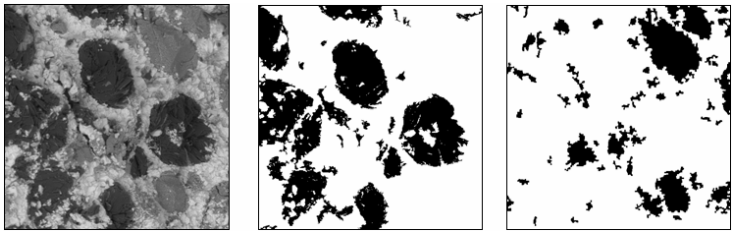

Figure 2. Left image is the BSE image, middle and right image are binary images of the same area where black phase are oil and brine, respectively.

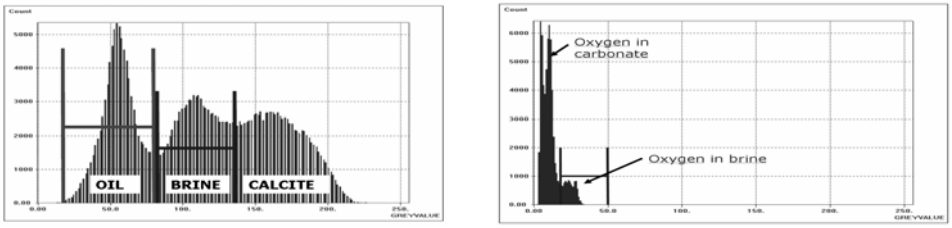

Figure 3. Histogram of pixel counts versus grey levels in the BSE image in Figure 2 and pixel counts versus grey levels in the oxygen X-ray image in Figure 4.

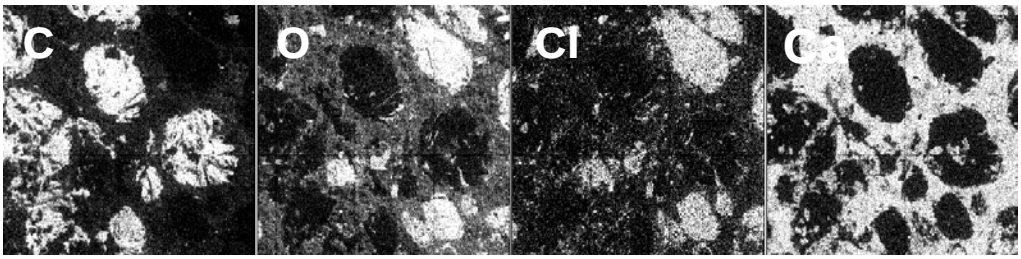

Figure 4. X-ray images from same area as Figure 2 of the elements carbon (C), oxygen (O), chloride (Cl) and calcium (Ca).

Seal peals with unknown fluid wetting properties can be studied. Valuable information can be obtained for designing the SCAL program and for better interpretation of log responses. An example of seal peel preserved core from a North Sea reservoir is shown in Figure 5. High magnification BSE image shows pores filled by a few oil droplets in brine. This indicates low oil saturation (So) and wetting condition towards water wet. Poorly consolidated reservoir rocks, that might be difficult or impossible to handle with respect to SCAL, can be studied in frozen state by the Cryo ESEM.

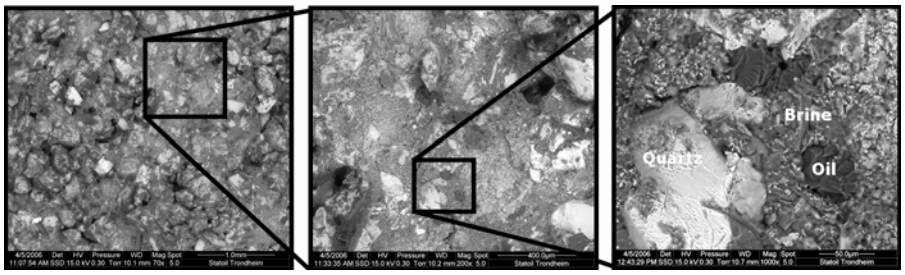

Figure 5. Seal peel core sample from a North Sea reservoir sandstone at 70X, 200X and 1000X.

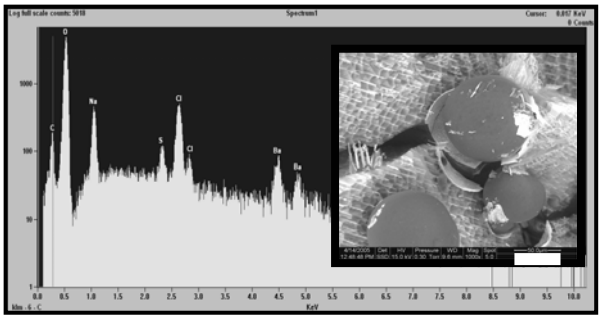

Figure 6. $BaSO_4$ particles on the surface of oil droplets in water (scale bar 50µm).

Figure 6 shows the cryo ESEM image of barium sulphate particles on the surface of oil droplets in water. The particles have aggregated at the oil-water interface and created shells covering the oil droplets. During the fracturing, the shells have broken up on some oil droplets, while on other (not shown) the shells are more intact. The EDS spectrum shows both Ba and S, indicating $BaSO_4$ particles, in addition to C (from oil) and O, Na and Cl (from water). Subliming the water phase makes low concentration of smaller oil in water emulsions easier to locate. Sublimation involves increasing the temperature to above -90^{o}C. This sublimation requires an uncoated sample surface. The structure of sublimed water is visible in the BSE image in Figure 6.

CONCLUSIONS

- Fluid distribution can be studied at pore scale by Cryo ESEM and X-ray spectroscopy/X-ray elemental mapping. Fluid distribution can be related to pore size and shape and to the mineralogy.
- Analysed area can vary from sub-micron to several millimeters.
- Fluid saturations can be quantified by image analyses of the BSE images and processed elemental X-ray images.
- Seal peel preserved cores can be analysed in their original state before cleaning and wettability restoration. Poorly consolidated reservoir rocks can be studied successfully.
- The method can be used to verify hypotheses of pore scale fluid distribution gained from SCAL experiments, NMR spectroscopy and computer tomography imaging.

- Sample preparation is relatively simple, in principle limited to freezing and fracturing. No sample coating is necessary. The method does not require any dopant added to one of the fluids in order to separate oil from brine, required by other analysis methods, i.e. computer tomography imaging.
- Inorganic particles at water/oil interfaces can be detected using the Cryo ESEM technique, utilizing both BSE images and X-ray elemental images.

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