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Fluid Flow, Pore Pressure, Wettability, and Leakage in Mudstone Cap Rocks

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ABSTRACT

This chapter considers some of the issues surrounding the modeling of one- and two-phase fluid flow in mudstones. For single-phase flow, key relationships include those between porosity and (1) effective stress, (2) permeability, and (3) capillary breakthrough pressure. All three relationships are strongly influenced by the grain-size distribution or clay fraction of mudstones, but a quantitative description is currently only available for the porosity-effective stress relationship. The importance of lithology or clay fraction as a control on the key flow properties of mudstones indicates the practical significance of estimating clay fraction directly from geophysical logs. We illustrate how artificial neural networks can be used to perform this task.

Having considered some of the basic flow properties of mudstones, the second part of the chapter discusses aspects of two-phase flow through mudstone pore systems. Rates, mechanisms, and pathways of petroleum leakage through mudstone pore systems remain poorly constrained. We combine field and experimental data with theoretical arguments to suggest that once a water-wet cap rock is breached, the leak path will become more oil wet as a result of sorption of hydrophilic and ultimately hydrophobic organic compounds onto mineral surfaces. Oil-water partition of hydrophilic organic compounds in reservoirs, followed by diffusion into cap rock pores may even create oil-wet pathways into cap rocks and permit leakage. In these cases, cap rocks simply retard the vertical migration of petroleum, and column height is a function of the rates of petroleum supply and loss. Modeling the rate of loss of petroleum requires a better understanding of mudstone relative permeability.

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INTRODUCTION

Compaction, absolute and relative permeability, pore pressure, and seal capacity are the inextricably linked properties of mudstone cap rocks that must be accurately described in two-phase fluid-flow models of petroleum systems. The three key relationships required for any Darcy-based flow models are those between (1) porosity (or void ratio, e) and effective stress (σ'), (2) flow rate and hydraulic gradient (Darcy's law), and (3) permeability and porosity. When modeling petroleum systems involving two- or three-phase flow, additional data requirements include (1) the relative permeability of the porous medium as a function of phase saturation and (2) the definition of a threshold capillary pressure that must be exceeded in a water-wet porous medium to allow passage of a nonwetting phase into and across a defined rock unit. Dynamic models in which rocks deform and lose porosity under the influence of increasing burial loads require a quantitative description of the way that these parameters evolve through time as a function of, for example, porosity.

This chapter is divided into two main sections. In the first part of this chapter, we consider some of the progress that has been made in providing the quantitative descriptions of the relationships required to model fluid flow in mudstones. We purposefully limit ourselves to a consideration of flow through the matrix pore structure and do not deal with the potentially catastrophic flow that may occur through fractures or faults. We show that the relationships between (1) porosity and effective stress, (2) porosity and permeability, and (3) porosity and threshold capillary entry pressure in mudstones are strongly influenced by grain size and describe how the grain size or clay fraction of mudstones may be rapidly and pragmatically estimated from downhole petrophysical logs. In this way, it becomes possible to rapidly estimate mudstone pore pressure and to populate basin models directly from downhole log inputs.

Having established some of the main controls on the basic flow properties of mudstones, the second part of the chapter focuses on issues related to the leakage or transmission of petroleum through mudstone pore systems. This is an area of petroleum geoscience where considerable uncertainty remains. Conventional descriptions of the system involve a water-wet cap rock pore system that will not transmit any petroleum until the buoyant force exerted by a petroleum column exceeds a critical capillary entry pressure dictated by the dimensions of the cap rock's pore-throat system. Flow is then generally assumed to occur across the cap rock according to a version of Darcy's Law, which is modified to consider two-phase flow. This common model raises several issues that are currently only partially resolved and that we discuss in this chapter. In particular, the following should be answered: (1) How do we define a critical or threshold capillary entry pressure of a heterogeneous cap rock sequence? (2) What is the initial wetting state of a mudstone pore system? (3) Is the wetting state of a mudstone pore system altered by leakage of petroleum, and how does this affect the way we assess seal capacity? (4) How do we define relative permeability curves for mudstones? (5) Where leakage has occurred, how can we estimate the amount of leaked petroleum?

COMPACTION AND FLUID FLOW

Porosity-effective stress

Mudstone compaction has commonly been described as a purely mechanical process in which porosity is lost in response to increasing effective stress. These concepts are rooted in soil mechanics (Terzaghi, 1943; Skempton 1970; Burland 1990) and have since been used to describe the higher stress, longer time, and higher temperature regimes relevant to sedimentary basins (e.g., Smith, 1971; Rieke and Chilingarian, 1974; Ungerer et al., 1990; Schneider et al., 1993; Jones, 1994; Audet, 1996; Karig and Ask, 2003). Because compaction represents a volumetric reduction of porosity, relationships between porosity and effective stress should strictly be couched in terms of mean effective stress. However, whereas vertical stress can generally be estimated quite accurately either directly from density logs or from well-established regional trends, estimates of minimum stress rely on high-quality leak-off test data; intermediate stresses are even less well constrained. Most commonly and pragmatically, therefore, porosity is related to vertical effective stress. In circumstances where the maximum principal stress is vertical, this will generally be acceptable. In circumstances where the maximum principal stress is not vertical, or where concerns about the magnitude of coupling between pore pressure and stress exist (e.g., Harrold et al., 1999), a more complex analysis may be required.

In soil mechanics, the relationship between porosity and effective stress is described as

$$e = e_{100} - \beta \ln\left(\frac{\sigma_v'}{100}\right) \quad (1)$$

$$\sigma_v' = \sigma_v - u \quad (2)$$

$$e = \frac{\phi}{1-\phi} \quad (3)$$

In these equations, ϕ is porosity, e_{100} is the void ratio at 100 kPa effective stress, and β is the slope of

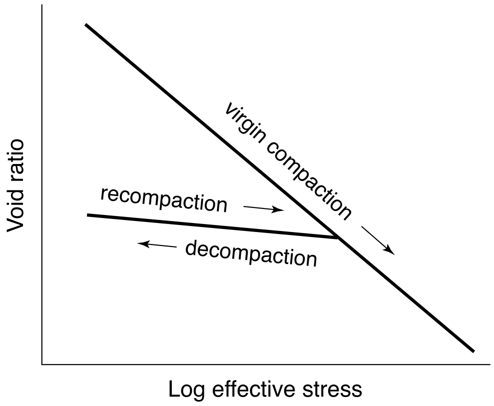

FIGURE 1. Soil mechanics-based description of the one-dimensional, mechanical compaction of fine-grained clastic sediments.

the linear relation between void ratio and the natural logarithm of vertical effective stress. Effective stress (σ'_v) is defined as the difference between total stress (σ_v) and pore fluid pressure (u). The form of equation 1 is such that void ratio is a linear function of the logarithmic value of effective stress. This is shown in Figure 1, which indicates the virgin compression line along which initial compaction occurs. Figure 1 also shows that because mudstone deformation is a predominantly plastic process, the major part of the deformation is not recovered when sediments are unloaded. If an unloaded mudstone is reloaded, the sediment returns to the virgin compaction line, after which, further increases in effective stress drives the mudstone along the virgin line. The porosity of a mudstone is thus an indication of the maximum effective stress to which it has been subjected.

It is also important to note that equations 1 and 2 can be used to estimate pore pressure from mudstone porosity, if the compaction is on the virgin compression line and the values of the compression coefficients in equation 1 are known (Alixant and Desbrandes 1991). This is useful because the low permeability of mudstones means that pore pressures cannot be measured using conventional measurement techniques.

Quantitative use of the porosity-effective stress equation as a means of (1) describing mudstone compaction and (2) evaluating pore pressure from mudstone porosity data requires us to know the numerical values of the two coefficients β and e_{100}. The work of Skempton (1944, 1970) and Burland (1990) showed that β and e_{100} are strongly correlated both with each other and with the sediment's void ratio at liquid limit (e_L). Although e_L is not a geologically useful term, it is strongly correlated to sediment clay fraction, where clay fraction is defined as the percentage of particles less than 2 μm in diameter (Skempton, 1944). Recently, Yang and Aplin (2004) have used data from both the soil mechanics literature and from geological samples to construct the relationship between clay fraction and compression coefficients. Using a large data set covering an effective stress range of 0.8–40 MPa collected from in-situ, geologically compacted, fine-grained clastic sediments from the North Sea and Gulf of Mexico, they constructed the following relationships:

$$e_{100} = 0.3024 + 1.6867 \text{ clay} + 1.9505 \text{ clay}^2 \quad (4)$$

$$\beta = 0.0407 + 0.2479 \text{ clay} + 0.3684 \text{ clay}^2 \quad (5)$$

Substitution of these coefficients in equation 1 allows one to describe mudstone compaction directly as a function of lithology. Three curves for mudstones with differing clay fractions are shown in Figure 2, illustrating the wide range of compaction behavior. In general, silty mudstones are deposited with lower porosities than more clay-rich materials but are less compressible. At high effective stresses, the porosity of mechanically compacted mudstones thus converge (Figure 2).

Pore Pressure

The low permeability of mudstones precludes direct determination of pore pressure by conventional techniques such as repeat formation tests. For this reason, and because of the safety and cost issues related to drilling through overpressured, mud-rich sequences, a strong drive has existed for many years to estimate

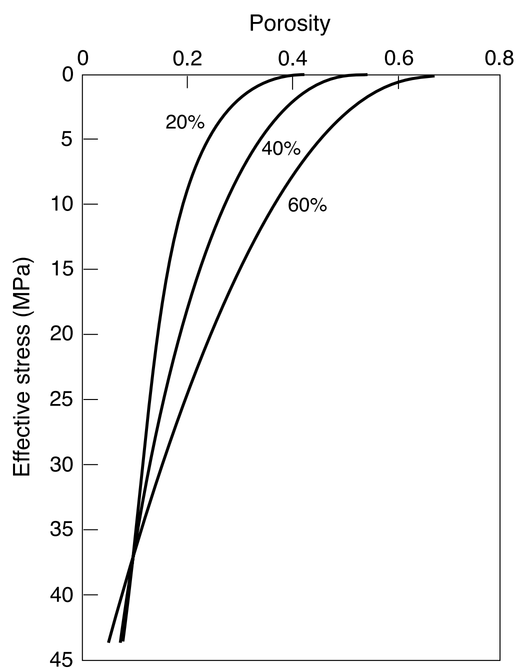

FIGURE 2. Porosity-vertical effective stress trends derived by Yang and Aplin (2004) for geologically compacted mudstones.

mudstone pore pressure indirectly from porosity. Older approaches based on primary mechanical compaction, such as those pioneered by Hottman and Johnson (1965) and Eaton (1975) have proved to be useful but suffer in two ways: first, they assume that all mudstones compact according to a single relationship; and second, their use requires the certain identification of hydrostatically (normally) pressured, shallow-buried sediments. Combining porosity data with an explicit effective stress relationship circumvents these difficulties in that it is based on an explicit physical principle and does not require local calibration to shallow and putatively hydrostatically pressured sections (Alixant and Desbrandes, 1991; Yang and Aplin, 2004). Using this approach, the basic compaction equation 1 can be rearranged such that effective stress can be evaluated if the void ratio (e) is known, and the compression coefficients e_{100} and β can be estimated from the clay content of the mudstone:

$$\sigma' = 100 \times \exp\left(\frac{e_{100} - e}{\beta}\right) \qquad (6)$$

Pore pressure is then the difference between total (vertical) stress and (vertical) effective stress. Examination of Figure 2 shows that estimates of effective stress and, thus, pore pressure could easily be 10 MPa in error if mudstone lithology is not considered.

Any quantitative approach to mudstone compaction using the Terzaghi approach should consider its several limitations. We have already mentioned that the model assumes that porosity loss is driven by increases in vertical effective stress instead of mean effective stress, but that this is unlikely to be a serious issue in many geological settings. Second, the model describes the porosity-effective stress relationship as an exponential relationship. This is convenient, and although it appears to work at stresses as much as 40 MPa (Yang and Aplin, 2004), other relationships may generate a more accurate description. Third, the relationships described here are only valid for mechanical compaction. At higher temperatures (above approximately 80–100°C), the recrystallization of clay minerals such as smectite plus the dissolution and remobilization of carbonates and opaline silica change the microfabric of mudstones (Ho et al., 1999; Aplin et al., 2003; Charpentier et al., 2003) and may lead to a loss of porosity that is independent of effective stress (e.g., Bjørlykke, 1999; Nadeau et al., 2002). Chemical compaction occurs extensively in both carbonates and sandstones (e.g., Garrison and Kennedy, 1977; Tada and Siever, 1989; Bjørkum, 1996), although its importance in clastic mudstones is less well constrained.

The fourth and perhaps most important limitation of the porosity-effective stress relationship is that the inelastic nature of mudstones means that it can only be used to estimate the maximum effective stress to which a mudstone has been subjected. Unloading because of uplift or the lateral transfer of pore pressure to basin highs along sands connected deeper into the basin (Yardley and Swarbrick, 2000), for example, will lead to a change in effective stress but essentially no change in porosity. Although this leads to an underestimate of present-day pore pressure using tools based on porosities evaluated from wireline or seismic data, it does give some insight into pore-pressure histories, for example, where pore pressures have increased as a result of recent, differential subsidence in the center of basins.

Porosity-Permeability

Hydraulic conductivity is the coefficient K (LT^{-1}) that relates the rate of fluid flow q (L^3T^{-1}) through a cross-sectional A (L^2) to the imposed hydraulic gradient in Darcy's Law:

$$q = KiA \qquad (7)$$

Permeability (k; L^2) is related to hydraulic conductivity through the viscosity (η) and unit weight of water (ρ_w):

$$k = K(\eta/\rho_w) \qquad (8)$$

Reviews by Neuzil (1994) and Dewhurst et al. (1999a) indicate that the hydraulic conductivity of mudstones ranges over eight orders of magnitude (10^{-8}–10^{-16} ms^{-1}) and by three orders of magnitude at a single porosity. As stated by Darcy's Law, fluid flux is directly proportional to permeability, so that a permeability uncertainty of three orders of magnitude is unacceptable for modeling purposes; the difference, for example, in dissipating overpressure over a period of 1 million or 1 billion yr.

One difficulty in modeling variations in permeability is the sparse database that exists for well-characterized mudstones. These were summarized by Dewhurst et al. (1999a), and very few new data have subsequently appeared in the literature (but see Hildenbrand et al., 2002). Much of the variation in the permeability of reasonably homogeneous mudstones at a given porosity can be explained by variations in grain size (Dewhurst et al., 1998, 1999b; Yang and Aplin, 1998). For example, Dewhurst et al. (1998, 1999b) measured hydraulic conductivities of the London Clay that varied by close to three orders of magnitude at a single porosity, quite close to the total range suggested by Neuzil (1994) for mudstone cores. The London Clay samples had clay fractions ranging from 27 to 65%, representing close to the full range measured in other studies (20–85%; e.g., Aplin et al., 1995).

Although we currently lack a quantitative model that describes the relationship between porosity and permeability as a function of clay fraction, it seems likely that a fairly strong relationship exists. At porosities for which we have permeability data for lithologically characterized mudstones (20–40%), permeability can be predicted to within an order of magnitude if the clay fraction of the sample is known. Although this is, by no means, perfect, it represents a two-orders-of-magnitude improvement over the full range. At lower porosities, the poroperm relationship as a function of clay content is still poorly established.

Relative Permeability

For two- or three-phase flow, relative permeability is the dimensionless variable that describes the ratio of the effective permeability with respect to a specific phase to the intrinsic permeability (k) of the porous medium. Relative permeability thus represents a semiempirical extension of Darcy's Law. The relative permeabilities of oil and water can be represented as k_{ro} and k_{rw} and have values between 0 and 1:

$$k_{ro} = \frac{k_o}{k} \text{ and } k_{rw} = \frac{k_w}{k}$$

An extensive literature exists describing the relative permeabilities of oil, gas, and water of reservoir lithologies with permeabilities above 1 md (e.g., Aziz and Settari, 1979; De Marsily, 1986). In contrast, very few relative permeability data have been reported for nonreservoir lithologies, not least because of the extreme difficulty of making measurements on samples that have intrinsic permeabilities on the order of 0.1–10 nd. In the absence of data for true mudstones, Okui and Waples (1993) and Okui et al. (1998) collected data from a range of clastic lithologies that varied in grain size from sands to silts. The data showed that with decreasing grain size, residual water saturation increases, flow of oil commences at increasingly small oil saturations, and the crossover point at which oil permeability becomes greater than water permeability occurs at increasingly low oil saturations. Extrapolating to finer grained lithologies, Okui et al. (1998) proposed the mudstone relative permeability curves shown in Figure 3, suggesting that water permeability may decrease to zero at water saturations of 70–80%, that flow of oil may occur at oil saturations of less than 10%, and that the effective permeability of oil may be substantial at oil saturations of greater than or equal to 20%. Although directly measured relative permeability curves for mudstones do not yet exist, the best supporting evidence for Okui and Waples (1993) ideas come from Hildenbrand et al. (2002) experimental determinations of both absolute and gas-phase effective permeabilities in a series of mudstones with porosities of 10–25%. Data in Hildenbrand et al. (2002) suggest that connected gas stringers may form at gas saturations significantly below 1%, and that at higher saturations, relative permeability data range to as much as 1, with many data between 0.1 and 0.4.

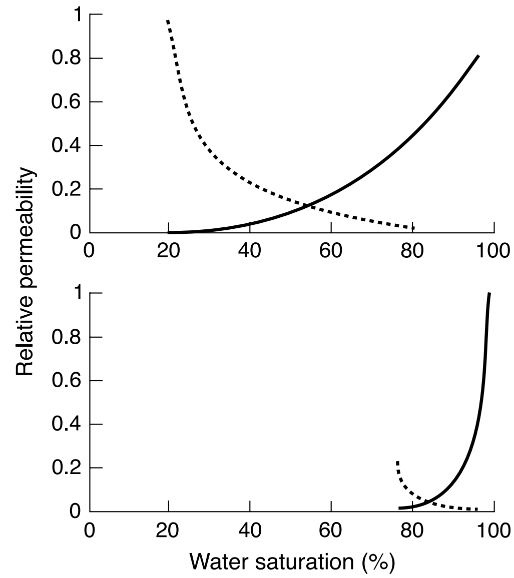

FIGURE 3. Relative permeability curves for sandstones (upper) and mudstones (lower) modified from Okui and Waples (1993).

Compared with sands, therefore, flow of petroleum through mudstone pore systems occurs at low saturations of the nonwetting phase. Substantial flow of petroleum at low saturations is consistent with both experimental data (e.g., Schowalter, 1979; Hildenbrand et al., 2002) and theoretical work based on the percolation theory (Hirsch and Thompson, 1995; Sahimi, 1995), which predicts that whereas saturations of 10–20% are required to form continuous filaments of petroleum across centimeter-scale volumes of homogeneous reservoir lithologies, saturations are scale dependent and decrease with increasing rock volumes. They are also qualitatively consistent with the permeability model developed by Yang and Aplin (1998), which estimates permeability from the pore-size distribution, calculating the contribution of individual pores to the total permeability. Because permeability is a function of the square of the pore diameter (e.g., Scheidegger, 1974), large pores contribute a disproportionately large fraction of the total permeability. Compared with sandstones, the relative importance of large pores is enhanced in mudstones by their relatively broad pore-size distributions, especially in less compacted material (Dewhurst et al., 1998; Yang and Aplin, 1998).

Threshold Capillary Entry Pressure

The threshold capillary pressure (CP_t) of a cap rock may be defined as the pressure that must be overcome to build a continuous filament of the nonwetting phase (petroleum) across a defined rock unit, thus allowing flow of the nonwetting phase. The pore size (or more properly, the pore-throat size) and, thus, the CP_t are generally assessed from mercury injection data, and a reasonably large public database of mudstone pore-size distributions now exists (Borst, 1982; Katsube et al., 1991; Katsube and Best, 1992; Katsube and Williamson, 1994; Kaldi and Atkinson, 1997; Schlomer and Krooss, 1997; Sneider et al., 1997; Dewhurst et al., 1998, 1999b; Yang and Aplin, 1998; Hildenbrand et al., 2002). Although the porosity of the samples analyzed in these studies is commonly reported, the lithology of the materials is sparsely quantified, so that we are still missing the framework with which to quantify the way in which CP_t evolves as a dual function of porosity and lithology. This problem is exacerbated by the difficulty of defining a CP_t from mercury injection data, reflected in the various estimation methods, including measurement of the 90th percentile on the cumulative pore-size distribution (e.g., Schowalter 1979; Schlomer and Krooss, 1997) and the pressure corresponding to the inflection point where, on a graph of pressure vs. saturation, the curve becomes convex upward (e.g., Katz and Thompson, 1987). Whereas this is close to the pressure at which a significant volume of the pore space becomes saturated with the nonwetting phase, flow of the nonwetting phase may occur at much lower saturations, perhaps below 1% (Hildenbrand et al., 2002). These methods are subjective and strictly work only for materials with unimodal pore-size distributions. For more complex materials, for example, core samples with bi- or trimodal pore-size distributions (Dewhurst et al., 1998) and sequences of lithologically heterogeneous mudstones (O'Brien and Slatt, 1990), it is much harder to define a CP_t. Definition of the connected weak point in a complex and heterogeneous mudstone cap rock system awaits methods to define the sedimentology of mudstone depositional systems.

Despite the difficulties involved in the precise definition of a CP_t from either mercury injection data or by laboratory flow experiments, data sets have been compiled from which correlations have been drawn between absolute permeability and some measure of CP_t (Ibrahim et al., 1970; Schowalter, 1979; Hildenbrand et al., 2002). Although the slope and intercept of the regression lines vary according to the data sets used, the correlations are quite strong, as would be expected, because both parameters strongly relate to the diameter of connected pore throats. It follows that because the permeability of mudstones at a given porosity is strongly influenced by lithology or grain-size distribution, the CP_t must also be a joint function of porosity and lithology. This is qualitatively clear in data sets such as those published by Dewhurst et al. (1998, 1999b) and Yang and Aplin (1998) and implicit in the comments by Krushin (1997) that mudstones with higher quartz contents (i.e., siltier) tend to display lower CP_t. Equally, Kaldi and Atkinson (1997) showed that the siltier mudstones deposited in higher energy environments in the upper Oligocene Talar Akar formation, offshore northwest Java, had relatively low CP_t.

Assessing Mudstone Lithology from Petrophysical Logs

It is clear that both the porosity-permeability and porosity-effective stress relationships of mudstones are strongly influenced by lithology, which can be expressed simply but robustly by clay fraction: the percentage of particles that have a diameter of less than 2 μm. It is also clear, although less well constrained currently, that the critical capillary entry pressure of mudstones is influenced, at a given porosity, by grain size. Estimation of mudstones' clay fraction thus yields a promising way of constraining the void ratio-effective stress, permeability-void ratio, and porosity-capillary entry pressure relationships, which are required both for basin modeling and pore-pressure evaluation.

Although clay fraction can be measured in the laboratory, a measurement-centered, particle-based approach to mudstone properties is unrealistic on a large scale. From a practical perspective, an approach using wire-line logs is thus appealing. Previous workers have used either the gamma-ray log or a combination of the neutron and density logs to assess the clay mineral content of mudstones (see Doveton 1994; Hearst et al., 2000). Developed largely for the log analysis of sandstones, the conventional approaches using gamma or neutron-density do not extrapolate easily to mudstones. Because the relationship between log response and clay fraction is quite complex and nonlinear, Yang et al. (2004) developed an artificial neural network (ANN) technique to estimate mudstone clay fraction from wireline data. The ANNs were trained, using a data set of around 530 analyzed mudstone samples, to estimate the clay fraction (and also grain density and total organic carbon) of mudstones from standard wire-line log data (gamma, resistivity, sonic, density, caliper). An example of the output from the program, which incorporates the ANNs as part of a procedure to evaluate mudstone pore pressure and permeability directly from wire-line logs, is shown in Figure 4.

Once clay content has been established from wireline log data, pore pressure can be evaluated using equation 6. The clay fractions determined from wireline data

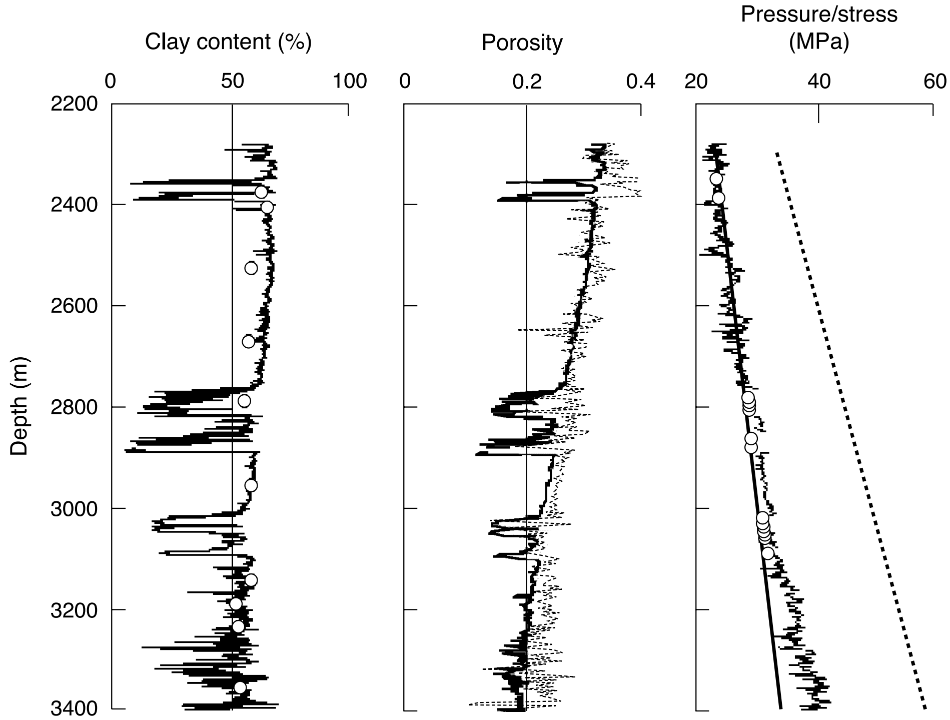

FIGURE 4. Estimation of pore pressure in a west African well from wire-line logs using the lithology defined porosity-effective approach encapsulated in equation 6 in the text. Laboratory-measured clay fractions are shown as open circles. Porosity estimates were made from a combination of the density and sonic logs. The modeled normal compaction curve represents the porosity the sediment would have if it was normally pressured. Depths are below kelly bushing (KB), and the depth between KB and the seabed is 771 m (2529 ft). Pore pressures determined with the repeat formation tester are shown as circles.

allow the compression coefficients to be calculated and, thus, the effective stress and pore pressure to be evaluated (Figure 4). Furthermore, once coefficients relating (1) porosity to permeability and (2) CP_t to porosity are known as a function of clay fraction, the same approach can be used to estimate those parameters directly from wireline data. These data can then be fed into fluid-flow models that use either (or both) Darcy or (and) percolation models to describe flow (Figure 5).

PETROLEUM LEAKAGE

The ideas presented thus far provide a basic framework within which to model fluid flow through mudstones. From the petroleum exploration point of view, fluid flow through mudstones critically manifests itself as the leakage of petroleum through cap rocks, or, from a different perspective, as vertical migration to stratigraphically higher prospects. Indeed, much of the world's petroleum has migrated vertically through large thicknesses of fine-grained sediments, although migration rates, mechanisms, and flow paths are poorly constrained (e.g., faults, fractures, and pores) and, thus, subject to considerable debate. The rest of this chapter considers the flow of petroleum through the bulk pore system of fine-grained sediments, concentrating, in particular, on geochemical evidence that, first, suggests that the wettability of cap rock pore systems may be altered once the cap rock has been breached and, second, helps to define the volume of petroleum that has migrated through the cap rock. The ideas are based on theoretical, experimental, and field evidence that all show that low-molecular-weight petroleum nonhydrocarbons, such as phenols (hydrophilic organic oxygen compounds) and carbazole derivatives (more hydrophobic nitrogen compounds), partition between oil, water, and rock according to rules that suggest substantial adsorption onto mineral surfaces and the distinct possibility that the wetting state will be altered from water- to oil- or mixed-wet (Larter and Aplin, 1995; Larter et al., 1996; Bennett and Larter, 1997; Taylor et al., 1997; van Duin and Larter, 2001).

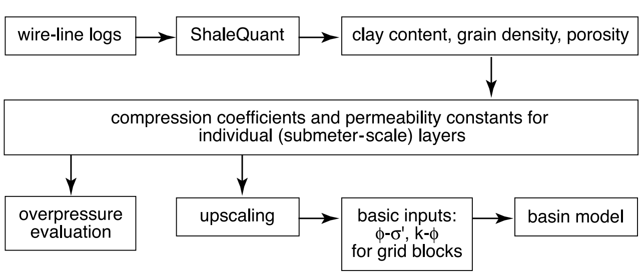

FIGURE 5. Workflow for estimating pore pressure and for obtaining key input data for flow models directly from wire-line logs. ShaleQuant is an ANN model that estimates mudstone clay fraction from wireline data.

Field Data: Snorre

Snorre is a large oil field in the Tampen Spur area of the Norwegian North Sea from which petroleum has leaked several hundred meters into the cap rock (Caillet, 1993; Leith et al., 1993; Leith and Fallick, 1997). Snorre contains approximately 300 m (1000 ft) of undersaturated oil in the Triassic and Jurassic Lunde and

Statfjord formations and is successively capped by the Lower Cretaceous Cromer Knoll Group (as much as 20 m [66 ft]) and as much as 600 m (2000 ft) of Upper Cretaceous Shetland Group and Tertiary Rogaland Group mudstones. Leakage through the Snorre cap rock is well documented geochemically (Leith et al., 1993; Leith and Fallick, 1997), with liquid petroleum having migrated vertically to as much as 600 m (2000 ft) through the cap rock succession, not only at the crest of the reservoir but across a broad front over most of the reservoir area (Leith et al., 1993; Bond, 2001).

Neither the timing nor the mechanisms of leakage in Snorre are perfectly constrained. Caillet (1993) argued that the currently substantial overpressure in the reservoir (14 MPa) may be high enough to cause hydrofracturing of the cap rock, whereas Bond (2001) suggests that sufficient column height exists in the reservoir to drive capillary failure. From a geochemical standpoint, the key point is that, whereas the hydrocarbons in the cap rock and reservoir are very similar and suggest a common origin (Leith and Fallick, 1997), the oil in the cap rock is enriched in both low- and high-molecular-weight nonhydrocarbons compared to the reservoired oil (Bond, 2001). We suggest here that the high concentrations of nonhydrocarbons in cap rock oils have implications for the wetting state of the pore system and serve as a marker for the volume of the oil that has migrated through the cap rock.

Among the many nonhydrocarbons that occur in oil, benzocarbazoles (aromatic nitrogen compounds) have been studied in some detail, because they sorb strongly to minerals and have thus been used to monitor the extent to which migrating oil has interacted with mineral surfaces (Larter and Aplin, 1995; Larter et al., 1996; Terken and Frewin, 2000). Loss of benzocarbazoles along migration pathways lowers their abundance in reservoired oils but should correspondingly increase their concentration in core extracts from migration pathways. High concentrations of benzocarbazoles in core extracts from cap rocks would thus be evidence for substantial migration through the cap rock pore system.

Figure 6 shows the total concentration of two nonhydrocarbons, benzo[a]carbazole plus benzo[c]carbazole, in solvent-extracted organic matter from the Snorre cap rock. Also plotted are equivalent data for core extracts from the reservoir and an unstained cap rock from the Shetland Group overlying the Troll field, which has not leaked oil. Core extracts from the reservoir have a mean benzocarbazole concentration of 2.3 ppm, whereas those from the Troll cap rock, representing benzocarbazole values from an unbreached cap rock, are close to 4 ppm. In contrast, many of the extracts in the cap rock have values between 5 and 7 ppm. The most logical explanation for this enrichment is that more than one volume of oil has passed

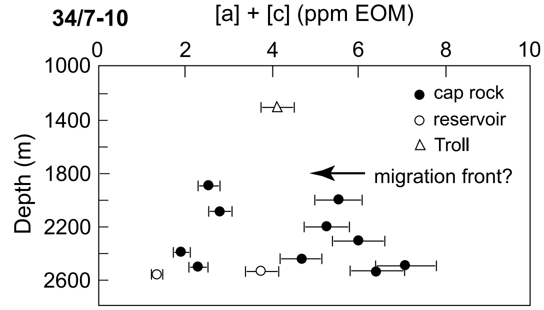

FIGURE 6. Benzo[a]carbazole plus benzo[c]carbazole data from core extracts taken from the Snorre field cap rock (circles) and reservoir (squares) plus the Troll Field cap rock (triangles). Concentrations are expressed in parts per million of the extractable organic matter (EOM). Data for Troll represent a background value for a cap rock that is similar to the Snorre cap rock but which has not suffered oil migration. Concentrations above those of the reservoir oil suggest that greater than 1 volume of oil has migrated through the pore system.

through the pore space, with partial or complete sorptive loss of benzocarbazoles from the migrating oil to mineral surfaces. In other parts of the cap rock, benzocarbazole concentrations are similar to or lower than those in the reservoir oil, suggesting loss of benzocarbazoles by sorption elsewhere on the leakage pathway.

Experimental Data

High concentrations of benzocarbazoles in Snorre cap rocks point to sorption onto mineral surfaces and the possibility that the sorption of polar molecules may result in changes to the wetting state of the cap rock pore system. However, benzocarbazoles are hydrophobic, begging the question of how they and other hydrophobic moieties become sorbed to minerals in water-wet pore systems. We suggest that the key compounds involved in sorption and, thus, the alteration of wetting state are actually small, hydrophilic molecules such as phenols. Strong evidence for this comes from a core flood experiment carried out under realistic subsurface conditions on a clay rich siltstone with a microdarcy-range permeability (Larter et al., 2000). Results showed that many nonhydrocarbons were removed on timescales of months from high API gravity oil during its passage through the initially water-saturated rocks. Small hydrophilic molecules such as phenols were rapidly removed and strongly retained in the cores (Figure 7). Comparison of the molecular composition of the oil exiting the core with that injected into the core indicated that predominantly low-molecular-weight polar compounds were removed, and that many of these are multifunctional compounds with mixed nitrogen and oxygen (and sulfur) functionality.

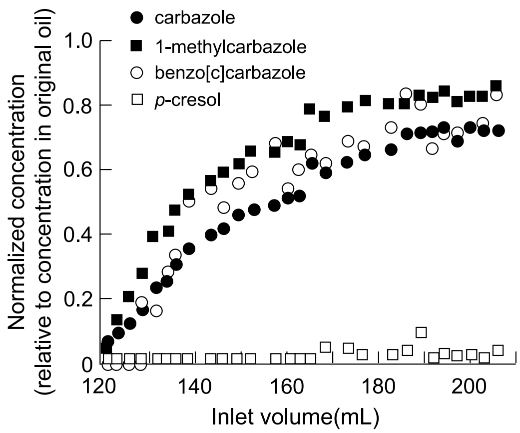

FIGURE 7. Variation in concentrations of selected, representative nonhydrocarbons in oil samples collected at the outlet of a siltstone core during a core-flood experiment in which, first, brine, and then, 41° API oil were flowed through the core (modified after Larter et al., 2000). Concentration data have been normalized to values obtained for the original (input) oil. Whereas both carbazoles and phenols are retained by the core, phenols (as exemplified here by *p*-cresol) show much stronger depletion than carbazole compounds, being strongly retained and essentially removed from the migrating oil in the core. The first oil was eluted from the core after about 120 mL of oil had been injected, the horizontal scale indicating the volume of oil injected. After the experiment, the core inlet showed a marked oil-wet character.

Furthermore, environmental scanning electron microscopy indicated that at the core inlet, the initially water-wet core had become strongly oil wet during the experiment, the oil wetness of the core decreasing toward the outlet of the core. These data strongly support the idea that the hydrophilic organic molecules such as alkyl phenols partition first into water and then onto mineral surfaces, altering the wetting state of the pore system and promoting the sorption of more hydrophobic compounds such as benzocarbazoles.

Theoretical Considerations

Theoretical considerations support the experimental and field data pointing to the sorption of polar organic molecules to mineral surfaces. Van Duin and Larter (2001) report a series of molecular dynamics chemical computational simulations of the phase behavior of organic-water mixtures in the presence of quartz and calcite surfaces. When changing the polarity of the organic phase in the simulations from a charge-neutral cyclohexane phase via apolar carbazole and polar phenol to highly polar acetic acid, distinct changes in the organic phase-water-mineral phase behavior were observed. Cyclohexane and carbazole form discrete organic phases separated from the mineral surfaces by a water film. In contrast, phenol and acetic acid show sufficient water solubility to penetrate through these films to compete with the water molecules for mineral surface adsorption sites. This is consistent with the rapid removal of phenols and other small hydrophilic moieties observed during the siltstone core flood (Larter et al., 2000). Further molecular dynamics simulations with preadsorbed phenol compounds on a calcite surface demonstrate that these small polar molecules can have a profound impact on surface wettability, making the mineral surface accessible even to completely nonpolar compounds, including high-molecular-weight hydrocarbons. This provides strong support for a two-stage process producing wettability changes in oil-water-mineral systems, commencing with small polar species partitioning from oil to water (Larter and Aplin, 1994, 1995; Taylor et al., 1997; Bennett and Larter, 1997) and sorbing to an initially water-wet mineral surface. Sorption results in a more hydrophobic mineral surface, after which water film rupture occurs and leads to the sorption of more apolar compounds (e.g., petroleum hydrocarbons) onto and around these polar surfactants. Mineral surfaces in siltstones and, by inference from the modeling and field observations, cap rocks can become oil wet on a timescale of months.

Wettability: Summary

Field and laboratory studies of fine-grained rocks clearly indicate that polar petroleum compounds are removed onto mineral surfaces, despite the initial presence of water films. Computational chemistry confirms that low-molecular-weight polar compounds, of which phenols are probably just one class, readily penetrate mineral water films to change surface properties, such that hydrocarbons can wet the mineral surfaces. Examination of siltstone cores flooded with brine, then oil, indicates that sorption of polar compounds appears to correlate with changes from an initially water-wet state to a more oil-wet state. The high abundance of benzocarbazoles in core extracts from the Snorre cap rock suggests that similar processes occur in natural systems, so that initial breaching of the cap rock pore network would result in a more oil-wet pore system.

We conclude that there is reasonable doubt that cap rocks in contact with oil would remain water wet. In this scenario, cap rocks then represent low-permeability chokes to petroleum systems instead of capillary seals. Failure could occur by a creep-seep mechanism by which low-molecular-weight hydrophilic oil components partition into cap rock porewaters and change wettability, allowing limited Darcy flow. This is then repeated until the seal is breached, and leakage by continuous Darcy flow occurs. In this case, mudstone cap rocks do not act as permanent seals but simply retard the inexorable flow of petroleum to the basin surface.

SUMMARY AND CONCLUSIONS

In this chapter, we have reviewed some of the issues relating to the understanding and modeling fluid flow in fine-grained sediments. From the practical standpoint of requiring well-constrained input data for flow models, it is apparent that for clastic mudstones, the relationships between (1) porosity and effective stress, (2) porosity and permeability, and (3) porosity and threshold capillary pressure are strongly influenced by the grain-size distribution or clay fraction of the sediments. Whereas coefficients that define mechanical compaction using soil mechanics (Terzaghi) theory have been reported as a function of lithology, quantitative descriptions of the porosity-permeability and porosity-threshold CEP relationships are still required.

Because lithology or clay fraction exerts a strong influence on the key flow properties of mudstones, a method to quickly determine clay fraction from geophysical logs is of practical importance. Among various approaches, we have used an ANN-based program to determine clay fraction directly from wireline data and then to estimate pore pressure using a mechanical compaction model.

Leakage or two-phase flow in cap rock pore systems remains poorly constrained. Accurate and agreed methods for estimating threshold capillary pressures are lacking both for homogeneous mudstones and especially for heterogeneous sequences, for which we are unable to define the critical leak path for petroleum. Field and experimental data combine with theoretical arguments to suggest that once a water-wet cap rock is breached, the leak path will become more oil wet as a result of sorption of hydrophilic and, ultimately, hydrophobic organic compounds onto mineral surfaces. Once this has happened, cap rocks simply retard instead of halt the vertical migration of petroleum. Indeed, oil-water partition of hydrophilic organic compounds in reservoirs, followed by diffusion into cap rock pores, may create oil-wet pathways into cap rocks and drive leakage even in the absence of any pressure gradient to drive Darcy flow. In this case, the rate of loss of petroleum through the cap rock is a function of its relative permeability.

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