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Review article

Predicting capillarity of mudrocks

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A B S T R A C T

This study provides a compilation, evaluation and correlation of published petrophysical datasets determined for 233 rock samples (165 mudrocks, 27 sandstone, 25 carbonate, 11 anhydrite and 5 marlstone datasets). With predominant focus on mudrocks a review of the methods used for determination of capillary breakthrough and snap-off pressures is given. Additionally, based on more recent data, previously published empirical correlations are critically investigated.

Knowledge about these two critical pressures is important for both, the prediction of the capillary sealing capacity of natural gas reservoirs or CO_2 storage sites, but also for production estimates from tight gas or shale gas plays.

Capillary pressure experiments, when performed on low-permeability core plugs, are difficult and time consuming. Laboratory measurements on core plugs under *in-situ* conditions are mostly performed using nitrogen, but also with methane and carbon dioxide. Therefore, mercury injection porosimetry (MIP) measurements are preferably used in the industry to determine an equivalent value for the capillary breakthrough pressure. These measurements have the advantage to be quick and cheap and only require cuttings or trim samples.

When evaluating the database in detail we find that (1) MIP data plot well with the drainage breakthrough pressures determined on sample plugs, while the conversion of the system Hg/air to gas/brine (e.g. CH_4, CO_2) using interfacial and wettability data does not provide a uniform match, potentially caused by different wettability characteristics; (2) brine permeability versus capillary breakthrough pressure determined on sample plugs shows a good match and could provide a first estimate of P_c-values since permeability is easier to determine than capillary breakthrough pressures. For imbibition snap-off pressures a good correlation was found for CH_4 measured on sample plugs only; (3) porosity shows a fairly good correlation with permeability for sandstone only, and with plug-derived capillary breakthrough pressures for sandstones, carbonates and evaporates. No such correlations exist for mudrocks; (4) air and brine-derived permeabilities show an excellent correlation and (5) from the data used we do not infer any direct correlations between specific surface area (SSA), mineralogy or organic carbon content with permeability or capillary pressure. However we were able to better predict permeabilities using a more sophisticated model that relies on a combination of these parameters.

1. Introduction

Low-permeability rocks (mudrocks, evaporites, carbonates, etc.) form part of every natural gas accumulation or CO_2 storage scenario in the sub-surface and special attention should be paid to the characterisation of these rocks. Historically, knowledge and expertise on conventional reservoir rocks was seen to be of priority for oil and gas exploration. Core material from reservoir rocks is regularly made available for proper petrophysical investigations, whereas caprock material (as less important for production) is mostly available only in the form of cuttings, which limits potential laboratory measurements to small sample sizes.

Regarding research of hydrocarbon entrapment over geological time scales, methane (and higher carbon number hydrocarbon gases) migration and dissipation is of interest, i.e. on hydrocarbon entrapment but also hydrocarbon leakage by diffusion or capillary leakage. Several conceptual, experimental or numerical modelling studies resulted in a good understanding of gas transport through low-permeability rocks (e.g. Amann-Hildenbrand et al., 2012; Berg, 1975; Schlömer and Krooss, 1997; Schowalter, 1979). Similar

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Symbols and abbreviations

k	permeability (m^2)
T	temperature (°C)
Φ	porosity (−)
P_c	capillary pressure (MPa)
$P_{c\_snap\text{-}off}$	"snap-off" pressure from imbibition tests: wetting phase displaces non-wetting phase (MPa)
P_{c_brkth}	capillary breakthrough (or threshold) pressure as determined from lab experiments: non-wetting phase displaces wetting phase during drainage measurement (MPa)
P_{c_entry}	capillary entry pressure from drainage tests: non-wetting phase displaces wetting phase during drainage measurement (MPa)
$P_{c\_Hg\text{-}air}$	drainage capillary pressure from mercury porosimetry tests (MPa)
$k_{eff(max)}$	maximum effective gas permeability determined from imbibition tests (m^2)
γ	interfacial tension (IFT) ($N\ m^{-1}$)
θ	contact angle (deg)
r	average pore radius determined from mercury porosimetry tests (m)
ρ_{bulk}	sample bulk density ($kg\ m^{-3}$)
ρ_{grain}	sample grain density ($kg\ m^{-3}$)
SSA, S	specific surface area determined by low pressure N_2 sorption (BET method) ($m^2\ g^{-1}$)
mineralogy	mineral or total organic carbon content (−)

processes apply for shale gas reservoirs where capillary pressure, diffusion coefficient, adsorption capacity, pore network characterisation and other parameters need to be determined for an improved prediction of gas production.

In carbon capture and storage (CCS) discussions, there is sometimes the general opinion expressed that seals that have trapped hydrocarbons for millions of years will do the same for CO_2. This neglects the differences in thermodynamic and geochemical behaviour (CO_2/brine/rock-interactions) of CO_2 compared to hydrocarbon gases. Various comparative studies performed during the last decade have shown that the critical capillary breakthrough pressure is lower for CO_2 than for N_2 and CH_4 (e.g. Hildenbrand et al., 2004; Li et al., 2005). Assuming the same wettability (perfect water wet) for the three gases the difference in breakthrough pressure is attributed to the difference in interfacial tension (higher for N_2 and CH_4 compared to CO_2). Although mineralogical and petrophysical characterization methods (e.g. porosity, permeability, rock density, mercury porosimetry, specific surface area) are essentially the same for research on CO_2 storage, shale gas reservoirs or nuclear waste storage, gas permeability and wettability might be different.

For CO_2 storage, seal characterisation requires a similar research focus, however for much smaller time scales compared to hydrocarbon plays or radioactive waste storage facilities. Instead of considering millions of years the focus is on <10,000 years. Another difference between these research fields is the gas type itself. Carbon dioxide forms a weak acid when dissolved in brine, reacts with the reservoir and the sealing rocks in time scales of 100s to 1000s of years. It may however influence surface properties of minerals and this again can be considered different to hydrocarbon gases, nitrogen or hydrogen, which are more or less inert when in contact with such minerals. This change in surface properties might result in changes in contact angles, which raises the possibility of different wettability states, i.e. CO_2 wetting versus CO_2 non-wetting. It can further be assumed that the wetting behaviour changes with time (or with progressive reaction of CO_2 with brine and minerals). Recent data that support this observation (e.g. Bikkina, 2011; Chiquet et al., 2007; Espinoza and Santamarina, 2010; Jung and Wan, 2012; Yang et al., 2007) and future research will have to pay more attention to this aspect, especially to understand wettability states of different rock types.

As critical capillary pressures of mudrocks are extraordinarily difficult to measure in laboratory and experiments often turned out to be extremely time consuming, the present study aims at finding "simple" rules and relationships with standard parameters like absolute water/gas permeability and porosity. This study reviews published petrophysical and mineralogical data of low-permeability mudrocks. Additionally, datasets determined on sandstones, carbonates, marlstones and anhydrites were included to extend the overall permeability and capillary pressure range. The entire dataset contains data from nuclear waste storage, hydrocarbon sealing and CO_2 storage research.

2. Database content

A total of 233 datasets were collected, providing mineralogical and petrophysical information of various rock types, e.g. porosity, permeability, capillary breakthrough pressure, mercury porosimetry data, and specific surface area. Rock types included are mudrocks (165), sandstones (27), carbonates (25), anhydrite (11) and marls (5). Main focus, however, was on mudrocks. Higher permeable rocks were included in order to increase the permeability/breakthrough pressure range and to potentially generalise certain trends for different rock types. A wide range of petrophysical rock properties, i.e. pore size distribution and porosity, could be correlated with capillary pressure by increasing the value range. We have highlighted potential shortcomings where identified useful. An overview of the published datasets used in this study is provided in Table 2 while the most relevant parameters used here and their original sources are listed in Table 3.

When collecting and comparing different petrophysical parameters we were aware that every measured parameter should be tagged with a certain error bar. Depending on the technical equipment values may be of different precision and accuracy. The latter is most influenced by the choice of the method. Although aiming at the same parameter different methods yield certain deviations from the "true" value. However, a quantification of the accuracy is very difficult, as the "truth" often depends on individual interpretation of experimental data and approximations of conversion factors. Therefore, it seems disproportionate to provide other researcher's data with error bars by making potentially unjustified predictions. Therefore, we want to point out that every data point has a certain imprecision or inaccuracy that needs to be kept in mind. In order to provide a basis for discussion different techniques used for the quantification of the capillary pressure and permeability are critically reviewed and explained in Section 3.

3. Terminology & background

In the following we provide an overview on terminology used in this study. The terminology for low-permeability rocks differs in

Table 1
Classification of mudrocks (Folk, 1980).

Grain size of mud fraction	Indurated, non-fissile	Indurated, fissile
>2/3 silt	Siltstone	Silt-shale
Silt ≅ clay	Mudstone	Mud-shale
>2/3 clay	Claystone	Clay-shale