Using a Compact Low Voltage FE-SEM in Evaluating Materials Nano-Porosity: Preliminary Study

Application Note

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Introduction

Porosity plays an important role in materials mechanical and physical properties [1]. The latter include, for instance, compression and tensile strength, density, and thermal conduction or expansion. It also impacts materials resistance to chemical corrosion. The ensemble of these properties defines the behavior of the material under a given set of physical conditions and its functionality as an intermediate or final product. In one case, high porosity is desired in the material if used for insulation or catalysis. In contrast, low porosity is preferred for materials used by virtue of their strength or their impermeability to fluids [2]. In natural rocks, like shale or sandstones for instance, pore volume is key to assessment of the capacity of the rock formation as a reservoir for economically exploitable fluids such as natural gas, oil, or water [3]. Generally, being able to estimate accurately the proportion of pore volume and size distribution reliably, quickly, and at lower cost is very important to many industries such as mining geology and oil industry.

There exist several methods for measuring porosity in materials. Brief reviews of these methods along with an in depth discussion of an individual technique are often presented [4–5]. A detailed discussion of these diverse methods is beyond the scope of this note. However, most of these methods in fact measure apparent porosity.

Closed porosity is difficult to estimate by most methods. Measuring total porosity therefore requires inclusion of the closed pores. Several physical methods are used for that purpose such as optical microscopy of petrographic thin sections; SEM imaging of polished or milled sections; X-ray micro-computed tomography (µCT); small angle X-ray scattering (SAXS); small angle neutron scattering (SANS). Some of these methods measure porosity in 2-D and others in 3-D. Each of these techniques has its advantages, disadvantages or limitations. Cost, easiness, and type of information obtained are among the most important factors that define the analyst choice.

Methodology

For porosity measurement with microscopy, whether optical or SEM, sample preparation is a critical step that needs extreme care. Both methods can be performed on polished petrographic thin sections whereas SEM can also be performed on polished section or on ion-milled surface. Since mechanical grinding and polishing is an easy and cost effective sample preparation method, a wide range of materials prepared by it shall be investigated in the near future. For this note, thus, only results obtained for an ion-milled shale sample are presented. The sample consists of a coupon ~ 10x10x5 mm cut from the rock and a triangular area roughly 2x2x3 mm near the edge was ion-milled to provide a flat and smooth

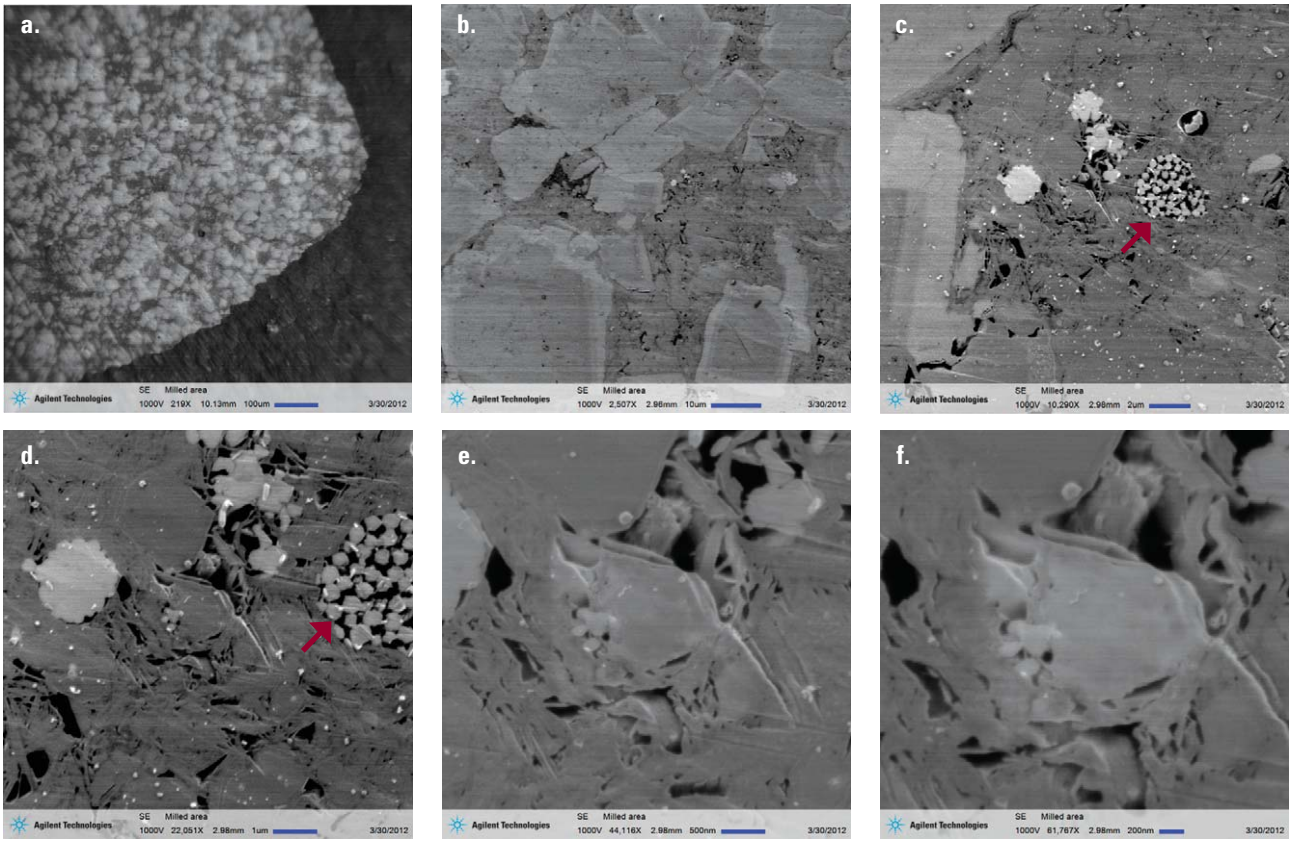

Figure 1. A sequence of SE images of the ion-milled shale sample acquired with the Agilent 8500 FE-SEM at increasing magnification (a – f) . Images show pores to be primarily present in the inter-granular clayey matrix (cement) and in the pyrite framboids (indicated by arrows in c and d).

surface (Figure 1a). The sample was adhered to an aluminum stub using conductive carbon tape and the stub was mounted on the microscope sample holder. The sample was imaged using an Agilent 8500 FE-SEM in high resolution mode with an accelerating voltage of 1 kV and a working distance of ~2.7–3.0 mm for high magnification and ~10.1 mm for low magnification. The Agilent 8500 FE-SEM is a low voltage, field emission SEM which employs a novel electrostatic lens design. This innovative design allows for high resolution imaging of insulating samples, typically without the need for metal coating.

Results and Discussion

Observation of the milled surface at low magnification shows the shale to comprise several mineral phases (Figure 1a). Pores are present mainly in clayey matrix, which makes up the intergranular cement of the rock (Figure 1b). To lesser extent, pores are also present in the pyrite spheres or framboids (Figure 1c, d). This heterogeneous distribution of pores among mineral phases implies that phase analysis (quantification) is needed for pore volume to be estimated correctly for the shale. Hence, knowing the proportions of clay and pyrite in the bulk sample would allow correct calculation of pore volume of the rock from 2-D SEM images. For instance, if the rock contains 30% clay and 8% pyrite by volume and SE image analysis gives pore volumes of 10% in clay and 5% in pyrite, then the total porosity due to these two phases is 0.1 x 0.3 + 0.05 x 0.8, which is 0.034 (or 3.4%). This calculation is possible once quantitative phase analysis of the shale rock is done, using image analysis of the 2-D image sequence acquired for the sampled surface [6–7].

Two different pore-related features have to be considered. The first is pore size distribution. In SE images obtained with Agilent 8500 and presented here (Figures 1 and 2), two size categories of pores are seen in this sample. Micron to submicron pores are present in both the clay mineral phase and the pyrite framboids. However, nano-pores are present only in the clayey matrix (Figures 1c through f, and Figure 2). The second feature, although not seen directly, it is inferred from the petrology. It stems from the fact that argillaceous sediments tend to be stratified and have highly preferred orientation of layered minerals such as clay mineral. Stratification in this case may create anisotropy in both pore distribution and orientation and hence permeability of the shale formation. Therefore, it is suggested here that imaging of a shale sample should be performed along two perpendicular directions in order to verify anisotropy in pore orientation/distribution.

The sequence of SE images presented in Figure 3 shows that some particular grains/crystals contain phase inclusions that might be mistakenly considered as pores. This confusion may occur

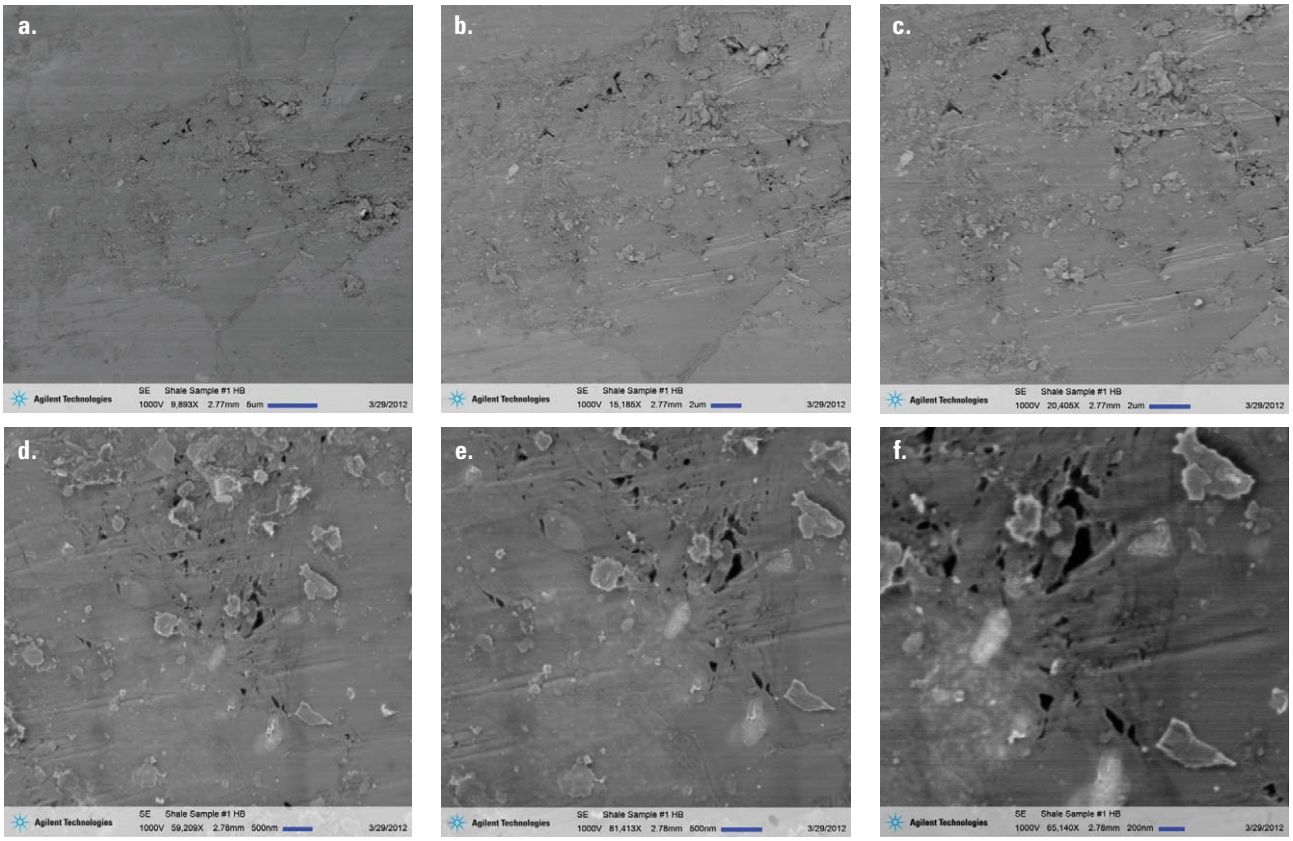

Figure 2. A sequence of SE images of the ion-milled shale sample acquired with the Agilent 8500 FE-SEM at increasing magnification. Images show pores to have different shape and size and are mainly present in the inter-granular clayey matrix.

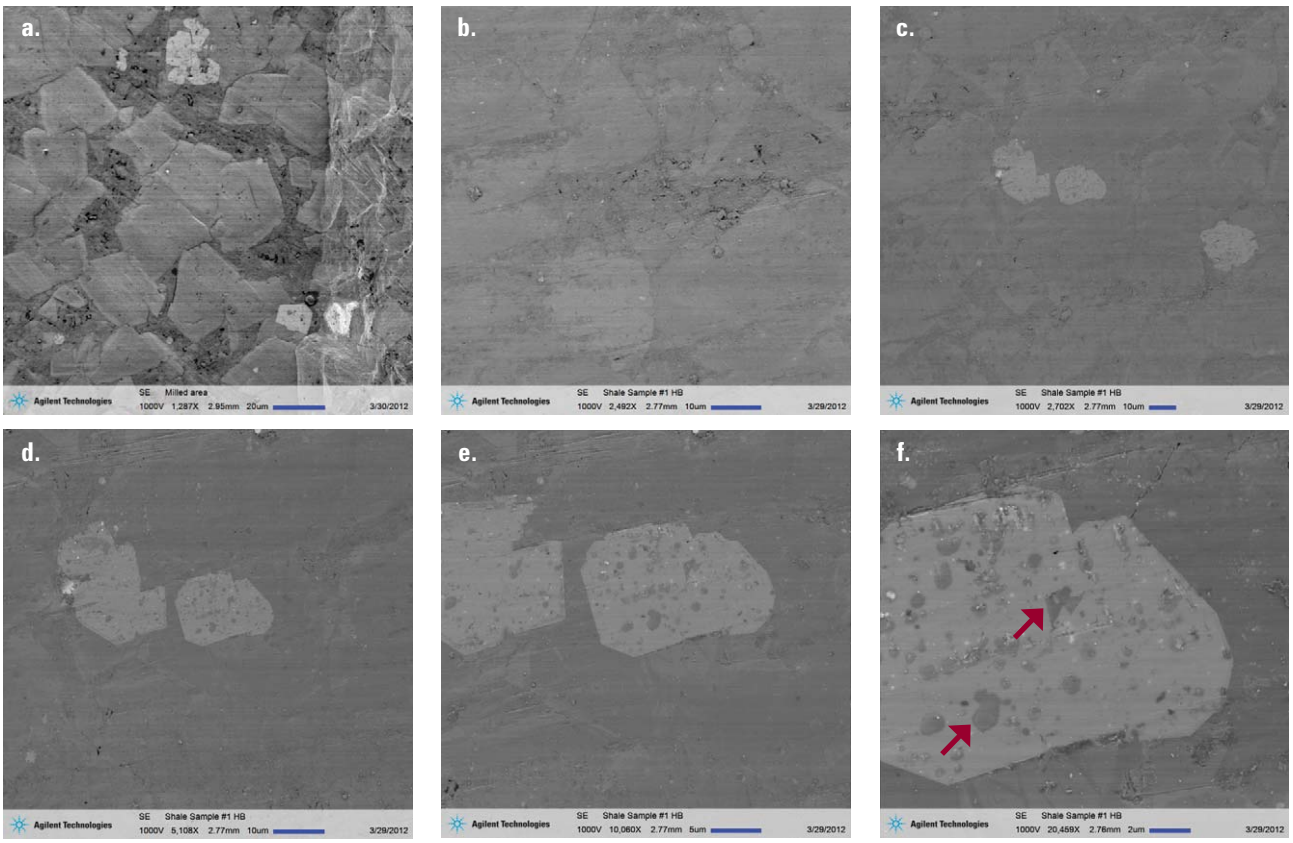

Figure 3. SE images of the ion-milled shale sample acquired with the Agilent 8500 FE-SEM. Images show the rock to have different mineral phases. Only inter-granular clayey matrix (cement) and occasionally pyrite framboids have significant amount of pores. The high-contrast grains in c through f (not determined) have inclusions that might be confused with pores in poor resolution images obtained with other FE-SEM's.

with poor resolution SE images obtained with other FE-SEMs. Hence, the high resolution and excellent contrast imaging of these grains with the powerful Agilent 8500 FE-SEM actually avoids EDS analysis of these inclusions when the purpose is uniquely measurement of porosity.

Conclusions

Using Agilent 8500 FE-SEM, it was possible to image a shale sample, with high resolution and excellent contrast. Indeed, it was not necessary to metal-coat this insulating material. These high resolution images of the milled surface have shown pores to be present in two mineral phases and have wide range of size distribution and most probably preferred orientation. The methodology followed here for porosity measurement flows straightforward. Image analysis would allow quantitative phase analysis of the shale and then quantification of pore volume in each individual phase. Total porosity can then be readily calculated.

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