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**Determination of Effective Porosity
of Mudrocks—A Feasibility Study**

Joachim Dorsch

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DEPARTMENT OF ENERGY

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**Determination of Effective Porosity
of Mudrocks
- A Feasibility Study**

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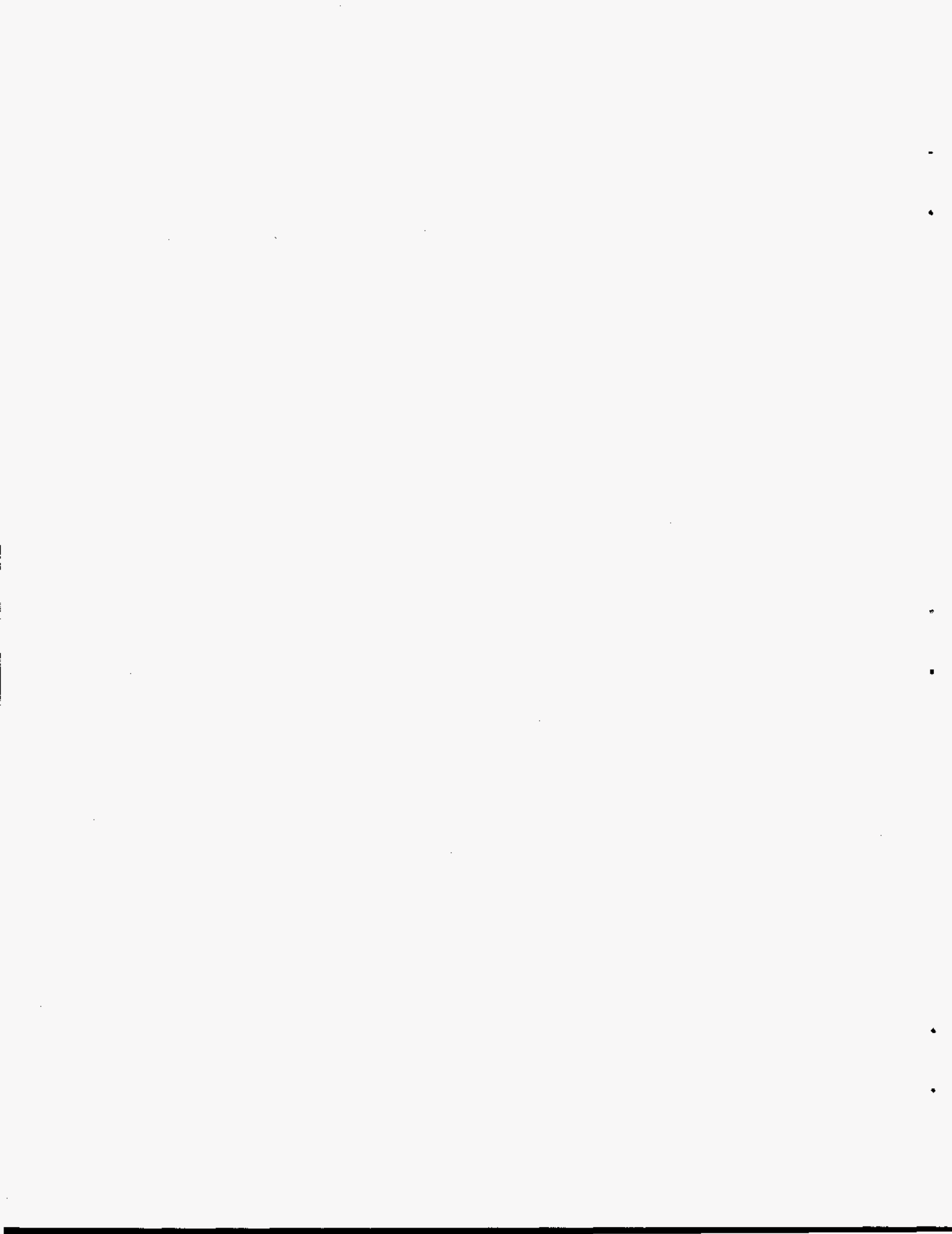


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Executive Summary

Matrix diffusion is believed to be an important transport process within the double-porosity (primary sedimentary porosity and secondary fracture porosity) mudrock-dominated stratigraphic units on the Oak Ridge Reservation (ORR). Effective porosity is identified as an important parameter for evaluating and modeling matrix diffusion as a transport process.

This report identifies, summarizes and evaluates several petrophysical techniques, which can be used to determine the effective porosity of mudrock. Most of the techniques found their original application in the petroleum industry for the evaluation of reservoir rocks.

Petrophysical techniques which are identified as useful in generating quantitative data on effective porosity of mudrock encompass: the water-immersion method, helium porosimetry, mercury porosimetry, and the radial diffusion-cell method. The water-immersion method, and helium and mercury porosimetry are well established techniques. They determine the effective porosity over a sample size of commonly less than ca. 6 cm³ (ca. 15 grams). The radial diffusion-cell method, on the other hand, is a recent technique, which is not yet tested on lithified mudrock. It also provides effective porosity data integrated over a much larger volume.

Helium and mercury porosimetry are very sophisticated techniques that require specialized laboratories. The water-immersion and the radial diffusion-cell method can readily be set up at the Environmental Sciences Division (ESD) at the Oak Ridge National Laboratory (ORNL). These methods are also much less expensive than helium and mercury porosimetry, in part because the necessary equipment is already available at ESD.

Effective porosity values derived from the water-immersion method, helium porosimetry and mercury porosimetry are generally judged to be reliable. Mercury porosimetry will provide the added advantage of providing quantitative data on the pore-throat sizes of the analyzed mudrock. The physical constraints imposed by the pore throats as the narrowest pathways within the interconnected pore system can impact diffusion rate. Furthermore, the size of the pore throats might cause exclusion of certain contaminant species from invading the matrix-pore space.

Introduction

Purpose

The feasibility study is intended to introduce and evaluate several methods, which can provide information on the effective porosity of fine-grained siliciclastic rocks. The study concentrates on laboratory methods, because these are considered to provide more detailed information on effective porosity than field-scale techniques. Several methods are introduced with their basic principle, a synopsis of their methodology, a summary of possible sources of error, and an estimate of the likely costs involved. Each method is then evaluated as to its accuracy and significance of the porosity values produced by the technique. Finally, the different methods are evaluated with respect to each other and final recommendations are made.

Knowledge of effective porosity of fine-grained siliciclastic rocks is important in evaluating the importance of matrix diffusion for contaminant transport in appropriate sedimentary successions (e. g., Germain and Frind, 1989; Toran et al., 1995). Diffusion as a transport mechanism is generally judged to be important in low-permeability deposits (Freeze and Cherry, 1979) which retain a certain level of space for the storage of fluid (porosity). Transport of ions and molecules by diffusion occurs within the pore space through the stationary fluid filling the pore space, while large volumes of material transport through actively moving fluid is severely curtailed.

Matrix diffusion, furthermore, is of special importance in stratigraphic units exhibiting a double-porosity nature (Sudicky, 1990). Fluid and contaminant transport might be dominated by a fracture system, constituting the fracture porosity. The porosity of the surrounding low-permeability rock volume (matrix porosity) might not contribute significantly to fluid/contaminant transport. Diffusion of contaminants from the fractures into the surrounding rock matrix, however, can significantly retard the spread of a contaminant plume (Neretnieks, 1980; Tang et al., 1981; McKay et al., 1993). Conversely, contaminants incorporated into the rock matrix through diffusion can be a severe obstacle to a speedy in-situ remediation effort (Germain and Frind, 1989; McKay et al., 1993). Matrix diffusion is considered an important mechanism for contaminant transport and retardation for the fractured mudrock-dominated stratigraphic units on the ORR (Wickliff et al., 1991; Solomon et al., 1992; Shevenell et al., 1994; Sanford et al., 1994). Knowledge of the effective porosity of these mudrock-dominated stratigraphic units is of paramount importance for evaluating the effects of

matrix diffusion, and for the prediction of contaminant behavior and the design of remediation measures (Toran et al., 1995).

Classification of Fine-Grained Clastic Sedimentary Rocks

Much confusion exists concerning the classification of fine-grained clastic sedimentary rocks. The classification scheme adopted for this report (tab. 1) is derived from Blatt et al. (1980). According to these authors, mudrock should be used as a *general term* for fine-grained clastic sedimentary rocks composed of silt, clay, or a mixture thereof, possessing fissility or not (Blatt et al., 1980). Shale, according to this scheme, is a suffix restricted to those fine-grained clastic sedimentary rocks exhibiting fissility (tab. 1).

Porosity

The total volume of a rock sample (V_b) is the sum of the volume of its solid material (grains: V_g) and the volume of its pore or void space (V_p) (v. Engelhardt, 1960). Porosity of a rock commonly is defined as the *percentage of rock volume consisting of voids or pores*. Porosity as a basic physical property of a rock, therefore, constitutes a measure of volume of pore space which is potentially available for the storage and/or passage of a fluid. Two types of porosity can be distinguished:

1) total porosity ϕ_T

$$\phi_T = V_p / V_b \cdot 100 = (V_b - V_g) / V_b \cdot 100,$$

2) effective porosity ϕ_E

$$\phi_E = V_{pinter} / V_b \cdot 100$$

ϕ_T = total porosity

ϕ_E = effective porosity

V_p = volume of pore space

V_{pinter} = volume of *interconnected* pore space

V_b = bulk sample volume

V_g = volume of the *solid* sample material: volume of grains.

Porosity, as the ratio of volume of pore/void space to total volume of the rock sample, is commonly expressed as a fraction or, when multiplied by 100, as a

Classification of Mudrocks

<i>ideal size</i>	<i>field criteria</i>	<i>fissile</i>	<i>nonfissile</i>
>2/3 silt	(abundant silt visible with hand lens)	silt-shale	siltstone
>1/3 <2/3 silt	(feels gritty when chewed)	mud-shale	mudstone
>2/3 clay	(feels smooth when chewed)	clay-shale	claystone

tab. 1: Classification of mudrocks (from Blatt et al., 1980).

percentage. Total porosity refers specifically to the cumulative void space of a rock sample, whereas effective porosity refers only to the interconnected void space. Effective porosity is the type of porosity believed to be important for diffusive processes in the low-permeability sedimentary rocks at the ORR, because the interconnected water-filled pore space can be used by diffusion for efficient material transport.

Another measure of pore space in a rock is
void ratio e

$$e = V_p \text{ [or } V_{pinter}] / V_g$$

e = void ratio.

Porosity and void ratio are related through (v. Engelhardt, 1960):

$$\phi_T \text{ [or } \phi_E] = e / (1 + e) \quad \text{or}$$

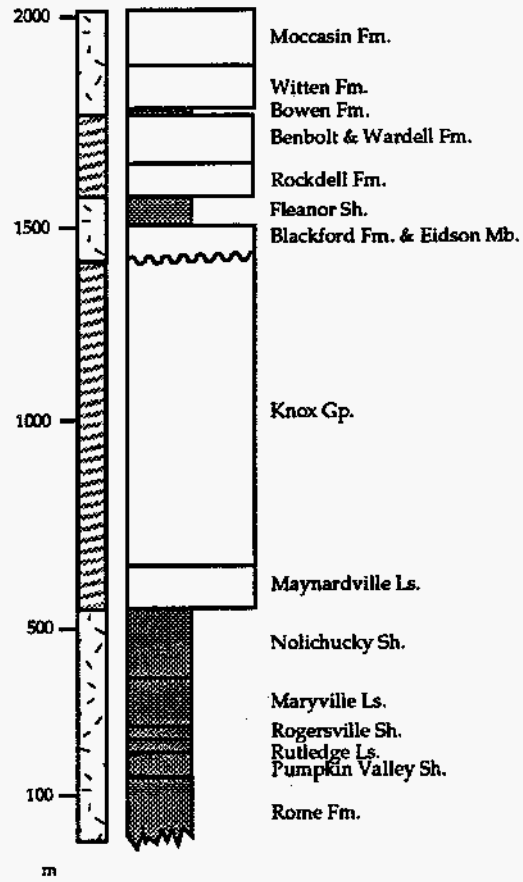
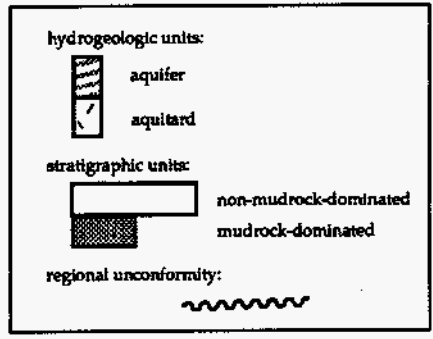
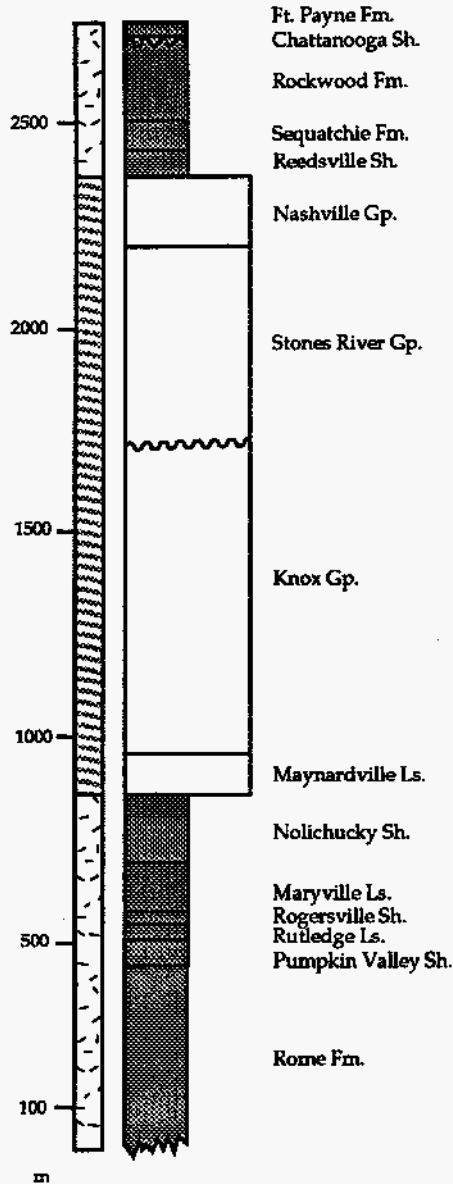
$$e = \phi_T \text{ [or } \phi_E] / (1 - \phi_T \text{ [or } \phi_E])$$

e = void ratio
 ϕ_T = total porosity.

A Framework for Mudrock Porosity at the ORR

The thickness and volumetric importance of the mudrock-dominated stratigraphic units at the ORR are displayed in stratigraphic sections for the Kingston thrust sheet (fig. 1a) and for the Copper Creek and Whiteoak Mountain Thrust sheets (fig. 1b). The porosity of mudrocks is influenced by many different variables (see summaries in Singer and Müller, 1983; Bennett and Hulbert, 1986), and a brief discussion of these different variables will help to provide a clearer picture of mudrock porosity and its evolution.

fig. 1: Stratigraphic sections for the Kingston thrust sheet (a) and the Copper Creek and Whiteoak Mountain thrust sheets (b) on the ORR. The vertical axis is in m displaying the importance and stratigraphic distribution of mudrock-dominated stratigraphic units. Thickness values are averages of measured stratigraphic thicknesses. Thickness data, stratigraphic ages, and distribution of aquifers and aquitards are derived from Hatcher et al. (1992).



b)

Upon deposition, mud possesses a high initial porosity as great as 90% (e. g., Singer and Müller, 1983). Initial porosity is strongly influenced by the amount of clay-size material within the mud (the higher the clay content the higher is the initial porosity; fig. 2), the clay-mineral composition (different specific surface areas for different clay minerals), and especially by the original depositional fabric. The original depositional fabric, in turn, is strongly influenced by the ambient environmental conditions (salinity, water turbulence, biogenic activity, particle concentration and size) at the time of sedimentation.

The initial porosity is altered soon after sedimentation, for example through biogenic activity, seismicity, or water movement (turbulence, currents, wave loading). The most important reduction of initial porosity in mud/mudrocks, however, occurs through compaction (figs. 3, 4, 5), which changes the depositional fabric by mechanical rearrangement of clay particles (e. g., Bennett and Hulbert, 1986). Precipitation and/or dissolution of cements within the existing fabric is commonly spotty in mudrocks and usually occurs at a later burial stage (note, however, 'early' calcite concretions) (Bennett and Hulbert, 1986). The occurrence of late-stage cements can add significantly to the reduction of (effective) porosity of mudrocks (Katsube et al., 1992a).

'Shales' (mudrocks in our terminology) possess an unimodal pore-size distribution (Katsube, 1992; Katsube and Best, 1992; Katsube and Issler, 1993), with the mean pore size decreasing with burial depth due to compaction (Katsube and Williamson, 1994; Katsube and Issler, in preparation; figs. 4, 5). The rate of this decrease in mean pore size is variable from basin to basin. The rate is reduced, for example, in basins of rapid subsidence (Katsube and Issler, in preparation; Katsube and Williamson, 1994). The pore space is considered to be interconnected and isolated pores are probably rare in mudrocks (Katsube et al., 1991).

Katsube and co-workers (Katsube, 1992; Katsube et al., 1990, 1991, 1992a, b; Katsube and Williamson, 1994) report some interesting observations obtained from tight 'shales' from a burial depth of 4400-5600 m. They report that nanopores ($\leq 3.0 - 14$ nm in width) constitute the main interconnected pore space in these tight shales (they consider nanopores as the pore throats). The nanopores/pores are characterized by a unimodal size distribution of 0.3 - 60 nm, with mean pore sizes/modes of 2.7 - 11.5 nm. These are some of the smallest pore sizes known from any rocks (Katsube et al., 1991). Pores larger than 25 nm exist in these tight mudrocks, but are rare and/or isolated (Katsube et al., 1992a; Katsube and Williamson, 1994). Katsube (1992) and Katsube et al. (1992a), furthermore, showed that $83\% \pm 4\%$ of the effective porosity of these tight 'shales' is contributed by nanopores.

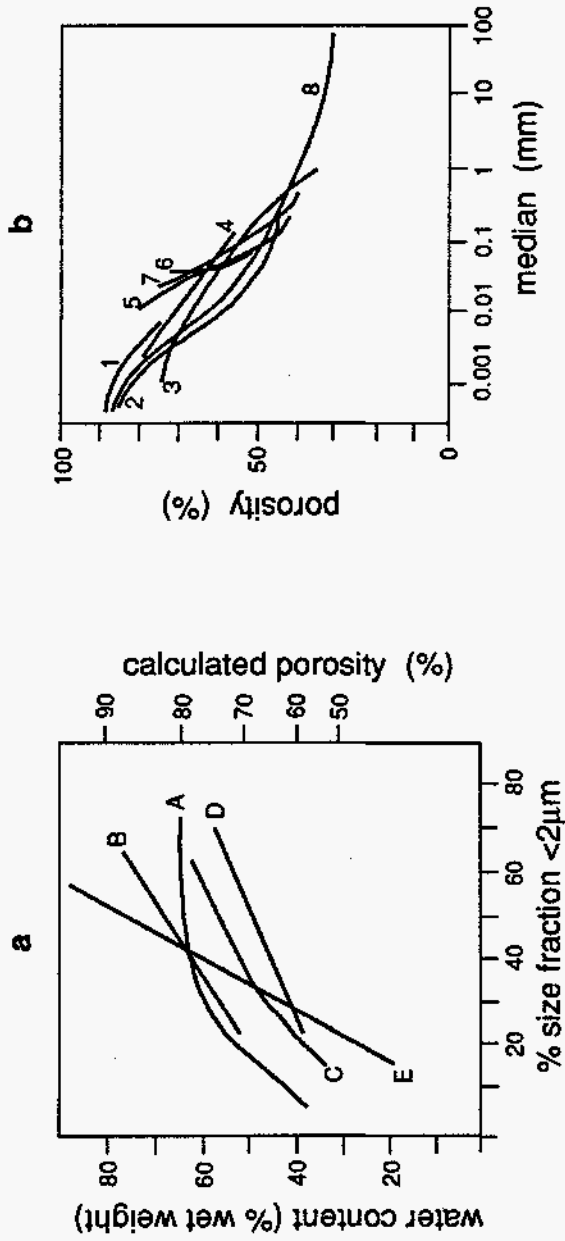


fig. 2: Relationship between water content/porosity of freshly deposited sediment in different sedimentary environments to grain size: (a) percentage of clay fraction [$<2 \mu\text{m}$] or (b) median;
 a) A = Lake Constance, B = Zuiderzee, C = Mississippi Delta, D = Gulf of Mexico (Rockport, TX), E = California Basin (based on Müller, 1967);
 b) 1 = Lake Mead, 2 = Lake Marlo, Venezuela, 3 = Lakes in the western USA, 4 = Gulf of Paria, 5 = North Sea, 6 = shelf off southern California, 7 = San Diego Bight, 8 = rivers in Japan, 9 = Pliocene and Pleistocene alluvial sediments of California (based on Meade, 1966);
 (modified from Heling, 1988).

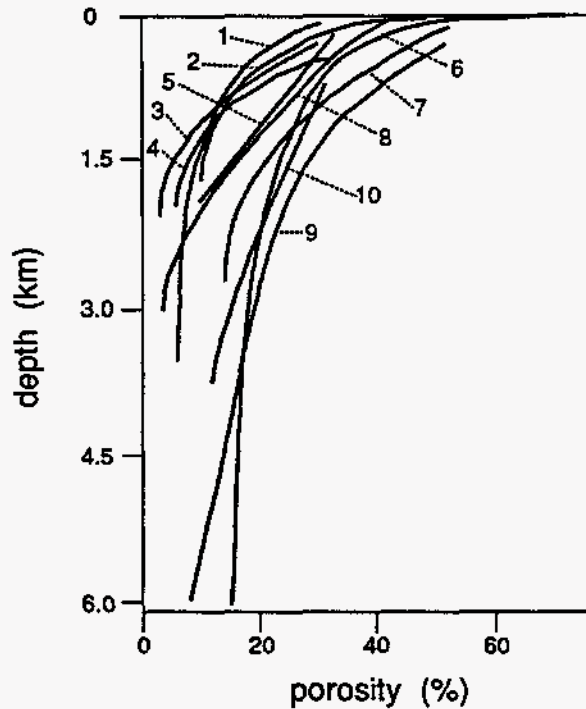


fig. 3: Porosity of mud and mudrocks in relation to burial depth: porosity-depth curve (based on Rieke and Chilingarian, 1974; modified from Heling, 1988);
 1 = mudrocks of the Lower Cretaceous, 2 = Recent to Miocene mud/mudrocks, 3 = Pennsylvanian - Permian of Oklahoma, 4 = Tertiary of Japan, 5 = Tertiary of Venezuela, 6 = Tertiary of the Gulf Coast, 7 = Shiunji Gas Field, Japan, 8 = O.F., 9 = data from Ham, 10 = data from Foster and Whalen; please refer to Rieke and Chilingarian (1974) for data sources;
 note rapid decrease in porosity over the first few hundred meters of burial and then decrease in rate of porosity reduction; the shape of the compaction curve is dependent on various factors (such as burial depth, tectonic stresses, lithology, temperature, time, loading rate, degree of cementation, presence of fluid-escape paths [summary in Singer and Müller, 1983]) and is therefore expected to be different for different sedimentary basins.

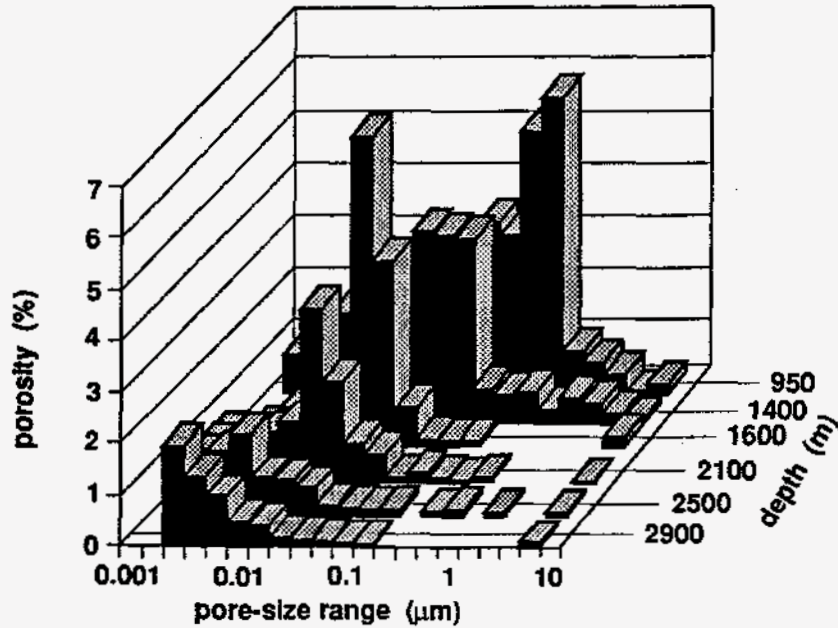


fig. 4: Pore-size distribution for mudrock samples from different depths in the Beaufort-Mackenzie basin (normally compacted zones); pore sizes (in μm) were obtained by mercury porosimetry; note: unimodal pore-size distribution, decrease in porosity with burial depth, narrowing of pore-size range with burial depth, and decrease in pore-size median with burial depth (from Katsube and Williamson, 1994).

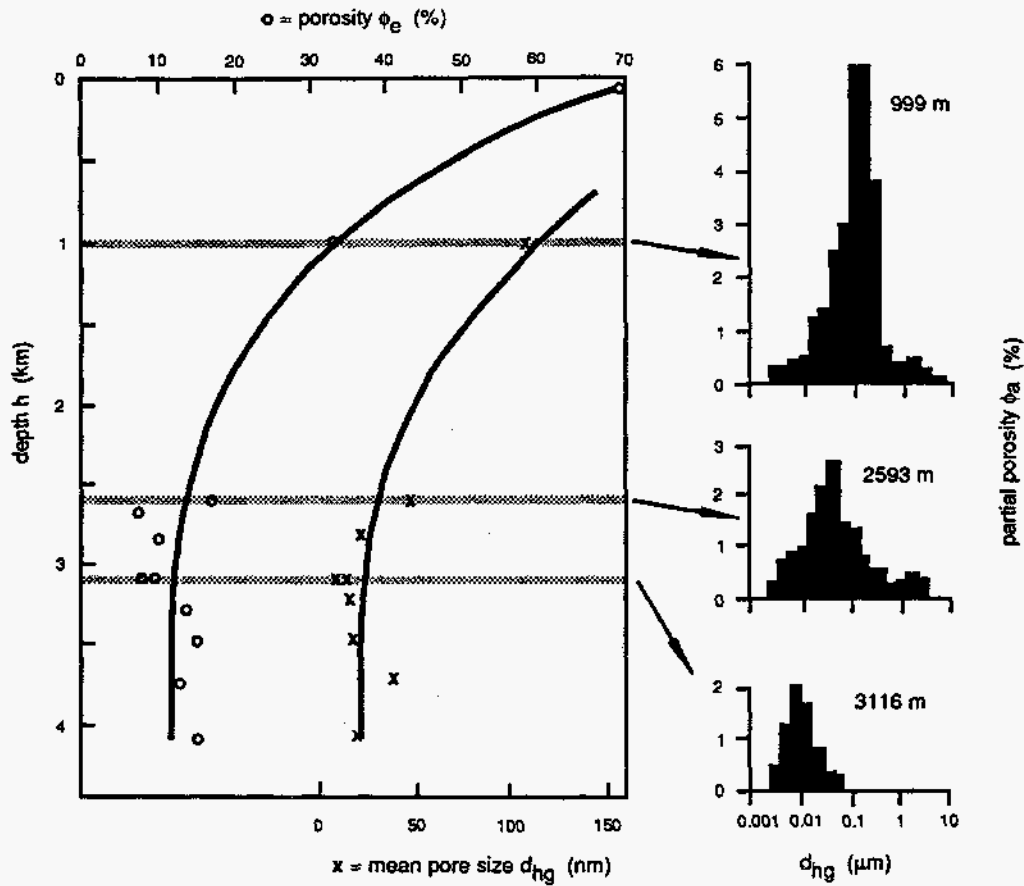


fig. 5: Decrease of effective porosity ϕ_e and of mean pore size d_{hg} with depth in mudrock samples from the Beaufort-Mackenzie basin; histograms display pore sizes and (unimodal) pore-size distribution for depths of 0.999, 2.593, and 3.116 km, and the change in pore-size distribution with depth (based on Katsube and Best, 1992; from Katsube and Williamson, 1994).

An interesting observation is reported by Melnyk and Skeet (1986). They showed an increase in effective porosity through an alteration zone along a traverse from parent rock to a natural fracture, but also a slight decrease in effective porosity immediately at the fracture when compared to the alteration zone (fig. 6). Although these measurements were undertaken on a granite sample, it is interesting to investigate whether a similar phenomenon can also be observed in mudrocks when moving closer to a fracture. Especially important is the interface between fracture and rock body where the available entry/open porosity provides access for contaminants (by diffusion) into the rock matrix. A decrease in effective porosity at the fracture surface in a mudrock seems highly probable, given that a fracture can serve as a flow conduit with the possibility of precipitation and introduction of mineral cement (calcite, quartz, etc.) into the pore space of the adjacent rock body. Effective porosity of mudrocks might be significantly different (reduced by cementation directly at the fracture surface, increased by weathering at a distance from the fracture surface) in the vicinity of a fracture when compared with the surrounding rock body.

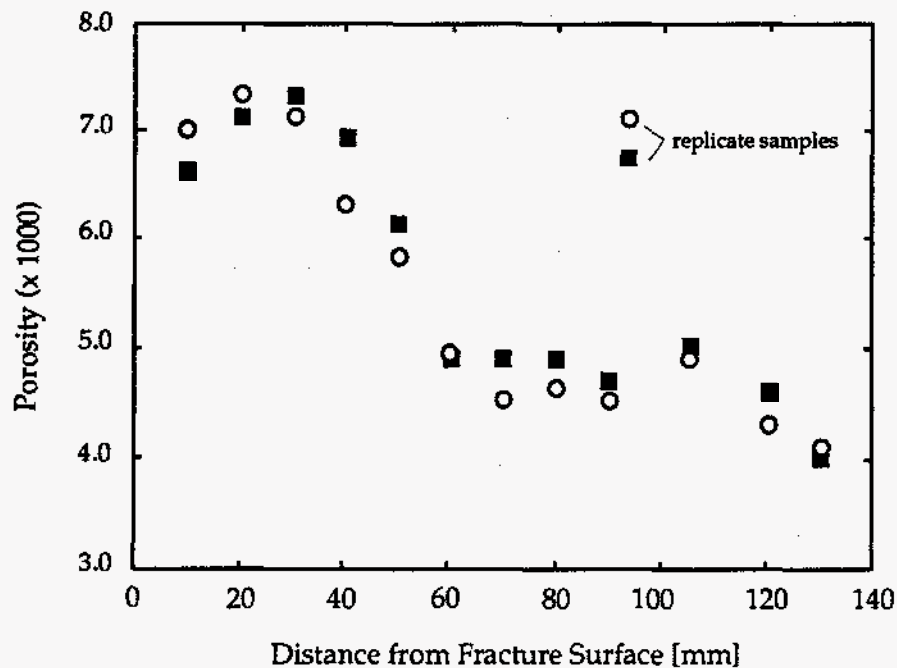


fig. 6: Porosity profile adjacent to a natural fracture surface in granite (modified from Melnyk and Skeet, 1986).

Techniques for Measurement of Porosity

Optical Methods

principle

Porosity is determined based on optical investigation of thin sections.

methodology

Several closely similar methodologies are available, but basically the determination of porosity with optical methods roots in the classic petrographic technique of point counting. Variations in the basic methodology are provided by the difference in thin sections used and their optical investigation. There are: a) standard thin sections and the standard polarizing microscope, b) polished thin sections and the scanning electron microscope (SEM), and c) polished thin sections and the transmission electron microscope (TEM). The SEM can also be applied to freshly broken mudrocks (investigating the face broken perpendicular to bedding). The investigation and point counting can be simplified and enhanced by various image-enhancing techniques.

possible problems and sources of error

- # subjectivity of the investigator;
- # thin section preparation: preparation of thin sections from fine-grained sedimentary rocks is not as straightforward as from other sedimentary rocks; plucking of small, rigid grains during sample preparation can artificially induce additional porosity, and thereby can provide a major source of erroneous porosity values;
- # measurement of 'total optical porosity' (TOP); TOP does not conform to effective porosity, because also isolated pores are counted;
- # to what degree is it possible to accurately define and image pores in fine-grained sedimentary rocks?

cost

The most significant costs are generated through the preparation of thin sections. Mudrocks are very tricky to prepare for optical analysis and expert preparation-technique is required. This is especially true for polished thin sections for SEM and TEM analysis. Petrographic analysis can be carried out at ORNL. A standard petrographic microscope coupled with a point counter is readily available, but access to SEM and TEM and expert help has to be secured separately at ORNL (and Y-12). Use of image-

enhancing techniques will make additional money necessary. Money will be used to purchase the necessary commercial software (including training) and computer, should suitable hardware not be available at ORNL.

evaluation: accuracy and significance of porosity values and of optical observations

The major problem with optical techniques is, of course, that they are measuring *total optical porosity* (TOP). TOP is different from effective porosity, and should yield porosity values larger than effective porosity values. This can be explained by the fact that optical techniques also image and tabulate isolated or pocket pores (either completely isolated within the rock matrix or isolated from the rest of the pore space through diagenetic plugging of the pore connections). These pores are by nature not linked to the interconnected pore space and, therefore, are not part of the interconnected effective porosity. The less isolated pore space exists within any given mudrock the closer the values of TOP and (true) effective porosity should be.

It is important to note the claim of Katsube et al. (1991), however, that the pore space in mudrocks does not contain much isolated pore space. This claim, however, awaits verification by further study (Katsube and Williamson, 1994).

Optical techniques, nevertheless, serve as an important tool for the overall characterization of mudrock-dominated stratigraphic units. The techniques provide an important source of information on the diagenetic history of the rocks, detail on the amount and type of coarser grained material, on grain-size sorting, pore structure and pore distribution. The type, occurrence, spatial and temporal distribution of diagenetic phases are important aspects of the petrophysical character of the deposits. Optical techniques also can serve to visualize pores in two dimensions and might help to identify the occurrence of isolated pores, pore occlusion, and of pocket or blind pores. Apart from detailing the characteristics of 'primary' (sedimentary) pores, also the contribution of 'secondary' pores (e. g., microcracks/microfractures) to matrix porosity might be addressed. All of these aspects of direct observation help in the interpretation of results obtained from laboratory-based petrophysical techniques (see below). They can, furthermore, serve as important pieces of evidence for petrophysical predictions for rocks in areas not yet characterized sedimentologically.

A study by Davies et al. (1991) displays the data which can be obtained through optical methods. It includes information on detrital and diagenetic phases, mudrock microfabrics, total (optical) porosity, extent of diagenetic modifications (e. g., cementation, dissolution, recrystallization), particle size and sorting, and pore structure (e. g., size, shape, internal surface characteristics). Davies et al. (1991) also point out

the discrepancy between porosity values obtained through optical and petrophysical techniques. This discrepancy might be either related to a faulty petrophysical method or to the optical porosity incorporating a large amount of pores not part of the interconnected pore network. Either explanation emphasizes the need to carefully evaluate measurement techniques and data output.

Immersion-Saturation Method

Much basic work to improve and standardize this technique was carried out recently. The technique was and is heavily used by researchers of the Geological Survey of Canada (GSC) in order to obtain porosity data for mudrocks. The methodology employed by researchers from the GSC roots in the claim that complete re-saturation of mudrocks with liquid can be accomplished. This results in obtaining meaningful and accurate values of mudrock porosity, which compare favorably with porosity values obtained by other techniques. The principal references for the immersion-saturation method following the GSC can be found in the publications of Katsube and his various co-workers. The immersion-saturation method was employed earlier, albeit with a different procedural protocol, by Goldstrand et al. (in review) on carbonate rocks from part of the Knox aquifer at the ORR.

principle

The basic tenet of the immersion-saturation method is the determination of the difference in sample weight between the fully saturated state and the dry state of the sample.

methodology

The immersion-saturation method is a simple technique of determining porosity. The porosity type measured is (most likely) effective porosity. Re-saturation of the sample with a liquid (deionized water) is believed to penetrate all of the interconnected pore space (Katsube et al., 1992b; Katsube, 1992; Katsube, pers. comm.).

Effective porosity can be calculated by:

$$\phi_{Ei} = \frac{W_w - W_d}{W_d} \cdot \frac{\rho_r}{\rho_w}$$

ϕ_{Ei} = effective porosity (determined with the Immers. Sat. Method)

ρ_r = bulk density of the rock sample

W_w = sample weight wet

W_d = sample weight dry

ρ_w = bulk density of the pore water.

The density of a rock sample can be obtained using the following equation:

$$V_b = \frac{W_d}{\rho_r}$$

V_b = bulk volume of sample

(this can easily be determined by caliper on a regularly shaped sample [e.g., cylinder]; ∂_r obtained in this way can be used/inserted in above formula to obtain V_b of an irregular shaped sample [same core, etc.]).

Effective porosity can also be calculated from:

$$\phi_{Ei} = V_p / V_b$$

$$V_p = \text{pore volume of sample} = (W_w - W_d) / \partial_w$$

∂_w = bulk density of water

V_b = bulk volume of sample.

The following analytical procedural steps for the immersion-saturation method are taken from Katsube and Scromeda (1991) and Katsube et al. (1992b). For a more detailed outline of the procedural steps see the appendix. Optimum conditions (e. g., drying temperatures, timing; see appendix) were detected by conducting the different parts of the analytical procedure in discrete increments, with sample weighing after each increment.

- 1) *vacuum drying*: drying and de-gassing sample under vacuum at room temperature
- 2) *vacuum saturation*: saturation of the sample: water is added to the vacuum chamber; the sample is left immersed under atmospheric pressure until weighing (W_w);
- 3) *oven drying*: drying of sample (heating at 105°C to 116°C) before weighing (W_d);

possible problems and sources of error

- # re-saturation: is water really penetrating all of the available interconnected pore space?
- # if not, what is the lower limit of pore-throat sizes accessed by re-immersion? are pores sheltered from immersion (and hence not imaged), because of small entry-pore throats?
- # mudrock samples have to be indurated enough, so that they do not disintegrate when immersed in water;
- # immersion liquid used: possible swelling of clay minerals with deionized water; is a brine better? does this (besides less/no clay-mineral swelling) also help prevent sample disintegration?
- # sample shape: the sample shape should conform to a simple geometry, such as a cylinder, for an easy and accurate determination of the dimensions and shape of the sample with a caliper; results of the measurements will form the basis for an accurate determination of the bulk sample volume;

- # drying technique: optimum conditions have to be determined;
- # optimum conditions for each procedural step have to be determined; they might be different for different basinal mudrocks, formations, etc.;
- # surface drying of sample following saturation: is all surface wetness removed, is no pore water removed, is no surface water added?

cost

The immersion-saturation method is by far the least expensive measuring technique covered in this report. The porosity measurements can be carried out at ORNL, as soon as a laboratory is set up and equipped. Equipment has to be purchased and includes as major items: a balance, a vacuum chamber with vacuum pump, and a laboratory oven. Most of it, however, is already available, because earlier porosity studies on carbonates (Goldstrand et al., in review) used a similar procedure. The experiments and measurements need a careful experimenter, but this can be handled with a minimal amount of training. After the experimental set up and procedural steps are established the laboratory should provide a speedy supply of effective porosity data.

evaluation: accuracy and significance of porosity values

The accuracy of the effective porosity values obtained with the immersion-saturation method depends on a) the complete saturation of the sample, and b) the exact determination of the wet (saturated) and dry (oven-dried) sample weight (Melnyk and Skeet, 1986).

The use of a humidity-controlled oven might not be as crucial for the immersion-saturation method than it might be for other methods. Both helium and mercury porosimetry employ drying before pore space is invaded and characterized. Faulty oven-drying can destroy/create porosity and therefore could introduce a significant error to the measurements. The question of what 'types of waters' (pore water, adsorbed water, structural water; see section on drying methods in Appendix I) should be characterized, however, still has to be determined, and the drying technique has to be selected thereafter.

Based on cross examinations on different and same samples using repeated measurements, different measurement methods on same and similar samples, and same measurement methods with altered procedural steps (temperature, duration, etc.), Katsube et al. (1992b) concluded that results can be interpreted *"to generally show relatively good consistency between porosities obtained by different methods, different procedures*

and different laboratories, except when damage is considered to have occurred as a result of repeated measurements" (p. 119). These findings support the contention that the immersion-saturation method provides (reasonably) accurate and reproducible results of effective porosity of mudrocks.

Effective porosity values obtained with the immersion-saturation method characterize the porosity over the extent of the sample. This should always be kept in mind. Other potential samples close by (from the same core) can yield deviating values for effective porosity, even if this core appears perfectly homogeneous. The values obtained *generally* will provide a good estimate of the effective porosity for a larger volume of rock (the size of the volume characterized in this way depends on the homogeneity of the chosen volume). Extrapolation of the *exact* effective porosity values obtained from a small sample volume to a larger rock volume (of variable chosen size), however, should always be treated with caution. This note of caution applies equally to other 'spot sample' methods (i. e., mercury porosimetry, helium porosimetry).

Penetration of water into pores and evacuation of water out of pores is important for the immersion-saturation method. Katsube (1992) reports the results of experiments and claims that water can invade pores smaller than 3 nm. A good correlation with effective porosity values obtained through other methods is interpreted to indicate that water both penetrates and can be evacuated from all nanopores (Katsube, 1992; Katsube et al., 1992b).

Radial Diffusion-Cell Method

principle

The method is based on the radial diffusion of a dissolved tracer in water from a cylindrical reservoir into the surrounding body of rock of finite dimensions.

methodology

A cylindrical sample core of known dimensions is set up with an internal (axial) reservoir of known dimensions (fig. 7). A tracer of known concentration/quantity is injected into the axial reservoir. The original (pre-injection) concentration of this tracer in the sample core is known, and the change in concentration within the reservoir is monitored. Solute migration within the sealed cylindrical core sample is possible only by matrix (molecular) diffusion.

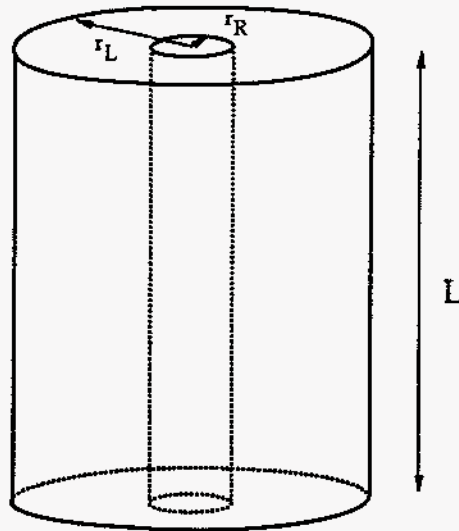


fig. 7: Typical diffusion cell used for the effective porosity measurement with the radial diffusion-cell method; L = length of the full core section used (typically 70 cm), r_L = full core radius, r_R = radius of the central reservoir

(from Novakowski and van der Kamp, unpubl. manuscript).

The effective porosity can be determined with the radial diffusion-cell method in different ways:

1) *directly*

(Novakowski and van der Kamp, unpubl. manuscript)

$$V_M = [V_R / C_{DR(\infty)}] \cdot V_R$$

V_M = volume of water present in the core sample

V_R = volume of the reservoir

$C_{DR(\infty)}$ = dimensionless residence concentration at equilibrium: C_R/C_0

(C_R = reservoir concentration; C_0 = initial reservoir concentration),

then:

$$\phi_{Ew} = V_M / \pi (r_L^2 - r_R^2) L$$

ϕ_{Ew} = (effective) porosity determined with the Radial Diffusion Method

L = length of core sample

r_L = radius of core sample

r_R = radius of reservoir

V_M = (s. above) value calculated with formula above;

2) *with use of the semi-quantitative model*

(Novakowski and van der Kamp, unpubl. manuscript:

ϕ_{Ew} will be calculated from β_1)

$$\beta_1 = C_{DR(\infty)} [r_{DL}^2 - 1] / 2 [1 - C_{DR(\infty)}]$$

β_1 = dimensionless mixing coefficient of the reservoir: $V_R / (R \cdot \gamma_R \cdot r_R)$

V_R = volume of reservoir

γ_R = cross sectional area through which diffusion occurs

[porosity · surface area of reservoir]

r_R = radius of reservoir

R = retardation factor

r_{DL} = dimensionless radius of the core sample: r_L / r_R

$C_{DR(\infty)}$ = dimensionless residence concentration at equilibrium;

3) *through effective pore volume with initial solute concentration known*

(van der Kamp et al., unpubl. manuscript)

$$\phi_{Ew} = V_{pe} / V_b$$

V_{pe} = effective pore volume: $V_{pe} = M_{xn} / C_{xn} - C_{x0}$

C_{x0} = initial pore water concentration of constituent (tracer) x

M_{xn} = total mass of constituent (tracer) x added to reservoir

C_{xn} = pore water concentration of constituent (tracer) x at time n

V_b = total (bulk) volume of the core sample;

note: there appear to be different values for effective porosity depending on the tracer used. Van der Kamp et al. (manuscript) attribute this to a variety of possible effects, such as ion exclusion, excluded pores, bound water, cation and anion exchange, precipitation, and dissolution.

possible problems and sources of error

- # the proposed technique (laboratory and field scale) is not yet tested and applied;
- # ensuring sample and pore space saturation: samples have to be sealed when retrieved; they have to come from the saturated groundwater-zone;
- # experimental design: a combination of design parameters has to be chosen which will ensure that very reliable results are obtainable in the shortest amount of time;
- # experimental set up: the manufactured equipment must be good enough to not interfere with experiments/measurements;
- # tracer: must exhibit a conservative behavior within sedimentary rock environments (i.e., no chemical interaction with the rock body, no decay or degradation);
- # drilling of reservoir: avoiding clogging of entrance pores by drilling 'cake'; clean up needed without creation of its own porosity (damage of sample core);
- # measurement of dimensions (radii/diameters, sample lengths, volumes): this is probably not quite as influential as for the other laboratory porosity-measurement techniques;
- # basic material has to be tested for use in experimental set up;
- # isolation of core: how snugly has the silicon jacket (or other material) to fit?
- # question of waters: pore water, adsorbed water, and structural water (part of structure of clay minerals); diffusion occurs within water of interconnected pore space; pore water with free water diffusion coefficient; how important is adsorbed water? should this also be characterized? diffusion coefficient for the latter is not the free water diffusion coefficient;
- # minimizing storage time following core retrieval to prevent fluid loss;
- # cleanliness during sample preparation and measurements;
- # influence of changing temperature and pressure: from original site of sample to the laboratory (any influence on pore-water chemistry or porosity?);
- # determination of initial concentration of tracer in pore water (prior to injection of test-tracer amount), and accuracy of it;
- # different effective porosities for different constituents/tracers: ensure to use a proven conservative tracer; compare data only with data obtained with the same tracer (then: what about data obtained with different laboratory methods?).

cost

There are no fixed costs at present. Service companies do not provide porosity measurements based on the radial diffusion-cell method, because this method is new and as of yet untested. The experimental set up appears to be simple enough that experiments can be carried out at ORNL (laboratory measurements only; field experiments are a completely different aspect and are not dealt with in this report). Laboratory space is necessary to carry out experiments undisturbed. Furthermore, raw material for manufacturing of equipment (reusable), time of technician to manufacture this equipment (either on-site or off-site), and equipment ordered from catalogues (reusable) has to be paid for. A pilot study is underway to investigate, among many other aspects, the experimental set up of this porosity-measurement technique, the equipment needed, and the performance of the equipment.

evaluation: accuracy and significance of porosity values

It is claimed that an accurate determination of effective porosity can be performed (Novakowski and van der Kamp, unpubl. manuscript; van der Kamp et al., unpubl. manuscript). The technique (experimental set up and calculations) is untested as of today, except for experiments carried out on Pleistocene glacial clay deposits. A test of the technique and its application to fine-grained clastic sedimentary rocks seems warranted. The technique is attractive because of its simplicity, the apparent low costs, and the claim of an accurate determination of effective porosity.

Effective porosity values obtained with the radial diffusion-cell method provide an integration over a larger sample volume when compared to the 'spot-sample' effective porosity values obtained with the immersion-saturation method, the helium-porosimetry or the mercury-porosimetry methods. Possible problems arising with this technique might involve the degree of sample heterogeneity, the minimum size of the sample required for experiments, and the apparently deviating effective porosity values obtained with different tracers (van der Kamp et al., unpubl. manuscript). Furthermore, the availability of suitable core material (especially the prerequisite of saturation) is an important factor in influencing the accuracy of the obtained effective porosity values.

Mercury Porosimetry

principle

Forceful injection of a non-wetting liquid (mercury) into a sample in discrete pressure steps. The required pressures to force mercury into the sample correspond to the size of openings (pore throats, pores) within the sample. The injection-pressure steps and the discrete volumes of intruded mercury are tabulated.

methodology

An excellent summary of the mercury-porosimetry method, its applications and the basic methodology is provided by Kopaska-Merkel (1991). This account provides the background information for much of the following synopsis. Other pertinent sources are Rootare (1970), Wardlaw (1976), Kopaska-Merkel (1988), Amthor et al. (1988), and Wardlaw et al. (1988).

Mercury porosimetry is carried out with the use of the mercury porosimeter. Only a small sample is required for analysis. Mercury, a non-wetting liquid, does not invade pore space unless pressure is provided. The mercury porosimeter provides the means for controlled mercury intrusion with varying intrusion pressures. With each increasing pressure step successively smaller pore throats are accessed by mercury. Mercury porosimetry finally provides capillary-pressure curves that plot the measured amount of intruded mercury (capacitance) versus measured injection pressure (fig. 8). The amount of intruded mercury can be converted to volume of mercury, and the injection pressure can be converted to diameter of pore throats (with the Washburn Equation). Mercury porosimetry, therefore, provides quantitative information on the distribution of pore-throat sizes. The sizes of pore throats are important, because they control access to larger pores. Pores of the same size might be accessed through throats of different sizes, but mercury enters the pore space only after a certain injection pressure is reached (fig. 9). The pore space with the larger sized pore throat will be accessed earlier than the pore space of equal size but with a smaller entry-pore throat (fig. 9).

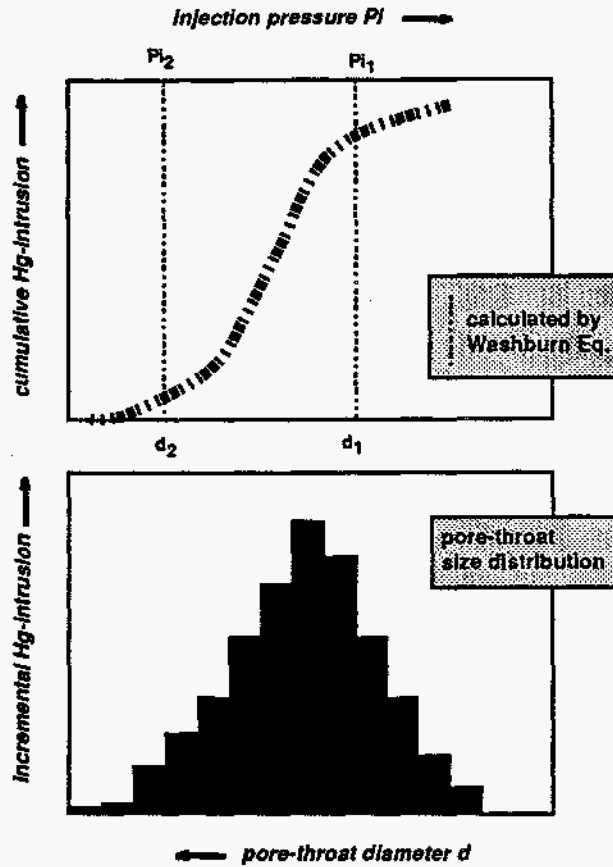


fig. 8: Capillary pressure curves, plotting the measured injection pressure and/or the calculated pore-throat diameter versus the amount/ volume of intruded mercury; the upper curve is a cumulative intrusion curve, where the total amount of intruded mercury can be read at the right side end of the curve; the lower plot is an incremental intrusion curve showing the amount/ volume of mercury intruded at the chosen consecutive pressure steps; arrows point toward higher values; note the pore-size distribution obtained in this way: it is unimodal which is typical for mudrocks (Katsube, 1992; Katsube and Best, 1992; Katsube and Issler, 1993); note that larger pore throats are invaded earlier at lower injection pressures.

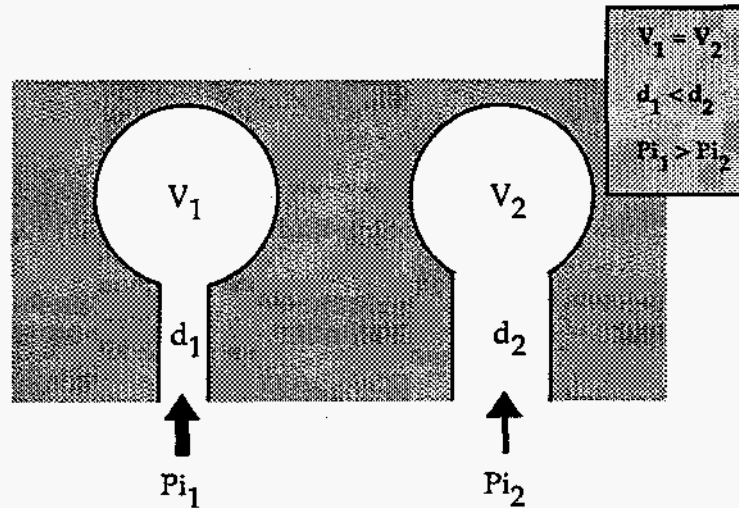


fig. 9: Illustration of the importance of pore throats for controlling access to pores; pores of the same size ($V =$ volume) are accessed by pore throats of different sizes ($d =$ diameter); mercury enters the pore throat only after a large enough injection pressure ($= P_i$) is reached to force mercury through the pore throat; the pore accessed by the larger pore throat will be invaded earlier at a lower injection pressure than the pore of equal size but with a smaller entry-pore throat.

Washburn Equation

The Washburn Equation relates the amount of pressure required to force mercury into pores to the pore-size diameter greater or equal to d (e. g., Katsube and Issler, 1993). For cylindrical pore shapes, assumed to characterize the pore system in mudrocks (Katsube and Issler, 1993),

$$d = (-4\gamma \cos\theta) / p$$

d = throat size

γ = interfacial (surface) tension (for Hg/vacuum = 0.48 N/m)

θ = contact angle (for Hg/vacuum = 30°)

p = intrusion pressure (psia).

With the help of the Washburn Equation a corresponding pore-throat size can always be calculated from a measured injection pressure.

Determination of effective porosity

Katsube and Issler (1993) provide an outline of the basic procedural steps to determine effective porosity based on mercury porosimetry. This is the methodology employed by the Geological Survey of Canada for its studies on mudrock-dominated basinal sections.

The mercury-injection pressure is increased successively in discrete steps (e. g., 56 steps from 0.14 to 420 MPa), equally dividing the available pressure range provided by the apparatus. Following each step, time is allotted for equilibration of the system, that is there is no change in volume of mercury taken up by the sample with time. Experience shows that this equilibrium time is about 40 s for high pressure steps ($p > 0.7$ MPa) and 10 s for low pressure steps ($p < 0.7$ MPa) for fine-grained sedimentary rocks. For each pressure step the volume of mercury intruding the sample is noted.

According to Katsube and Issler (1993), each discrete pressure step corresponds to a certain pore size (more correctly: to a certain pore-throat size), based on the Washburn Equation, and the volume of mercury intruding the sample at each pressure step can be converted into the porosity for that pore size (more correctly: for that pore-throat size and for pores accessed through pore throats of that size).

Partial porosity ϕ_a refers to the porosity contributed by each discrete pore-size range (Katsube and Issler, 1993). It is calculated for each pore-size range by using the volume of the intruded mercury at this size range and the bulk volume of the sample. The sum of all partial porosities gives the effective porosity ϕ_{Em} as determined by mercury porosimetry. Katsube and Issler (1993) split ϕ_{Em} into a ϕ_{Em1} (sum of all ϕ_a from pore sizes $\leq 10 \mu\text{m}$) and a ϕ_{Em2} (sum of all ϕ_a from pore sizes $\leq 250 \mu\text{m}$). The reason for this split is that ϕ_{Em2} might contain measurement errors (e.g., errors induced by the space left between sample and penetrometer wall) more likely than ϕ_{Em1} , which is more likely to reflect the effective porosity of the sample.

Alternatively, the effective porosity ϕ_{Em} can be determined by using the cumulative volume of intruded mercury (obtained at the conclusion of the experiment following the application of highest pressure) and converting this cumulative volume to porosity (i.e., side-stepping the calculation of partial porosities ϕ_a and summing these up) by maximum cumulative intrusion volume divided by bulk sample volume (e. g., Amthor et al., 1988):

$$\phi_{Em} = V_{Hgintr.} / V_b$$

$V_{Hgintr.}$ = max. cum.mulative intruded volume of mercury

V_b = bulk sample volume.

The bulk-sample volume can be determined by caliper or any other appropriate method. Melas and Friedman (1992) use a method employing the mercury porosimeter directly:

$$V_b = V_{pen} - V_{Hg}$$

V_{pen} = volume of penetrometer (to be determined by calibration runs)

V_{Hg} = volume of mercury; = M_{Hg} / D_{Hg}

D_{Hg} = density of mercury

M_{Hg} = mass of mercury; = $M_1 - M_2$

M_1 = mass (penetrometer+sample+mercury*)

M_2 = mass (penetrometer+sample)

* as a non-wetting liquid mercury will/should not penetrate pore space without applied pressure (even pores at the sample surface).

For a more accurate determination of effective porosity of a mudrock based on mercury porosimetry, Katsube (1992) suggests the determination of 'missing porosity' $\Delta\phi$ (fig. 10). $\Delta\phi$ is defined as that part of the effective porosity of a sample which cannot be characterized by mercury porosimetry, because of equipment limitations. The mercury porosimeter is limited at the higher pressure steps. The smallest sized nanopore throats might therefore not be accessed with the available pressures. The *corrected* (not measured!) effective porosity, as determined from mercury-injection data, is:

$$\phi_{Emc} = \phi_{Em} + \Delta\phi$$

ϕ_{Emc} = corrected effective porosity based on mercury porosimetry

ϕ_{Em} = effective porosity based on mercury porosimetry

$\Delta\phi$ = 'missing porosity'.

The 'missing porosity' is estimated by fitting a normal distribution curve to the nanopore (-throat) size distribution (fig. 10), assuming that the nanopore (-throat) sizes exhibit an unimodal distribution (Katsube, 1992). The extent of the curve-fitting (i. e., the size of $\Delta\phi$) depends directly on the analytical capabilities of the mercury porosimeter used.

The computer attached to the mercury porosimeter provides a series of data manipulation steps, and can provide a variety of outputs based on data analysis. Some types of output offered include: incremental and cumulative pore-throat sizes, average and median pore-throat size, apparent skeletal density, and others.

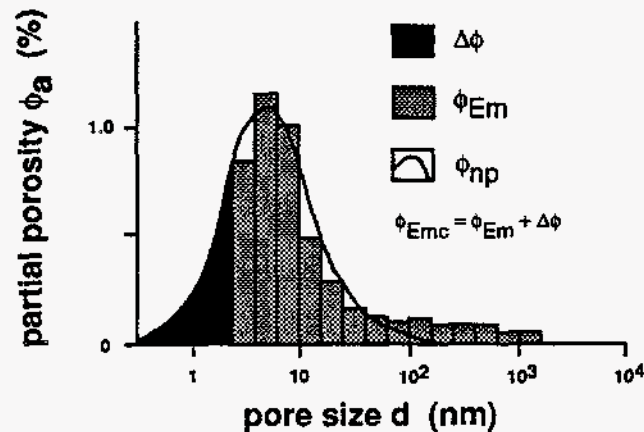


fig 10: Unimodal distribution of nanopores (0.3 - 60 nm) characteristic of tight mudrocks; $\Delta\phi$ = 'missing porosity', ϕ_{np} = nanopore porosity, ϕ_{Em} = effective porosity based on mercury porosimetry, ϕ_{Emc} = corrected effective porosity based on mercury porosimetry (based on Katsube, 1992; from Katsube and Williamson, 1994).

Pore-throat sizes

The determination of pore-throat sizes and their distribution is an important aspect of mercury porosimetry with regard to diffusion as a transport process. The pore throats are the smallest and narrowest pathways within the interconnected pore network of a mudrock. Material transport by diffusion is accomplished within this interconnected pore network. Therefore, the physical constraints provided by the narrowest pathways can significantly impact diffusion as a transport mechanism by influencing diffusion rate. Furthermore, the pore throats can put a size limit on diffusion by denying access to the matrix-pore space to contaminant species too large for the dimensions of the pore throats.

possible problems and sources of error

- # inexperienced laboratory technicians;
- # 'philosophy' of the service company/laboratory;
- # temperature control: mercury expands/contracts with changing temperature;
- # size of penetrometer (sample chamber): more than 5% of the penetrometer-stem volume should be occupied by the sample during experiments;
- # accurate determination of volume of penetrometer: this necessitates the very accurate calibration of the penetrometer (series of calibration runs; recommended accuracy = 0.001 cm^3);
- # correction for differential compression (due to exposure to high pressures) and differential expansion (due to temperature increase at high pressures) by use of 'blank analyses';
- # lower detection limit of equipment: smallest available nanopores might not be characterized (and therefore be neglected);
- # neglect of 'missing' porosity; it is imperative to determine 'missing' porosity in order to obtain meaningful effective porosity values with mercury porosimetry (Katsube, 1992); the extent of uncharacterized pore space depends on the capabilities of the mercury porosimeter;
- # ensuring that equilibrium conditions have been reached for each step of mercury injection (especially important for the tortuous pore system of mudrocks);
- # selection of appropriate values for contact angle and mercury-surface tension (to be used in the Washburn Equation);
- # pore-shape concept: cylindrical vs. sheet-like pore shapes; is chosen pore-shape concept really closely resembling the pore shape in mudrocks?
- # determination of sample bulk volume;
- # for the ORR: are there fluids present in the rocks which are wetting or partially wetting (i.e., wetting phases spread out on and covering the pore walls which do not 'bead up' like non-wetting phases)?
- # presence of continuous open fractures;
- # development of induced microfractures at higher injection pressures?
- # boundary effect: enhanced access of mercury to pores and pore throats exposed at the sample margin (rapid intrusion of mercury at lower injection pressures);
- # shielding effect: small pore throats near the sample margin might shield larger pore throats within sample from mercury intrusion until the marginal small pores are intruded;

apparent mercury intrusion: caused by either compression of mercury, or by intrusion of mercury into microscopic crevices of the penetrometer.

cost

Mercury porosimetry is a very sophisticated technique. Handling of mercury, furthermore, is potentially hazardous. The method, therefore, should be performed at specialized service companies/laboratories with experienced technicians. Projected costs are ca. \$400/sample (J. Katsube, pers. comm.). Prices might be variable and negotiable, though, and a survey of commercial service companies should be conducted. The ORNL-Metals & Ceramics Division has state-of-the-art equipment and information about analysis costs should be obtained. Former supervisor Dr. L. Fuller would charge \$100/sample, but the laboratory capacity and equipment time is severely limited because of ongoing research; new supervisor Dr. T. Burchell would charge more (approaching \$400/sample), but with no restriction on sample number (it is important to investigate, however, whether expertise in handling of mudrocks already exists at the Metals & Ceramics Division).

evaluation: accuracy and significance of porosity values

Detailed evaluation of machine error was not carried out for the Autopore II 9220. Calculations for a precursor model (Pore Sizer 9305) yielded a measurement accuracy for volume of intruded mercury of $\pm 0.0015 \text{ cm}^3$ (Kopaska-Merkel, 1988). The error for the Autopore II 9220 should be smaller, but certainly not larger, than this value (Kopaska-Merkel, 1991).

The accuracy of porosity determination with mercury porosimetry will be increased substantially by estimation and incorporation of 'missing' porosity values (Katsube, 1992). This 'missing porosity' depends solely on the capacity of the porosimeter used: the greater the capacity of the mercury porosimeter, the more complete should be the characterization of the interconnected pore space within a sample. Calculation of the 'missing porosity' requires a curve-fitting procedure (as described in Katsube, 1992) using the acquired incremental capillary-pressure curve. The resulting estimated effective porosity (i.e., the sum of the statistically estimated 'missing porosity' based on the incremental capillary-pressure curve and the total intruded volume of mercury based on the cumulative capillary-pressure curve) compares favorably with effective porosity values obtained with the immersion-saturation method (Katsube, 1992; Katsube et al., 1992b).

The derivation of mudrock pore-throat sizes and their distribution is an additional plus of mercury porosimetry. The small pore-throat sizes might impose physical constraints on diffusion as a transport mechanism. They might severely influence diffusion rate and might cause the exclusion of certain contaminant species from invading the matrix-pore space because of their size.

Helium Porosimetry

principle

Based on the Boyle-Mariotte Law: $p \times V = \text{const.}$ ($T = \text{const.}$). A change in volume V or pressure p causes a commensurate change in pressure or volume, given that the temperature T remains constant. Important for helium porosimetry: an increase in available volume causes the gas (helium) to expand resulting in the decrease in gas pressure.

methodology

In principle there are two different ways to determine porosity with expanding helium (much detailed information is contained in Luffel and Howard, 1988, and American Petroleum Institute, 1960):

1) helium expands isothermally into a core plug (rubber-sealed on the sides and ends, with low sleeve pressure) from a gas reservoir of known reference volume and helium pressure, until equilibrium pressure is reached. From the new gas pressure V_p (pore volume) can be calculated. V_b (bulk volume) is then determined by either caliper (measuring the dimensions of the core plug) or by immersion of the core plug in mercury (either measuring volume of mercury displaced from a pycnometer, or measuring the buoyant force).

Derivation of porosity

$$\phi_{Eg} = V_p / V_{bimm.}$$

ϕ_{Eg} = effective porosity as determined by He-porosimetry
 $V_{bimm.}$ = bulk volume measured through Hg-immersion
 V_p = pore volume;

2) the core plug is placed into a steel chamber of known volume. Helium isothermally expands into the chamber from a reservoir of known volume and pressure until equilibrium pressure is reached. From the new gas pressure V_g (grain volume) can be calculated. This method is significantly faster than method 1, because helium can permeate over a larger exposed surface area.

If V_p was measured directly (s. method 1):

$$\phi_{Eg} = V_p / (V_p + V_g)$$

also: $V_p = V_b - V_g$

$$\phi_{Eg} = (V_{bimm.} - V_g) / V_{bimm.}$$

V_g = grain volume

V_b = bulk sample volume

V_b : $V_{bc} = V_{bimm.} = (V_p + V_g)$; these all should correspond;

V_{bc} = bulk volume measured with caliper.

CORAL - experimental set up

(based predominantly on Randolph, 1983; Soeder and Randolph, 1987; Soeder, 1988; Soeder and Chowdiah, 1990; *note*: specific information on sample-preparation techniques [for mudrocks] are contained in Soeder, 1988: 118; Soeder and Chowdiah, 1990: 422).

CORAL stands for computer-operated rock analysis laboratory. It provides high precision core analysis and is housed at the Institute of Gas Technology (IGT) in Chicago, Illinois. Measurement of porosity is based on the methods outlined above, using a gas (He, N). Listed advantages of the CORAL experimental set up include:

- # higher precision than other helium porosimeters;
- # electronic data acquisition, electronic tabulation and interpretation;
- # *stable temperature control*: the entire system is contained within an isothermal chamber (temperature stability to within 0.03 °C, at a normal operating temperature of 355 °K [81.85 °C = machine operating temperature?]);
- # gas-flow rates (min. of 10^{-6} cm³/s) are accurately monitored;
- # four simultaneous measurements are possible;
- # application of confining hydrostatic pressure to simulate "reservoir" conditions (max. 69 MPa = 10 000 psi).

CORAL is at its best when a suite of parameters is determined for the samples. Measuring only one property (e. g., porosity) is less advantageous, because 8-12 hours are required to obtain temperature stability following sample changes. A highly simplified diagram of the general set up for porosity (and permeability) determination are given in fig. 11.

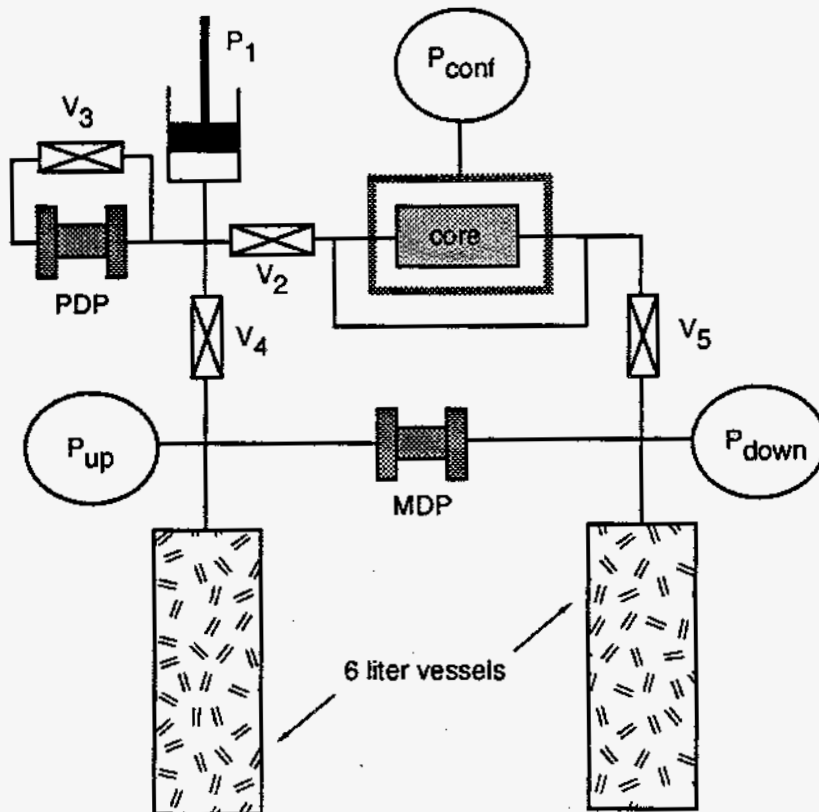


fig. 11: Sketch of analytical set up at CORAL used for the determination of effective porosity at the Institute of Gas Technology at Chicago (from Randolph, 1983).

possible problems and sources of error

(summarized from Luffel and Howard, 1988)

Aspects which have to be considered during a) sampling, b) sample preparation, and c) experiments/measurements:

- # condition of the core plug (cleanliness; approaching shape of cylinder [length measurements with caliper at different positions should be within 0.003 cm/0.001 in.; top and bottom ends should be within 0.1° of perpendicular to core-plug axis], edges should not be eroded, not be chipped, etc.): important especially for caliper measurements (core plug should be of sufficient size/dimensions);
- # a general problem which affects samples used for any of the petrophysical measurement techniques: evaluation of the possibility of microfracturing during a) coring and b) return of samples from depth to surface;
- # V_p determination (rubber-sleeve method): core ends should be plane and smooth and perpendicular to core-plug axis; rubber sleeve has to conform to core-plug grain texture, and should have just the right amount of sleeve pressure ('pressing' rubber sleeve onto core plug); allow enough time to reach pressure equilibrium;
- # exact calibration of reference volume, dead volume, and pressure gauge;
- # ability to maintain constant temperature around measurement apparatus ($<0.3^\circ\text{C}/<0.5^\circ\text{F}$);
- # adsorption of gas on grain surfaces;
- # measurement of V_b with mercury immersion: possibility of trapped air at the core plug/mercury-interface (remember: mercury is a non-wetting liquid); possible measurement errors when determining amount of mercury displaced (in pycnometer) or weighing buoyant force;
- # measurement of V_b with caliper: the more deviant the core plug is from an exact cylinder, the higher the inaccuracy in V_b will be; fractured and/or chipped samples are not suited for caliper measurement at all;
- # larger volume core plugs yield more accurate porosity values;
- # proper drying method (see appropriate chapter below);
- # periodic repeat tests (on 10-20% of the samples);
- # cross check: V_{bc} should very closely match V_b obtained through adding of measured $V_p + V_g$;
- # inexperienced laboratory technicians;
- # 'philosophy' of the service company/laboratory.

cost

Helium porosimetry is a very sophisticated technique. It has to be carried out at service companies. CORAL and its advantages are provided at the Institute of Gas Technology (IGT) in Chicago. Current cost estimates per sample are not provided by IGT. According to the latest information from IGT (Misra, pers. comm.; Chowdiah, pers. comm.), CORAL is being disassembled and moved to a new location. Running of ORR-samples will necessitate to assemble CORAL again, which would be figured into the overall costs (but wouldn't CORAL be assembled anyway?). The final costs also depend on the number of samples to be analyzed: the more samples the cheaper the costs per sample. Other service companies/laboratories charge ca. \$30/sample (J. Katsube, pers. comm.) using helium porosimetry, but probably do not follow the analytical guidelines set forth for CORAL.

evaluation: accuracy and significance of porosity values

It is claimed that (effective) porosity can be measured with an accuracy of $\pm 2.0\%$ (Soeder, 1988). Because it is more advantageous to measure several petrophysical parameters concurrently with CORAL, it appears to be appropriate to add other measurements than (effective) porosity to the experiments. The measurement of permeability is an obvious choice, given that a) the costs are not inflated, and b) that core plugs were obtained horizontally (that means parallel to either bedding or stratification). As was the case for mercury porosimetry and for the immersion-saturation method, the measured effective porosity obtained by helium porosimetry characterizes a sample volume the size of a standard core plug, or the size of a disk cut from the plug.

Issler and Katsube (1994) claim that helium porosimetry values are more reflective of the total interconnected pore space (effective porosity) than values obtained by mercury porosimetry. According to these authors, then, helium porosimetry should be emphasized over mercury porosimetry. Values for effective porosity published by workers of the Geological Survey of Canada (Katsube and co-workers) involved the type of helium porosimetry available at commercial service companies. It has to be investigated in how far these service companies supply the technological sophistication obtained by CORAL. The final decision between CORAL and a service company has to be based on the costs involved and on an independent investigation into the capabilities of helium porosimeters (and philosophy) provided by service companies. Despite these considerations, values of effective porosity obtained by helium porosimetry are generally considered as "good numbers."

Recommendations

Of general importance for the samples shipped out to commercial or other laboratories (i.e., core-analysis procedures not performed in personam) is:

a) a shared responsibility in the progress of the analyses (with quality control, based on every aspect available*), and

b) a close contact between the principal investigator and the laboratory carrying out the measurements (Luffel and Howard, 1988). Luffel and Howard (1988), furthermore, list a series of recommendations which should be fulfilled by any analytical laboratory:

- # repeat tests;
- # checking the consistency of results;
- # availability of all individual V_p , V_g , and V_b measurements;
- # reporting of caliper measurements;
- # reporting of dry weights;
- # reporting of all data from repeat measurements;
- # reporting of all anomalous results;
- # access to a laboratory diary;

(*repeat tests on 10-20% of the samples; comparison of obtained porosity values to other available data [permeability, grain density, lithology]; consistency of data; comparison to auxiliary data [wireline logs, familiarity with rocks]) (Luffel and Howard, 1988).

The most promising techniques for measurement of effective porosity of mudrocks appear to be:

- 1) immersion-saturation method
- 2) radial diffusion-cell method
- 3) helium porosimetry
- 4) mercury porosimetry.

The accuracy of the different techniques might be variable. Certain researchers emphasize one technique, while others dismiss the same. Much research within this area of petrophysics is being conducted at the moment, the state of the art seems to be 'in flux' (based on readings and especially on conversations with researchers in academia, petroleum companies, petrophysical service companies, and Geological Surveys).

Should the immersion-saturation method perform accurately, it would be by far the most attractive technique, because it is relatively simple and inexpensive. It has to be evaluated, however, as to its suitability for ORR-mudrocks (e. g., the possibility of sample disintegration).

The radial diffusion-cell method appears to be promising. As soon as the experimental set up is established, it should be a relatively simple and inexpensive technique. In order to establish diffusion cells it needs, however, cores of a "certain" length and diameter which must have been sealed upon recovery. The other three methods (1, 3, 4), in contrast, can work with much less sample material. The radial diffusion-cell method has not yet been tested and verified. Experiments to evaluate set up/design, experimental procedures and accuracy are needed. It also has to be investigated whether ORR-mudrocks are useful for this method. The method, furthermore, provides effective porosity integrated over a larger volume (no chips, no plugs, but core of decimeter length) in contrast to the "spot" measurements of the other methods.

Methods 1 and 2 are comparatively simple and straightforward enough to be set up at ORNL. Methods 3 and 4 are sophisticated and very complicated. Service companies are needed to conduct the analyses. Therefore, these methods are more expensive. It is important to check and "control" the service laboratories before and during analyses.

Helium porosimetry generally is cheaper than mercury porosimetry. Helium porosimetry provides effective porosity values, whereas mercury porosimetry provides pore-throat sizes and size distribution. The latter needs corrections for obtaining accurate effective porosity values (see work by Katsube, Issler). The extent of the corrections depends on the capabilities of the mercury porosimeter used in the experiments.

A pilot study is necessary to:

- a) test laboratory set ups (1, 2),
- b) test techniques (1, 2),
- c) establish technique (2),
- d) generate numbers for a cross-comparison (1, 2, 3, 4), and sensitivity-interpretation assessment. Eventually, the pilot study should be expanded to a larger, systematic and comprehensive effective porosity study of a chosen mudrock-dominated stratigraphic unit on the ORR.

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Appendix I: More detailed Outline of Analytical Procedures

Samples for effective porosity measurement are retrieved by a) drilling of core plugs from split core intervals, b) slicing of discs from the core plugs for the various measurement (fig. 12). This is the standard procedure for the immersion-saturation method, helium porosimetry, and mercury porosimetry. The radial diffusion-cell method, on the other hand, uses sections of whole cores (fig. 7). Alternatively, also irregularly shaped samples can be used for the immersion-saturation method, helium porosimetry, and mercury porosimetry.

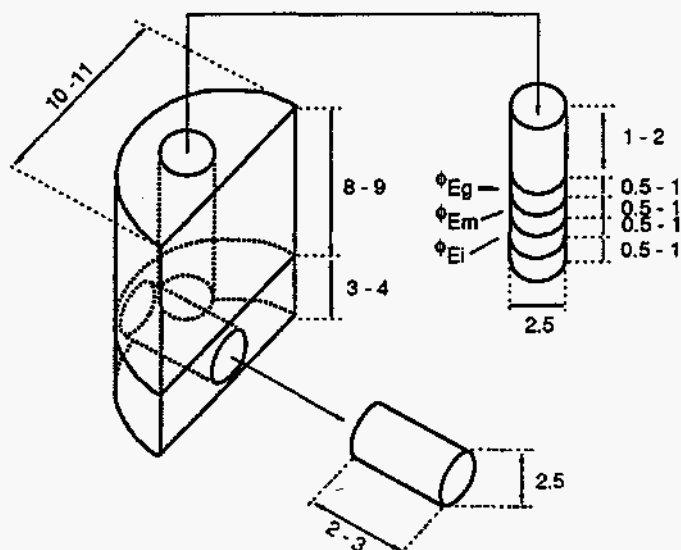


fig. 12: Example of sample retrieval for different kinds of petrophysical measurements; standard core plugs are drilled from split cores, the core plugs are then cut to provide the samples for various measurements (dimensions are in cm); porosity measurements using mercury porosimetry (ϕ_{Em}), helium porosimetry (ϕ_{Eg}), and the immersion-saturation method (ϕ_{Ei}) commonly use disks up to 1 cm thick and about 2.5 cm in diameter (from Katsube et al., 1991).

Immersion-Saturation Method

(from Katsube and Scromeda, 1991; Katsube et al., 1992b; optimum durations from Katsube et al., 1992b)

1) Vacuum Drying

- # drying the sample at room temperature (sample is "air dried");
- # placing the sample into glass beaker with tweezers;
- # placing beaker into vacuum chamber;
- # applying vacuum at 760 mm Hg (duration: period chosen arbitrary);
- # sample is weighed (sensitivity of balance: ± 0.1 mg);
- # sample is returned for (a) period(s) of additional vacuum drying
(period durations are variable), followed by weighing; this procedure is repeated until a constant weight is reached (duration: suggested **optimum total vacuum-drying time = 735 min**);

question: selection of period durations: can we go with suggested (total) optimum duration from the onset to shorten experiments? minimize considerably the repeat periods? (this holds also for the other procedural steps).

2) Vacuum Saturation

- # applying vacuum for de-gassing of sample (duration: 15 min)
- # saturation of sample: introducing saturation liquid (deionized and distilled water) to the vacuum chamber (duration: until vacuum chamber is filled with liquid);
- # applying vacuum for de-gassing of sample (duration: 15 min);
- # sample left under atmospheric pressure (duration: variable, suggested period 1-60 min);
- # weighing of sample: removal of the sample from beaker, outer area is dried with kimwipe (no sheen left on the sample surface indicative of moisture films); note: keep this drying process consistent from sample to sample!
- # sample is returned to beaker, immersed under atmospheric pressure for (a) period(s) (variable min), and weighing procedure is repeated; this is to be continued until a *constant weight* is obtained (indicating *full saturation*: W_w); (suggested **optimum total saturation time = 285 min**).

3) Oven Drying

(following completed saturation)

- # sample placed in a beaker;
- # heating in oven at 105-116°C; note: experiments are ongoing with different temperatures and durations; especially temperature is in question (duration: variable, suggested period 30-? min);
- # cooling the sample in a desiccator (duration: variable, suggested period 7-20 min; longer cooling periods required for longer heating periods; question: what decides the duration of the cooling period?);
- # weighing of the specimen;
- # reheating, drying (duration: variable periods), and weighing until a *constant weight* is obtained (indicating *complete dryness*: W_d);
(duration: optimum total oven-drying time = 690 min [at 116°C])

note: minimize deviations from the procedural steps to ensure consistency in measurements!

This procedural outline is employed for step-wise analysis, providing a multitude of intermediate data before complete vacuum drying, water saturation, and oven drying are reached. This data will enable to calculate the degree of saturation for each incremental analysis step, and to plot saturation curves.

Degree of Saturation S_r : to be computed after each increment of treatment and weighing

$$S_r = \Delta W_r / (W_w - W_d)$$

ΔW_r = weight of the water content at any given time: $= (W_r - W_d)$

W_r = weight of sample at any given time

W_w = wet sample weight (constant weight, considered fully saturated)

W_d = dry sample weight (constant weight, considered completely dried)

$(W_w - W_d)$ = weight of the maximum water content.

S_r should be calculated for each measuring step (weighing, obtaining W_r) for all three parts of the experimental procedure. This enables to plot S_r versus time, giving

- a) vacuum-drying curve (vacuum drying of the air dried sample),
- b) saturating curve (saturation under atmospheric pressure), and
- c) oven-drying curve

for each studied sample (fig. 13, from Katsube and Scromeda, 1991).

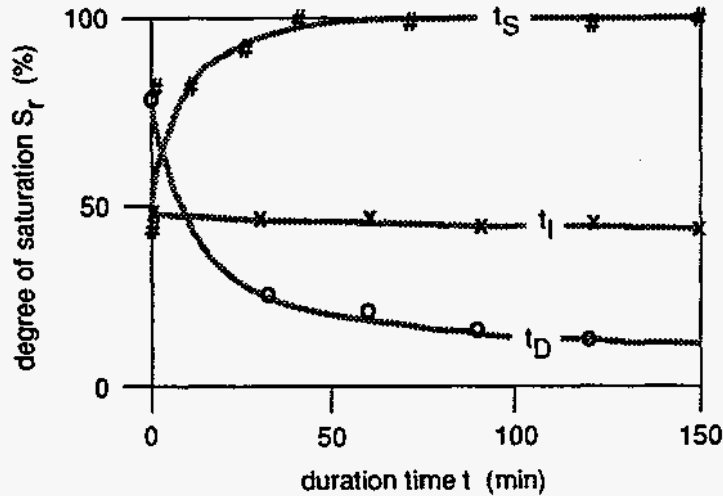


fig. 13: Plotting degree of saturation (S_r) versus time (t); t_s represents the saturation curve (#), t_D the oven-drying curve (o), and t_l the vacuum-drying curve (x) (from Katsube and Scromeda, 1991).

Melnyk and Skeet (1986) use a different analytical procedure. According to these authors the sample is dried in a vacuum chamber for 24-48 hrs, equilibrated to laboratory air for 60 min (no condensation of water into pore space?), and then weighed. This procedure is to be repeated until a constant (± 0.5 mg) weight is obtained (W_d , is not obtained by/after oven-drying!). This is followed by de-gassing of the sample under vacuum, and immersion of the sample in de-gassed deionized water within the vacuum cell. W_s (water-saturated surface-dry weight) is obtained through the establishment of drying curves, and W_a (submerged sample weight) is obtained using a buoyancy method. Effective porosity, then, is determined according to the equations provided (Melnyk and Skeet, 1986, p. 1069). An interesting discussion on obtaining the 'water-saturated but surface dry weight' from drying curves is included.

Helium Porosimetry (via CORAL)

(the most detailed description of the experimental set up can be found in Randolph, 1983; details on sample preparation specifically for mudrocks are outlined by Soeder, 1988, and Soeder and Chowdiah, 1990; the following summary is based on the mentioned references)

1) Sample Preparation:

- # horizontal plug drilled from a core (horizontal, i.e., parallel to stratification/bedding, is necessary for permeability determination, but is not as important for porosity determination); coolant: tap water; diamond coring bit diameter: 1.5 in (3.8 cm); plug: 1 in (2.5 cm) in diameter and ca. 5-6 cm in length;
- # trimming ends of plug flat (thin diamond blade of a metallurgical saw); squaring off of ends with light sanding (400-grit carborundum paper);
- # caliper measurement of dimensions of core plug;
- # weighing of core plug.

2) Oven Drying

- # in controlled-relative-humidity oven, with intermittent weighing (duration: variable, until weight of sample is constant, temperature: 60°C [140°F], relative humidity: 45%);
- # dry weight: weighing of sample under a tared inverted beaker (after weight stabilization is reached).

3) CORAL

- # covering sample with a rubber sleeve (modified technique: using thin lead sheaths), inserting into coreholder of CORAL;
- # establish confining pressure, activation of temperature control system for isothermal enclosure;
- # system left overnight (check for leaks, achieving temperature stability);
- # increase in confining pressure;
- # porosity (and other) measurements are carried out: a detailed account of this procedure is provided by Randolph (1983), but is not summarized here; estimation of "reservoir" stress.

Mercury Porosimetry

(the brief notes on mercury porosimetry are taken from Kopaska-Merkel, 1991, which are based in part on information provided by the manufacturer of the porosimeter)

The porosimeter used at the Metals & Ceramics Division at ORNL (supervisor: formerly Dr. L. Fuller, now Dr. Tim Burchell), and also at the Geological Survey of Alabama (supervisor: Dr. D. Kopaska-Merkel), is the Autopore II 9220 manufactured by Micromeritics Instrument Corporation. Mercury porosimetry with the Autopore II provides the possibility to determine porosity more accurately, because the pressure range available ensures that the available pore-throat size range will be covered (Kopaska-Merkel and Amthor, 1988, for carbonate rocks). Most commercial service laboratories do not possess these capabilities and, therefore, most of their porosity values should be considered as suspect (Kopaska-Merkel, 1991). A wide range of possible intrusion pressures is especially important for the study of mudrocks given their small pore-throat sizes.

The Autopore II is a computer-controlled mercury porosimeter. It can generate injection pressures ranging from 1.5 psia (0.01 MPa) to 60 000 psia (414 MPa) (90 000 psia according to L. Fuller, pers. com.). Injection pressure can be increased or decreased incrementally, allowing the separate reading of a maximum of 250 pressure steps and correlated capacitance (amount of intruded mercury) values. The computer is programmed with certain run conditions (such as pressure steps, equilibrium times, etc.) specified by the operator and the investigator. Data output is variable and a wide variety of data displays are available.

1) Decisions to be made

- # determination of appropriate equilibrium times (conservative values);
- # determination of the number of pressure steps and pressure increments (design of pressure tables);
- # selection of a maximum specific-intrusion volume; this causes the apparatus to collect additional data points, if there is a lot of intrusion between already planned data points.

2) Sample Preparation

- # sample size: has to fit into penetrometer, can be very small;
- # cleaning and drying of sample (the "proper" drying technique should be selected);
- # determining the dimensions of the sample (caliper);

weighing of clean and dry sample.

3) Analysis

sample put into penetrometer (sample chamber), sealed off;

weighing of penetrometer (containing sample);

application of vacuum to penetrometer;

introduction of mercury and filling of penetrometer;

incremental increase in injection pressure causing corresponding intrusion of mercury into sample; conducting low pressure and high pressure experiments, with weighing of penetrometer in-between.

Drying Method

The process of drying can introduce errors to the determination of porosity and/or permeability of clay-rich material. The drying of mudrocks in preparation for measurement experiments or as part of the measurement experiments should be carefully evaluated. In all cases of laboratory investigations the drying procedure used should be reported. The standard drying procedures during core analysis involve suggested operating temperatures of 116°C (at atmospheric pressure) or 93°C (under vacuum) (American Petroleum Institute, 1960; Scromeda and Katsube, 1993).

Different types of water can be distinguished for clay-rich material such as mudrocks (Grim, 1962; Bush and Jenkins, 1970; Scromeda and Katsube, 1993). The first type of water is the pore water (free water), i.e. the water contained within the pore space of the rock. A second type is water adsorbed to clay minerals (adsorbed water), whose (about) three molecular layers closest to the clay mineral should be considered as part of the clay mineral (nonordinary/nonliquid water) and not as part of the open pore space (Grim, 1962; Bush and Jenkins, 1970). The properties of this nonordinary water are strongly modified by the adjacent solid surface (Grim, 1962; Bush and Jenkins, 1970; Drost-Hansen, 1991). A third type of water is the crystal-lattice water (structural water), which is an integral part of the clay mineral (Grim, 1962; Bush and Jenkins, 1970). Pore water and adsorbed water will be lost in an unhumidified oven at temperatures of 180°F (82°C) or higher (>100°C according to Scromeda and Katsube, 1993), whereas the crystal-lattice water will be lost at temperatures above 570°F (> 300°C) (Bush and Jenkins, 1970).

Bush and Jenkins (1970) recommend the use of a humidity-controlled oven run at 40% relative humidity and at an operating temperature between 140-145°F (60-63°C). This will ensure that 1 to 2 molecular layers of adsorbed water (nonordinary water) are retained at clay minerals (as part of the clay mineral) and that the pore water and excessive adsorbed water - not part of the clay mineral - is driven off. Measurement of porosity on samples dried in this fashion will most closely characterize porosity under reservoir conditions (Bush and Jenkins, 1970; Soeder, 1986). Following Keelan (1982), Soeder (1986) used a humidity-controlled oven with operating conditions of 45% relative humidity and 145°F (63°C) for preparation of samples to be run at CORAL. Samples to be analyzed for effective porosity at CORAL (using helium porosimetry) most likely will be treated in the same way. Drying of mudrocks at lower temperatures without control of relative humidity will simply slow down the rate of dehydration and eventually will lead to a complete loss of all adsorbed water (Bush and Jenkins, 1970).

It is important to know the type of clay minerals present in the samples to be analyzed. Keelan (1982) reported that different species of clay minerals exhibit different degrees of 'sensitivity' to the drying procedure. He ranks montmorillonite as the clay mineral most sensitive to drying, with chlorite being only slightly sensitive, and illite and kaolinite as almost insensitive to drying.

Soeder (1986) pointed out that smectites (such as montmorillonite) and mixed-layer smectite/illite collapse and change chemically and physically to illite during complete drying in a non-humidity-controlled oven. This substantially increases the permeability (and porosity) of the sample. Knowledge of the clay-mineral composition of the samples (stratigraphic unit), therefore, is very important. Extreme care should be taken, if smectites are present (e. g., Krushin, 1994).

An aspect to consider, however, is that diffusion of chemical species will occur through the whole cross section of water available between the physical confines provided by the framework minerals (clay minerals, quartz, feldspar, etc.). The water-cross section, accordingly, would comprise the normal pore water and the adsorbed water including the few molecular layers of nonordinary water. It should also be considered, however, that the properties of the nonordinary water differ from the properties of the pore water (bulk or ordinary water). This is even more complicated, if one adopts the notion of vicinal water, where solid surfaces exert modifying influence upon water beyond the 2 to 5 molecular layers of nonordinary water to up to 50 molecular diameters (Drost-Hansen, 1991). The changed properties of the water-molecule layers along solid surfaces, when compared to pore water (bulk/ordinary water properties), will likely influence the diffusion characteristics of chemical species (e. g., Drost-Hansen, 1991). According to Drost-Hansen (1991) vicinal water, in fact, is the likely type of water contained within the pore spaces of fine-grained sedimentary rocks, given the small pore sizes and the proximity of the confining solid surfaces of the framework minerals holding up the pores. The thickness of the nonordinary water (and of vicinal water) can be estimated by assuming a thickness of about 0.25 nm for one molecular layer of water (Bush and Jenkins, 1970; Soeder, 1986).

Scromeda and Katsube (1993), on the other hand, dismiss drying of mudrocks at temperatures below 100°C. They claim that it is necessary to dry rock samples at operating temperatures above 100°C (either under vacuum or at atmospheric pressure) in order to drive off all adsorbed water. Drying at operating temperatures below 100°C most likely will prevent the measurement of true effective porosity (Scromeda and

Katsube, 1993). Should drying according to the specification of the Geological Survey of Canada (Scromeda and Katsube, 1993) not physically alter mudrock samples (presence/absence of smectites) and also drive off *all* of the adsorbed water (including the nonordinary water), then it appears to be the technique most promising for determining the true effective porosity of mudrocks.

To end on a positive note: indurated fine-grained siliciclastic rocks are by far less susceptible to any possible negative modifications imposed by the drying procedure than are unconsolidated or weakly consolidated clayey sediments (Bennett and Hulbert, 1986).

Appendix II: Addresses of Laboratories and Service Companies*Core Laboratories*

1875 Monetary Lane
Carrollton, TX 75006
(214) 466-2673

Terra Tech

420 South Wakara Way
Salt Lake City, Utah 84108
(801) 584-2400

K&A Energy Consultants

6849 East 13th Street
Tulsa, OK 74112
(918) 835-9524

(contacts: Bob Easterly, John Correa)

Institute of Gas Technology

3424 South State Street
Chicago, Illinois 60616

(contacts: Brij Misra, Prasan Chowdiah)

Geological Survey of Alabama

420 Hackberry Lane
P.O. Box O
Tuscaloosa, AL 35486-9780

(contact: D.C. Kopaska-Merkel)

Spectrum Petrographics

499 Dillard Gardens, Suite 2
Winston, OR 97496

(contact: Michael DePangher)

Appendix III: Notations and FormulasVolumes

V_p = pore volume (volume of pore space)

V_{pinter} = volume of *interconnected* pore space

V_b = bulk volume (bulk sample volume)

$V_{bimm.}$ = bulk volume measured through Hg-immersion

V_{bc} = bulk volume measured with caliper

$V_b = W_d / \partial$

∂ = bulk density of the rock sample

W_d = sample weight dry

V_g = grain volume (volume of the *solid* sample material: volume of grains)

$V_p = V_b - V_g$

$V_b \rightarrow V_{bc} = V_{bimm.} = (V_p + V_g)$: these all should correspond

Porosities

ϕ_T = total porosity

ϕ_E = effective porosity

ϕ_O = (total) optical porosity (TOP)

$\phi_T = V_p / V_b \cdot 100$

$= V_p / (V_p + V_g) \cdot 100$

$= (V_b - V_g) / V_b \cdot 100$

$\phi_E = V_{pinter} / V_b \cdot 100$

Void Ratio

$e = V_p \text{ [or } V_{pinter}] / V_g$

e = void ratio

Relationship between Porosity and Void Ratio:

$\phi_T \text{ [or } \phi_E] = e / (1 + e)$

$e = \phi_T \text{ [or } \phi_E] / (1 - \phi_T \text{ [or } \phi_E])$

Effective Porosities

A. ϕ_{Eg} = effective porosity measured with helium porosimetry (g = gas)

1) $\phi_{Eg} = V_p / V_{bimm.}$

2) $\phi_{Eg} = V_p / (V_p + V_g)$

3) $\phi_{Eg} = (V_{bimm.} - V_g) / V_{bimm.}$

B. ϕ_{Em} = effective porosity measured with mercury porosimetry (m = mercury)

$$d = (-4\gamma \cos\theta) / p \quad (\text{Washburn Equation})$$

d = throat size

γ = interfacial (surface) tension (for Hg/vacuum = 485 dynes/cm)

θ = contact angle (for Hg/vacuum = 130°, measured in Hg)

p = intrusion pressure (psia).

$$1) \phi_{Em} = V_{Hg\text{intr.}} / V_b$$

$V_{Hg\text{intr.}}$ = max. cum. intruded volume of mercury

2) ϕ_{Emc} = corrected effective porosity measured with mercury porosimetry

$$= \phi_{Em} + \Delta\phi$$

$\Delta\phi$ = 'missing porosity'

$$V_b = V_{pen} - V_{Hg} \quad (\text{using the mercury porosimeter})$$

V_{pen} = volume of penetrometer (to be determined by calibration runs)

$$V_{Hg} = \text{volume of mercury; } = M_{Hg} / D_{Hg}$$

D_{Hg} = density of mercury

M_{Hg} = mass of mercury; = $M_1 - M_2$

M_1 = mass (penetrometer+sample+mercury*)

M_2 = mass (penetrometer+sample)

* as a non-wetting liquid mercury will/should not penetrate pore space without applied pressure (even pores at the sample surface).

C. ϕ_{Ew} = effective porosity measured with the radial diffusion-cell method

(w = 'Waterloo')

$$1) V_M = [V_R / C_{DR(\infty)}] - V_R$$

V_M = volume of water present in the core sample

V_R = volume of the reservoir

$C_{DR(\infty)}$ = dimensionless residence concentration at equilibrium: C_R / C_0

(C_R = reservoir concentration; C_0 = initial reservoir concentration)

then:

$$\phi_{Ew} = V_M / \pi (r_L^2 - r_R^2) L$$

L = length of core sample

r_L = radius of core sample

r_R = radius of reservoir

V_M = (s. above) value calculated with formula above

2) ϕ_{Ew} calculated from β_1

$$\beta_1 = C_{DR(\infty)} [r_{DL}^2 - 1] / 2 [1 - C_{DR(\infty)}]$$

β_1 = dimensionless mixing coefficient of the reservoir: $V_R / (R \cdot \gamma_R \cdot r_R)$

V_R = volume of reservoir

γ^P = cross sectional area through which diffusion occurs
[porosity · surface area of reservoir]

r_R = radius of reservoir

R = retardation factor

r_{DL} = dimensionless radius of the core sample: r_L / r_R

$C_{DR(\infty)}$ = dimensionless residence concentration at equilibrium

$$3) \phi_{Ew} = V_{pe} / V_b$$

V_{pe} = effective pore volume: $V_{pe} = M_{xn} / C_{xn} - C_{x0}$

C_{x0} = initial pore water concentration of constituent (tracer) x

M_{xn} = total mass of constituent (tracer) x added to reservoir

C_{xn} = pore water concentration of constituent (tracer) x at time n

D. ϕ_{Ei} = effective porosity measured with the immersion-saturation method (i = immersion)

$$1) \phi_{Ei} = \frac{W_w - W_d}{W_d} \cdot \frac{\partial_w}{\partial_r}$$

∂_r = bulk density of the rock sample

W_w = sample weight wet

W_d = sample weight dry

∂_w = bulk density of pore water

$$2) \phi_{Ei} = V_p / V_b$$

$V_p = (W_w - W_d) / \partial_w$

∂_w = bulk density of water

$V_b = W_d / \partial$

$$S_r = \Delta W_r / (W_w - W_d)$$

S_r = degree of saturation

ΔW_r = weight of the water content at any given time: = $(W_r - W_d)$

W_r = weight of sample at any given time

W_w = wet sample weight (constant weight, considered fully saturated)

W_d = dry sample weight (constant weight, considered completely dried)

$(W_w - W_d)$ = weight of the maximum water content

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