Osmotic effects on the microstructure of Ashfield shale

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ABSTRACT

Preliminary results of a comprehensive microstructural investigation aimed at studying the influence of osmotic effects in Ashfield shale, a low permeability sedimentary rock from the Sydney Basin (Australia), are presented in the paper. Natural rock specimens were exposed to different brine solutions to assess their influence on rock microstructure. Qualitative as well as quantitative experimental techniques were used to evaluate changes in mineralogical composition (XRD analysis), Cation Exchange Capacity (CEC), cation/ion concentration (chromatographic analysis), specific surface, structural arrangement (Scanning Electron Microscopy) as well as pore size distribution (Mercury Intrusion Porosimetry). Test results show an important influence of the applied osmotic potential on specific surface, CEC and pore size distribution and to a lesser extend the structural arrangement assessed via SEM. These changes occur without important variations in the mineralogical composition of the rock.

Keywords: osmotic effects, shale, rock microstructure, pore size distribution, cation exchange capacity.

1 INTRODUCTION

Shale deposits are complex sedimentary clayey rocks commonly found in engineering practice. Most of these materials are prone to modify their engineering properties once they are exposed to environmental actions (e.g., Bjerrum, 1967; van Eeckhout, 1976; Seedman, 1987; Ballard et al., 1994; Botts, 1998; Wong, 1998; Vales et al., 2004; Pineda et al., 2014a,b; Ewy, 2014; to name a few). Although several studies have focused mainly on the effects of stress relief and cyclic moisture variations, rock degradation caused by physico-chemical interactions is nowadays attracting more attention mainly as a consequence of the development of nuclear waste disposal facilities and hydrocarbon (well-bore stability) production. The fluid-rock interaction plays a major role on the engineering behaviour of shales. Better characterization of rock microstructure is nowadays possible thanks to the combination of advanced laboratory techniques from which qualitative and quantitative information may be obtained.

This paper explores the influence of osmotic effects on the microstructure of Ashfield shale from the Sydney Basin (Australia). Preliminary results presented here highlight changes in mineralogical composition, cation exchange capacity, cation/ion concentration, specific surface area, structural arrangement and pore size distribution due to rock exposure to brine solutions.

2 MATERIAL TESTED

The material tested in this study is Ashfield shale, a low porosity rock from the Sydney region (New South Wales). Core specimens (62 mm in diameter) were obtained from a vertical borehole drilled at Lindfield site (NSW). The Ashfield shale formation comprises a pro-delta sequence which is subdivided into four strata located between 2.5 and 26 m depth. Groundwater at depths where Ashfield shale is encountered is saline, with maximum solubility around 31.6 g/l of NaCl. Samples tested in this study were obtained between 19.8 – 26.0 m depth. Sub-horizontal stratification is clearly observed in the cores shown in Figure 1 as well as joints (cracks) with low dip angles (~ 20º). Small cylindrical specimens (13 mm in diameter and 6 mm in height) were used in
the geochemical tests described in the next section. Tested specimens were drilled using a diamond core bit under dry conditions. Dry coring was preferred due to the high sensitivity of clayey rocks to liquid water. Compressed air was used to prevent overheating of the drill bit. Finally, dry polishing was applied to top and bottom ends of each specimen prior testing.

A qualitative XRD analysis performed on a representative specimen shows that Ashfield shale tested in this paper is mainly composed by kaolinite (31.4 %), quartz (27.7 %), illite (21 %), muscovite (15 %) and siderite (4.8 %). The fine fraction (<425 µm) has a liquid limit of 26.8 % and a plasticity index of 9.4 %. Additional characterization test results are described in the following sections.

3 EXPERIMENTAL PROGRAM

The influence of osmotic effects in Ashfield shale was studied by means of immersion tests. Small specimens of around 4 gr in mass were immersed into brine solutions within reaction (closed) vessels until equilibrium was achieved (see Figure 2). A liquid/rock ratio of 10 (g/g) was adopted in all tests. An small sample size was preferred here to speed up the thermodynamic equilibrium between the rock and the surrounding pore fluid. Reaction vessels were sealed and stored under controlled rock temperature (20 ± 0.1°C). The reaction time between the rock and the brine solutions was 120 days. Once the reaction time was completed, each sample was rinsed with alcohol to wash out any salt excess and dissolved soil. Brine solutions of 0 (distilled water), 0.1, 0.5 and 2 mol of NaCl / litre of deionized water were used in this study. The osmotic potential of brine solutions was estimated via the van Hoff’s equation (e.g., Mitchell & Soga, 2005):

\[ \pi = RT \Sigma (c_i - c_0) \]

where R is the gas constant (8.314462 J/mol*K), T is the absolute temperature (°K) and Σ(ci-ci0) refers to the molar concentration of the solute (both cations and anions). According to Eq. (1) the brine solutions used in this study imposed osmotic potentials equal to 0 (deionized water), 0.49 (0.1 mol/l), 2.46 (0.5 mol/l) and 9.86 MPa (2.0 mol/l). Tested samples were duplicated to ensure enough specimens for the microstructure analyses described below.

Microstructural tests aimed to estimate changes in mineralogical composition (XRD analysis), Cation Exchange Capacity (CEC), cation/ion concentration (chromatographic analysis), specific surface area (SSA), structural arrangement (Scanning Electron Microscopy) as well as pore size distribution (Mercury Intrusion Porosimetry).

XRD analysis as well as the Cation Exchange Capacity (CEC) test were performed using crushed material sieved through the 75 µm sieve. The CEC was estimated following the methodology described in Savoye et al. (2001).

Two methods were adopted to obtain the SSA of Ashfield shale specimens. The total specific surface area (SSA_tot) was calculated, for the intact material only, using the Ethylene Glycol Monoethyl Ether (EGME) method (e.g. Cerato & Luteneger, 2002). On the other hand, nitrogen adsorption (BET) tests were carried out to estimate the specific surface area (SSA_BET) using the 212 – 512 µm fraction.

Scanning Electron Microscopy (SEM) analysis was employed to assess variations in the structural arrangement of the rock after the interaction with different brine solutions. A Zeiss Sigma VP FESEM (Bruker light element SSD EDS detector) device was used for this purpose. As observed in Figure 1, the horizontal bedding planes indicate high degree of anisotropy. To assess this aspect, both horizontal (i.e. parallel to the bedding planes) and vertical (perpendicular to the bedding planes) specimens were cut and exposed to different brine solutions prior SEM analysis. Moreover, the pore size distribution of the rock was estimated via MIP tests in an AutoPore IV 9500 porosimeter (Micromeritics®). In both tests, SEM and MIP, specimens were previously subjected to the freeze-drying process following the procedure described in Delage et al. (2006).
4 RESULTS

4.1 Intact material

The intact material (natural state) is characterized by a total specific surface area $SSA_{\text{total}} = 51.36 \text{ m}^2/\text{g}$. The specific surface area, estimated from nitrogen adsorption tests ($SSA_{\text{BET}}$), is equal to $8.13 \text{ m}^2/\text{g}$ whereas the cation exchange capacity (CEC) is about $10.59 \text{ meq/100 g}$. Both $SSA_{\text{BET}}$ and CEC are within the range reported by Mitchell & Soga (2005) for kaolinite, the predominant mineral in Ashfield shale. Results from chromatographic analysis shows that concentrations for calcium ($Ca^{2+}$), potassium ($K^+$), magnesium ($Mg^{2+}$) and sodium ($Na^+$) are equal to 81.4, 82.8, 66.3 and 37.6 mg/l, respectively.

Figure 3 shows the pore size density function PSD, estimated from the derivative of the cumulative intrusion curve as $PSD = -\frac{\delta \log (e_{\text{MIP}})}{\delta \log (d)}$ (where $d$ is the pore entrance diameter). As observed, the capacity of the porosimeter (220 MPa) is not enough to obtain the complete PSD for the intact material. Nevertheless, a dominant pore size below 10 nm (micro-pores) may be distinguished from this figure. Meso-pores around 0.5 – 3 $\mu$m (500 - 3000 nm) as well as macro-pores about 200 - 300 $\mu$m seem to be predominant in the intact rock. The macro-pores reported in this figure are attributed here to joints and micro-cracks.

SEM microphotographs presented in Figure 4 show good agreement with MIP results. The structural arrangement of Ashfield shale is composed by a dense clayey paste which hosts large-size detritic minerals such as quartz, illite, pyrite and siderite. The microphotograph shown in Figure 3a corresponds to a horizontal section, i.e. parallel to the bedding planes, where meso-pores around 20 - 30 $\mu$m (indicated as black holes) may be identified. The arrangement observed in Figure 3b, that shows a vertical section (perpendicular to the bedding planes), suggests the predominance of meso-pores (1-2 $\mu$m) as well as micro-pores whose dominant diameter cannot be visually identified.

4.2 Natural rock exposed to brine solutions

Figure 5 shows the diffractograms obtained from (qualitative) XRD analysis on specimens previously exposed to different brine solutions. As could be expected, XRD analysis shows negligible changes in the mineralogical composition of the natural rock due to the interaction with brine solutions.
The variation of the SSA\textsubscript{BET}, the CEC and the main cations with the applied osmotic potential, $\pi$, is reported in Figure 6 and Tables 1 and 2. The SSA\textsubscript{BET} reduces whereas the CEC increases with increasing the osmotic potential. SSA\textsubscript{BET} reduces from 9.56 m\textsuperscript{2}/g ($\pi = 0$ MPa) to 6.24 m\textsuperscript{2}/g ($\pi = 9.86$ MPa). The CEC increases from 11.71 meq/100 g to 15.85 meq/100 g for the same variation in $\pi$. The reason for the increase in CEC with $\pi$ is related to cation replacement ($\text{Ca}^{2+}$ and $\text{K}^+$ by $\text{Na}^+$) as also indicated in Figure 5. $\text{Ca}^{2+}$ reduces from 122.79 mg/l to 23.52 mg/l. $\text{K}^+$ and $\text{Mg}^{2+}$ reduce from 52.76 mg/l to 20.62 mg/l and from 41.58 mg/l to 5.75 mg/l, respectively. On the other hand, $\text{Na}^+$ increases from 17.41 mg/l up to 323 mg/l. It is worth noting that by adopting the salinity reported above for the intact material (31.6 g of NaCl/litre of pure water) which represents an osmotic potential $\pi \approx 1.9$ MPa, the SSA\textsubscript{BET} and CEC for the natural rock seem to follow the trends depicted in Figure 6.

Figure 7a shows the void ratio ($e_{\text{MIP}}$) estimated from MIP tests using the cumulative intruded volume of mercury. The maximum intruded void ratio for the natural state is about $e_{\text{MIP}}=0.04$ whereas the total void ratio, obtained from mass ad volume measurements, is 0.05. It can be seen that $e_{\text{MIP}}$ increases with decreasing the osmotic potential. For the specimen exposed to deionized water ($\pi=0$ MPa), the maximum $e_{\text{MIP}}$ is more than twice the value obtained for the natural specimen. This result indicates the progressive expansion of Ashfield shale caused by a reduction in rock salinity. As observed in Figure 6b, the reduction in osmotic potential leads to modifications in the PSD. Two new dominant pore sizes are observed in the PSD of specimens exposed to brine solutions lower than 0.1 mol/l ($\pi<0.49$ MPa). The first one locates around 70 nm (micro-pores) whereas the second one falls about 1000 nm (1 $\mu$m) (meso-pores). Macro-pores are also detected in Figure 6b, which are attributed to the growth of pre-existing micro-cracks and joints.
| State                  | π (MPa) | SSA\textsubscript{BET} (m\textsuperscript{2}/g) | CEC (meq/100 g) |
|------------------------|----------|----------------------------------|-----------------|
| Natural state          | -        | 8.13                             | 13.35           |
| Deionized water        | 0        | 9.56                             | 11.71           |
| 0.1 mol/l              | 0.49     | 8.89                             | 12.34           |
| 0.5 mol/l              | 2.46     | 7.54                             | 14.83           |
| 2.0 mol/l              | 9.86     | 6.24                             | 15.85           |

| State                  | π (MPa) | Ca\textsuperscript{2+} (meq/100 g) | K\textsuperscript{+} (meq/100 g) | Mg\textsuperscript{2+} (meq/100 g) | Na\textsuperscript{+} (meq/100 g) |
|------------------------|----------|----------------------------------|---------------------------------|---------------------------------|----------------------------------|
| Natural state          | -        | 81.36                            | 82.84                           | 66.27                           | 37.58                            |
| Deionized water        | 0        | 122.8                            | 52.76                           | 41.58                           | 17.41                            |
| 0.1 mol/l              | 0.49     | 28.22                            | 35.45                           | 40.40                           | 153.1                            |
| 0.5 mol/l              | 2.46     | 24.81                            | 40.41                           | 51.50                           | 190.0                            |
| 2.0 mol/l              | 9.86     | 23.52                            | 20.62                           | 5.75                            | 323                              |

Figure 7 compares two microphotographs obtained at the same magnification for two specimens cut parallel to the bedding planes. One specimen was exposed to deionized water (π=0 Mpa) (Figure 8a) whereas the second sample was put in contact with a brine solution with a concentration of 2mol/l (π = 9.86 MPa) (Figure 8b). Despite the minor differences in pore size between these two specimens, a bit denser clayey paste may be observed for the sample exposed to the brine solution. The interaction between the natural rock and deionized water causes an increase in the size of platy minerals, mainly illite and kaolinite. This increases the size of micro-pores and meso-pores as observed in Figure 8b. A similar trend is observed in Figure 9 for specimens cut perpendicular to the bedding planes. The expansion of clay minerals by the interaction with deionized water (see Figure 9a) is clearer compared to the specimen cut parallel to the bedding planes shown in Figure 8a. Although the stratification of clay minerals may be identified in Figure 9b, the brine solution inhibits the expansion of the clay minerals and maintains the original arrangement of the natural rock (see Figure 9b). The creation of new micro pores (within clay aggregates) and meso-pores is consistent with the shifting of the PSD observed in Figure 7.

5 CONCLUDING REMARKS

The dependency of osmotic effects on rock microstructure in natural Ashfield shale was evaluated in this paper. Natural rock specimens were put in contact with a range of brine solutions under controlled conditions aimed at evaluating changes in rock microstructure caused by the rock-fluid interaction.

Microstructural tests showed a reduction in the specific surface area with increasing the osmotic potential, π. On the contrary, the cation exchange capacity increases with π. As could be expected
cations like Ca$^{2+}$, K$^{+}$ and Mg$^{2+}$ were replaced by Na$^+$. This led to a progressive modification of the pore size density function PSD of the rock with $\pi$. This phenomenon was corroborated using microphotographs obtained from SEM analysis. Rock anisotropy was clearly identified using SEM images. Specimens cut perpendicular to the bedding planes showed larger modifications in the rock structural arrangement compared to samples cut parallel to the bedding planes.

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