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The effect of divalent ions on the elasticity and pore collapse of chalk evaluated from compressional wave velocity and low-field Nuclear Magnetic Resonance (NMR)

Konstantina Katika*, Mouadh Addassi, Monzurul M. Alam, Ida L. Fabricius

Technical University of Denmark, Denmark

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ABSTRACT

The effects of divalent ions on the elasticity and the pore collapse of chalk were studied through rock-mechanical testing and low-field Nuclear Magnetic Resonance (NMR) measurements. Chalk samples saturated with deionized water and brines containing sodium, magnesium, calcium and sulfate ions were subjected to petrophysical experiments, rock mechanical testing and low-field NMR spectroscopy. Petrophysical characterization involving ultrasonic elastic wave velocities in unconfined conditions, porosity and permeability measurements, specific surface and carbonate content determination and backscatter electron microscopy of the materials were conducted prior to the experiments. The iso-frame model was used to predict the bulk moduli in dry and saturated conditions from the compressional modulus of water-saturated rocks. The effective stress coefficient, as introduced by Biot, was also determined from density and ultrasonic velocities measured on core plugs. Low-field NMR spectroscopy was used in addition to the mechanical testing to prove any changes observed after the saturation related to the surface-to-volume ratio of the pore space in each of the samples or to surface relaxivity. Backscatter-electron (BSE) images were recorded in order to identify the texture of the core plugs under investigation.

The experimental results revealed that both elasticity and pore collapse are influenced by the presence of divalent ions in distinct ways. Compressional wave velocities indicate that saturation with water rich in magnesium and calcium ions softens the contact among the mineral grains. Pore collapse strength is deteriorating after the saturation of chalk with water rich in divalent ions. The presence of calcium and sulfate ions in the saturating fluid results in pore collapse at lower stresses than in the case when samples are saturated with deionized water or sodium chloride solution. Low field NMR spectrometry revealed precipitation of crystals in the pore space of chalk saturated with Mg-rich brine. The precipitation of Mg-carbonates was not used to explain the deteriorating pore collapse strength and effects on the elasticity after the saturation since none of the other plugs saturated with divalent ions (Ca^{2+} and $SO_4{}^{2+}$) experienced it.

1. Introduction

The mechanical strength of chalk is related to the porosity, the stiffness properties of the grains and how well the grains contact each other. The strength can also be related to the fluid used for saturation (Risnes et al., 2003; Andreassen and Fabricius, 2010; Megawati et al., 2012; Nermoen et al., 2015).

One of the ongoing challenges of the oil and gas research is to enhance the oil recovery by altering the salinity and the relative concentration of the ions in the water used in advanced waterflooding. Low salinity flooding method has been successfully used in sandstone reservoirs (Seccombe et al., 2008) and effects of changing the composition of the injecting water have been observed in chalk (Austad et al., 2007; Strand et al., 2006). A number of studies have shown $SO_4{}^{2-}$, Ca^{2+} and Mg^{2+} to be potential determining ions to be injected in order to enhance the oil recovery in chalk reservoirs (Zahid et al., 2011). Laboratory experiments have shown that variation in the salinity and of ionic composition can improve the oil recovery in carbonates (Webb et al., 2005). Meanwhile, studies have shown that the chemical composition of the fluid used for saturation and flooding affects the mechanical strength of the chalk (Risnes et al., 2003; Korsnes et al., 2006; Madland et al., 2011; Nermoen et al., 2015). The effects include decreased pore stiffness and subsequent compaction (Delage et al.,

* Corresponding author.
E-mail address: koka@byg.dtu.dk (K. Katika).

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1996; Kristiansen et al., 2005). These phenomena can be related to a variety of parameters; including precipitation and dissolution reactions, as well as adsorption reactions and changes in wettability.

Nermoen et al. (2015) observed the effect of various brines and oil on the elastic properties (as derived from mechanical testing) of Liege chalk from Belgium. The proposed mechanism is that chalks saturated with brines that cause high electrostatic potential on the surface of chalk are the weakest. Nermoen et al. (2015) introduced the repulsive electrostatic stresses as a mechanism that separates the grains of chalk and therefore weakening the saturated sample. They introduced the electrostatic stress in the effective stress relation, as a mechanism that decreases the effective stresses in chalk under the presence of certain fluids and ions. Relevant to this study, they examined the electrostatic stresses of potential ions in brines; such as NaCl, $MgCl_2$ and Na_2SO_4. Based on this mechanism, chalk saturated with NaCl and $MgCl_2$ are stronger than chalk saturated with Na_2SO_4. Previous work (Katika et al., 2013) has shown that potential determining ions as Mg^{2+} and Ca^{2+} may change the specific surface of chalk from Stevns Klint and affect the mechanical properties of the rock. Chalk from Stevns Klint is usually used as a rock analog for the reservoir chalk from the North Sea of Tor formation due to their similar petrophysical properties (Fabricius et al., 2003). By varying the ionic composition of the brine used for saturation, the mechanism behind pore water action in the chalk can be revealed. Checking the effects of each of the responsible divalent ions on chalk from Stevns Klint could help us identify how each ion affects the pore stiffness in chalk and lead to better predictions of the chalk reservoir response to water injection. Ultimately, brine injection could be applied in the larger scale of a chalk reservoir in order to enhance the oil recovery with minimized effects on the mechanical strength of the rock.

In the present study, we use low field NMR to determine changes in the specific surface and surface relaxivity of the plugs after the saturation. This technique has proved to be useful for porosity and pore size distribution assessment. For the past decades NMR logging has been widely used to identify lithology independent porosity, type of saturation and pore size distribution of the reservoir (Coates et al., 1999). The past few years, low-field NMR at laboratory conditions has started to evolve as part of research in chalk (Megawati et al., 2012; Katika et al., 2013). In those studies, NMR spectroscopy was used to illustrate the pore structure, the type of saturation, the interactions between the pore fluids and the rock and to determine wettability.

In the current study we conducted rock mechanical testing on high porosity chalk from Stevns Klint and observed the influence of specific ion content (Na^+, Mg^{2+}, Ca^{2+} and $SO_4{}^{2-}$) of the saturating fluid on the elasticity, derived from ultrasonic data, and stress of pore collapse. We present petrophysical data, including low field NMR, illustrating the interaction of individual ions with the surface of this porous medium. Overall, this study provides valuable information about the elasticity and pore collapse mechanisms of chalk under the presence of potential determining ions used in waterflooding experiments and reservoir injection.

2. Theory

2.1. Elasticity of rocks

The velocity of elastic waves is the primary data available for acquiring information about the subsurface. Therefore, ultrasonic wave velocity has been used as a tool to evaluate changes in petrophysical and rock mechanical properties. The elastic response of a porous material may be significantly affected by the pore fluid. In order to detect changes in chalk elasticity due to the saturating fluid, ultrasonic velocities were measured in different states; in dry and saturated conditions as well as during pore collapse. Several authors have described the mechanical behavior of chalk in the laboratories while saturated with deionized water (Fruth et al., 1966; Xie and Shao, 2006), sea water (Teufel et al., 1991) or at dry conditions. These studies emphasized on the behavior of the rock when subjected to external stress regardless of the fluid used for saturation or injection. Other studies (Risnes et al., 2003; Korsnes et al., 2006; Madland et al., 2011; Katika et al., 2013) described the mechanical behavior of chalk as related to the chemistry of the fluid used for saturation.

Mechanical rock testing and ultrasonic elastic velocities measurements provide information about the static and dynamic elastic moduli respectively when combined with the density of the material. For rock mechanics, when calculating the elastic moduli using dynamic or static measurements the results are not always found to be equal. Experiments show that difference can be of one order of magnitude or more. In general the dynamic modulus is expected to be bigger than the static one. The weaker the rock is the bigger is the difference (Mavko et al., 1998). A main reason for this discrepancy is that static measurements give the drained modulus whereas the dynamic measurements give the undrained modulus. In the case of dry chalk, where both moduli are drained, the static and dynamic moduli are found to be similar (Olsen et al., 2008). In the current study, we describe elasticity from the undrained modulus.

In order to evaluate the stiffness of the rock we calculated the elastic moduli that are related to the dynamic properties of the rock. The compressional wave modulus, M, is a parameter related to the compressional wave velocity, V_P, and the density, ρ, and the shear wave modulus, G, is related to the shear wave velocity, V_S, and the density. Those two moduli provide information about the bulk modulus, K, of the rock as shown in the following equations:

$$M = \rho V_P{}^2 \quad (1)$$

$$G = \rho V_S^2 \quad (2)$$

$$K = M - \frac{4}{3}G \quad (3)$$

2.2. Pore collapse

The elasticity of a porous material is a term that describes its ability to recover from a force driven deformation. When this deformation is irreversible and a sudden increase in compressibility is observed; the phenomenon is known as pore collapse (Smits et al., 1988). Pore collapse is a phenomenon widely studied in chalk (e.g. De Gennaro et al., 2004; Xie and Shao, 2006). It can be observed from a sudden decrease in the modulus during loading; at this point the material proceeds from elastic to inelastic behavior. In the current study, pore collapse is studied at uniaxially confined strain conditions based on stress strain diagrams. Pore collapse is a failure mode where the grains start loosening or even breaking due to compaction. The process occurs in porous material with high porosity. In a stress–strain curve, pore collapse takes place by the end of the linear elastic phase.

2.3. Effective medium modeling

For a given elastic modulus, a given porosity and mineralogy, the iso-frame model can be used to quantify the amount of resistance that the pore fluid can offer against the overburden stress in a cemented rock frame. This model is based on the upper