

# DENSITY STUDIES IN CLAY-LIQUID SYSTEMS, PART II: APPLICATION TO CORE ANALYSIS

*by*

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## ABSTRACT

In Part I (Deeds and van Olphen, 1961) pycnometric data on expanding clays in water and in other displacement fluids were analyzed in terms of inaccessible void space within aggregates and of possible density anomalies of the adsorbed fraction of the displacement fluids.

Further details of this work are reported, and the consequences for the interpretation of core analysis data are discussed. It is concluded that in core analysis the density of the connate water can be assumed to be normal while the fraction of the total pore space which is filled with oil is computed, provided that the total pore space is determined by using water or a polar organic liquid. If a hydrocarbon liquid or an inert gas is used, a small correction for inaccessible pore space can be applied.

## INTRODUCTION

In petrophysical practice the determination of grain densities and of the porosity of the extracted cores is based on the measurement of the volume of a liquid (or gas) displaced by the solid phase. Furthermore, the fraction of the pore volume occupied by water is derived from the amount of water which can be extracted from the core.

Apart from the many uncertainties involved in relating core properties to actual reservoir properties, several questions have been raised regarding the interpretation of the results of core analyses in terms of the properties of the recovered core as such.

First, the grain density or pore volume of the core is often determined from the displacement volume of toluene or of another hydrocarbon liquid of the extracted core. Particularly for cores containing finely divided clays, the possibility has been considered that narrow pores occur in the core which are inaccessible for hydrocarbon fluids but into which water can penetrate. Hence, when connate water is present in the original core, the pore space derived from tests with hydrocarbon fluids may not be representative of the pore space that is actually occupied by the fluids in the core.

<sup>1</sup> Publication no. 291.

TABLE 1.—APPARENT DENSITIES IN NON-PENETRATING LIQUIDS

Clay material	Pycnometer fluid	Sample weight, g	Apparent density, g/cm <sup>3</sup>
Sodium Wyoming Bentonite (flakes from unfractionated suspension) Wyoming Bentonite (powder)	<i>n</i> -decane	9.4024	2.689
		6.0935	2.686
	<i>n</i> -decane	35.3129	2.691
		20.4554	2.692
		23.5527	2.691
		26.5879	2.688
		45.0071	2.707
		24.4159	2.692
	Benzene $\gamma$ -collidine* toluene	41.4130	2.702
		47.0931	2.698
		27.4546	2.701
average standard deviation (11 determinations)			2.694
			0.006
Sodium Hectorite (powder)	cyclohexane	20.1965	2.683

\* Although  $\gamma$ -collidine is a polar liquid, bentonite does not swell in this liquid.

TABLE 2.—APPARENT DENSITIES IN WATER

Clay material	Pycnometer fluid	Sample weight, g	Apparent density, g/cm <sup>3</sup>
Sodium Wyoming Bentonite (freeze-dried powder) (flakes)	water	2.4926	2.791
		2.1657	2.794
		1.8298	2.782
		3.8524	2.800
		4.7358	2.791
		4.1187	2.816
average standard deviation (6 determinations)			2.795
			0.01
Wyoming Bentonite (powder)		7.7719	2.835
Sodium Hectorite (powder)		10.5498	2.844
		4.0921	2.812

Second, in the derivation of the actual pore volume occupied by water from the amount of extracted water, the possibility has been considered that the fraction of the water in the core which is adsorbed by the clays in the core may have an abnormal density.

TABLE 3.—APPARENT DENSITIES IN POLAR ORGANIC LIQUIDS

Clay material	Pycnometer fluid	Sample weight, g	Apparent density, g/cm <sup>3</sup>	Basal spacing, Å
Wyoming Bentonite (powder)	1, 4-dioxane (water)	25.6508	2.843 (2.840)	14.5
Sodium Wyoming Bentonite (flakes)	ethylene glycol (water)	3.3823	2.818 (2.795)	17.0

TABLE 4.—APPARENT DENSITY OF LLANO SODIUM VERMICULITE IN WATER, POLAR ORGANIC LIQUIDS, AND NON-POLAR ORGANIC LIQUIDS

Clay material	Pycnometer fluid	Sample weight, g	Apparent density, g/cm <sup>3</sup>	Basal spacing, Å
Sodium Llano Vermiculite (powder)	water	8.2495	3.037	14.82
		5.1212	3.043	14.82
		6.7742	3.055	14.82
	average	3.045		
<i>n</i> -decane	ethylene glycol* pyridine*	7.9946	2.726	9.82
		7.7761	2.741	9.82
		10.2298	2.742	9.82

\* This vermiculite does not swell in either ethylene glycol or pyridine.

In Part I the significance of these two factors in expanding clay-liquid systems has been analyzed. The results will be reviewed briefly. Detailed tables of the results of the pycnometric determinations are incorporated (Tables 1-4). Some of the data on average values differ very slightly from those presented in Part I. Some additional data on non-expanding clays and

sand are reported in Table 5, and all the density data are summarized in Table 6. Crystallographic densities are computed in an appendix.

Finally, the consequences of this work for the interpretation of core analysis data will be discussed.

TABLE 5.— APPARENT DENSITIES OF NON-EXPANDING CLAYS AND SAND IN WATER AND IN *n*-DECANE

Material	Pycnometer fluid	Sample weight, g	Apparent density, g/cm <sup>3</sup>
Sodium Fithian Illite*	<i>n</i> -decane	25.0783	2.758
	water	20.0594	2.798
Kaolinite†	<i>n</i> -decane	26.3562	2.608
		9.8363	2.602
	water	19.3894	2.634
Potassium Llano Vermiculite		16.8150	2.627
	<i>n</i> -decane	13.9800	2.689
	water	12.4658	2.794
Ottawa Sand (44 $\mu$ ) (alpha-quartz)	<i>n</i> -decane	42.0768	2.652
	water	32.0459	2.641
Sodium Wyoming Bentonite dehydroxylated at 900° C (non-expanding)	<i>n</i> -decane	12.3622	2.491
	water	31.2182	2.490

\* Source Illinois; locality Fithian, described in A.P.I. Project 49. Cation exchange capacity, 24 meq/100 g.

† Commercial product, source unknown. Cation exchange capacity, 2 meq/100 g.

## INTERPRETATION OF DENSITY DETERMINATIONS

### *Expanding Clays*

By the assigning of normal densities to the displacement fluids used, "apparent" densities or "apparent" specific volumes of clays were computed from pycnometric measurements. Crystallographic densities of the clays in the non-expanded state were derived from the unit cell weight (obtained from chemical analysis and standard clay formula calculations) and from the unit volume (determined by X-ray diffraction).

The apparent densities of expanding clays in "non-penetrating liquids" (fluids in which these clays do not expand), e.g. hydrocarbon liquids, are about 4 percent lower than the crystallographic densities of the clays in the non-expanded state. This difference is assumed to be due to the presence of a void space between partially overlapping unit layers within clay aggregates,

TABLE 6.—CRYSTALLOGRAPHIC AND APPARENT DENSITIES, SPECIFIC VOLUMES OF EXPANDING AND NON-EXPANDING CLAYS, AND SPECIFIC VOID SPACES

Material	Crystallographic density (spec. vol.), g/cm <sup>3</sup> (cm <sup>3</sup> /g)	Apparent density and specific volume		Specific void volumes	
		in water, g/cm <sup>3</sup> (cm <sup>3</sup> /g)	in hydrocarbon, g/cm <sup>3</sup> (cm <sup>3</sup> /g)	Inaccessible, cm <sup>3</sup> /g	Selectively accessible, cm <sup>3</sup> /g
Na-Bentonite	2.798 0.3574	2.795 0.3578	2.694 0.3711	0.014	0.013
Na-Hectorite	2.8030 0.3567	2.812 0.3556	2.683 0.3727	0.016	0.017
Na-Vermiculite	2.827 0.3537	3.045 0.3284	2.726 0.3668	0.013	0.038
K-Vermiculite	2.816 0.3551	2.794 0.3579	2.689 0.3718	0.017	0.014
Kaolinite	2.630 0.3802	2.630 0.3802	2.605 0.3838	0.003 <sub>s</sub>	0.003 <sub>s</sub>
Na-Illite	2.780* 0.3597	2.798 0.3573	2.758 0.3625	0.003*	0.005
Sand (alpha-quartz)	2.649 0.3775	2.641 0.3786	2.652 0.3770	0	0

\* Estimated from data in the literature on composition and cell dimensions of illites.

which is inaccessible to the non-penetrating liquids. We assume that any density anomalies near the clay surfaces can be neglected because of the low adsorption energy and small contact area involved.

The apparent densities of expanding clays in penetrating liquids (fluids in which the clays expand) such as water are higher than those in non-penetrating liquids. For most expanding clays, the apparent density in water is actually equal to the crystallographic density of the non-expanded clay. The difference between the apparent densities of the clays in water and in hydrocarbon liquids may be formally attributed to the presence of an apparent selectively accessible void space which is inaccessible to hydrocarbons but accessible to water and which will be completely filled by water when normal density is assigned to all the water in the system. Because of the identity of the apparent density in water and the crystallographic density of the clay, the inaccessible void space as defined above is equal to the apparent selectively accessible void space. It is therefore assumed that both relate to the same real void space within aggregates. Then, the system in water behaves as if the density of water throughout the system is normal, including the adsorbed water between the unit layers of the clay.

In the hydrous system, however, the clay no longer exists in the non-expanded state, and hence, the crystallographic density of the non-expanded clay is not necessarily the true reference density of the clay. In the unexpanded state, the unit layers are held apart a few tenths of one Ångström unit by the exchange cations; moreover, there are some holes in the centers of hexagonal rings of oxygen atoms in the unit layer surface. In the unexpanded state, these spaces between the unit layers are occupied only by the exchange cations. In the hydrous system, on the other hand, the unit layers are completely parted by the water molecules, which may touch the unit layers and partially fill the holes in the surface of the unit layers. Although the clay system behaves as if a sheet of water of normal density enters between the unit layers without filling the space that was vacant in the unexpanded clay, the interlayer water may in reality expand to fill this space and assume a lower density. The true reference density of the clay would then be the crystallographic density of the unit layers separately, which is higher than that of the unexpanded packet of unit layers. No precise data can be given on this reference density, but a rough estimate of the possible degree of expansion of the interlayer water shows that the "density" of the interlayer water would at most be 5 percent below normal. Obviously, no exact information on this matter can be obtained from bulk measurements of clay densities.

An exceptional behavior is shown by sodium vermiculite. For this material, the apparent density in water is much higher than the crystallographic density of the unexpanded clay. The apparent density in water is approximately the same as the estimated crystallographic density of the separate unit layers. Therefore, when a normal density is assigned to the water between the unit layers, the space between the unit layers is completely filled, and no room remains for expansion as in the bentonite clays. This exceptional behavior is probably due to the large attraction between the negative unit layers and the comparatively large number of exchange cations which are positioned midway between the unit layers in this clay.

#### *Non-expanding Clays and Sands*

The apparent densities of non-expanding clays and sands in hydrocarbon liquids are equal to, or at most 1 percent lower than, the apparent densities in water (Table 5). The latter are practically identical with the crystallographic densities.

In analogy with the results obtained for expanding clays, the slight differences, if any, between the densities in hydrocarbon liquids and water are attributed to void spaces in the systems which are inaccessible to hydrocarbon liquids rather than to abnormal densities of the small fractions of the liquids which are adsorbed on the exterior surfaces of the comparatively thick particles of these clays.

The void spaces probably occur between partially overlapping particles. Since these particles are thicker, more rigid plates than those of the bentonite and hectorite clays, they will be less perfectly stacked in aggregates; hence, the channels connecting the voids with the bulk pore space are probably rather

wide. Only a few of these channels may be small enough to block the passage of hydrocarbon molecules. Water molecules still may be able to pass through these channels since they can widen the gap between overlapping plates because of their high adsorption energy; this is analogous to the mechanism of their penetration between the unit layers of expanding clays. In kaolinite and in illite, the void space amounts to about 1 percent of the specific volume of these clays; for sand the void space is negligible, whereas for vermiculite in the non-expanding potassium form, the void space is comparable with that in the expanding clays, probably because of a more perfect parallelism of the rather perfect crystallites in the aggregate stack.

Table 6 gives a survey of apparent and crystallographic densities and specific volumes of both expanding and non-expanding clays with data for the void spaces in these systems.

### APPLICATION TO CORE ANALYSIS

The total pore space of a core is the difference between the volume of the core and the volume occupied by solid matter. The latter is determined by measuring the volume of a liquid (or a gas) displaced by the solid. The fraction of the total pore space occupied by water is found from the volume of water extracted from the core. The fraction of the total pore space occupied by oil is found by subtracting the fraction occupied by water from the total pore space.

If the liquid used in the determination of the displacement volume of the solids cannot fill part of the pores (the inaccessible void space), the total pore space is underestimated. If the density of the adsorbed part of the water in the core should be greater than normal, and if the fraction of the pore space filled with water is considered equal to the volume of the extracted water, this fraction is overestimated. The difference between the two volumes, which is occupied by oil, would then be doubly underestimated. However, if the density of the adsorbed water should be smaller than normal, the two effects would partially cancel. It has often been wondered whether such errors might not be considerable in those cores containing large proportions of expanding clays for which both effects possibly could be rather significant.

We have seen that abnormal fluid densities and inaccessible void spaces indeed occur in clay systems. However, as will be shown, no quantitative knowledge of such effects is required in the interpretation of core analysis data under certain conditions.

In Part I the apparent density of an expanding clay in water was reported to be equal to that of the same clay with a small amount of pre-adsorbed water immersed in *n*-decane. The clay with pre-adsorbed water contained about 300 mg of water per gram of clay. This observation indicates that any water in the system in excess of 300 mg per g has a normal density.

Figure 1 shows a comparison of the situation in a core having at least 300 mg of connate water per gram of expanding clay (b) with the core completely filled with water after extraction of water and oil (a). The total

volume of the core is divided schematically into the clay volume, the volume of 300 mg of water per gram of clay, the volume of remaining water, and the volume of oil.

In the core completely filled with water, a normal density can be assigned to all the water except to the 300 mg per gram of clay, the density of which is unknown. By subtracting the volume of the water not associated with the clay from the total volume, the true volume of the clay plus the 300 mg of water per gram is obtained.

In the original core, the clay combined with 300 mg of water per gram occupies the same true volume. Then, when a normal density is assigned to the rest of the water, the true volume of the oil can be obtained.<sup>1</sup>

(a) Volume distribution in extracted core filled with water.

clay	300mg   of   water   per g   of   clay	total water minus 300 mg per g of clay
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(b) Volume distribution in original core.

clay	300 mg   of   water   per g   of   clay	volume of ex- tracted water minus 300 mg per g of clay	volume of oil
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FIGURE 1.—Schematic representation of volume distributions in cores.

We do not have to know how the true volume of the clay plus the 300 mg of water per gram is divided between the clay and the water, and we can assign any density to either one as long as their combined volume is equal to the true volume. We can thus assign normal density to the 300 mg of water per gram of clay and the apparent density value defined before to the clay.

Therefore, the true volume of the oil can be found by the following method: Determine the total pore space with water as the displacement fluid, and assign normal density to the water in the computation; calculate the fraction of the pore space occupied by water by assigning a normal density to the water extracted from the core; compute the true volume of the oil by subtracting the fraction of the pore space occupied by water from the total pore space.

Obviously, both the total pore space and the fraction occupied by water

<sup>1</sup> A core commonly contains more connate water than the amount corresponding with 300 mg of water per gram of expanding clay present in the core.



determined in this way represent "apparent" pore spaces, but their difference—the fraction occupied by oil—is a true pore space.

Instead of water, some polar organic liquid which gives the same apparent density values for the clay can be used. Dioxane seems to be an appropriate alternative.

If the use of a hydrocarbon liquid such as toluene is preferred, as is common practice, the results obtained with such a liquid require a correction for the determination of the apparent pore space which would be obtained with water or a polar organic liquid as the displacement fluid. This correction amounts to the addition of the selectively accessible pore space to the total pore space determined with a hydrocarbon. The correction is about 0.015 ml for every gram of expanding clay present in the core.<sup>1</sup> In order to apply the correction, the amount of expanding clay must be estimated from X-ray diffraction and a base exchange capacity determination of the core solids.

Since this correction is rather small and hence negligible for most practical purposes, there is no compelling reason to abandon the present method for determining grain density, in which toluene is used as the displacement fluid. However, for extremely shaly cores, and when high precision is required, a correction to the results of the toluene method or the use of dioxane or water as the displacement fluid might be considered. In an extreme example, if 100 ml of a core contains 40 g of an expanding clay, the total pore volume, and thus the volume of oil in place,<sup>2</sup> must be corrected by adding  $40 \times 0.015 = 0.6$  ml if toluene was used in the measurements. If it is assumed that the core contained 10 ml of oil in addition to connate water, this correction amounts to 6 percent of the oil in place. The correction for even this extreme case is relatively inconsequential in view of the uncertainties in relating core analysis data to actual reservoir conditions.

## APPENDIX

### COMPUTATION OF CRYSTALLOGRAPHIC DENSITIES

The crystallographic density of a montmorillonite clay in the unexpanded state, i.e. of the dry clay immersed in a hydrocarbon fluid, can be derived from the unit cell dimensions and the unit cell weight. The cell dimensions are determined by X-ray diffraction; the cell weight is determined analytically. To illustrate the procedure, the calculations for sodium Wyoming bentonite will be discussed in detail.

#### *Sodium Wyoming Bentonite*

*Average unit cell weight of sodium Wyoming bentonite.*—With the procedure of Ross and Hendricks (1945), as proposed by Marshall (1935), the formula of the average unit

<sup>1</sup> For sodium vermiculite the correction would be larger (0.038 ml/g), but this mineral is unlikely to occur in cores.

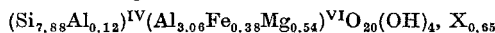
<sup>2</sup> It should be clearly understood that we are dealing with the volume of oil in the core which is derived from the difference between the total pore volume and the volume of connate water in the core, not with the volume of oil derived from the weight of the oil. The latter is determined by subtracting the weight of the dry extracted core plus the weight of the water in the core from the original weight of the core. This procedure is not always considered reliable.

cell of a montmorillonite clay can be computed from the results of a chemical analysis of the constituent elements of the clay and the cation exchange capacity.

Chemical analysis of the Clay Spur Wyoming bentonite gave the following results:  $\text{SiO}_2$ , 55.4 percent;  $\text{Al}_2\text{O}_3$ , 19.0 percent;  $\text{Fe}_2\text{O}_3$ , 3.6 percent;  $\text{MgO}$ , 2.5 percent.

The cation-exchange capacity of the clay is 86 meq/100 g.

From these data the following unit cell formula is calculated:



in which X stands for a monovalent exchange cation, which in this clay is Na.

According to this formula, there are 745 atomic units per cell. Since the mass of an atom of unit atomic weight is  $1.660 \times 10^{-24}$  g, the weight of the unit cell equals  $1237 \times 10^{-24}$  g ( $\pm 0.25$  percent).

*Unit cell dimensions of sodium Wyoming bentonite.*—The following unit cell parameters were determined directly from X-ray diffraction patterns:

$$a_0, 5.15 \text{ \AA}; b_0, 8.93 \text{ \AA}; c_0, 9.60 \text{ \AA}.$$

These parameters agree with those reported in the literature (MacEwan, 1951, p. 104). Empirically, it has been found that the *a* and *b* dimensions of montmorillonite clay cells vary with the amounts of substitution in the following manner:

$$b_0 = 8.90 + 0.06r + 0.033s + 0.047t \text{ \AA},$$

in which 8.90 represents the  $b_0$  dimension of the unsubstituted prototype mineral pyrophyllite,  $r = \text{Al}$  in tetrahedral coordination,  $s = \text{Mg}$  in octahedral coordination, and  $t = \text{Fe}$  in octahedral coordination. Hence, for the Wyoming bentonite clay, we obtain  $b_0 = 8.94 \text{ \AA}$ . The  $a_0$  dimension is calculated from the  $b_0$  dimension as  $a_0 = b_0/\sqrt{3} = 5.16 \text{ \AA}$ . Hence, the volume of the unit cell ( $a_0, b_0, c_0$ ) is between 441.5 and  $442.8 \times 10^{-24}$  cm<sup>3</sup>.

*Crystallographic density of sodium Wyoming bentonite.*—The crystallographic density of sodium Wyoming bentonite is  $1237 \times 10^{-24}/442.1 \times 10^{-24} = 2.798 \pm 0.012$  g/cm<sup>3</sup>.

#### *Crystallographic Density of Sodium Hectorite*

Chemical analysis:  $\text{SiO}_2$ , 57.54 percent;  $\text{MgO}$ , 25.90 percent;  $\text{Li}_2\text{O}$ , 0.80 percent.

Cation-exchange capacity: 83 meq/100 g.

Unit cell formula:  $(\text{Si}_{8.0})^{\text{IV}}(\text{Mg}_{5.34}\text{Li}_{0.66})^{\text{VI}}\text{O}_{20}(\text{F}, \text{OH})_4, \text{Na}_{0.66}$ .

Unit cell weight:  $762 \times 1.660 \times 10^{-24} = 1265 \times 10^{-24}$  g (based on 40H).

Unit cell dimensions:  $a_0 = 5.24 \text{ \AA}$ ,  $b_0 = 9.07 \text{ \AA}$ ,  $c_0 = 9.60 \text{ \AA}$ .

Unit cell volume:  $a_0 \times b_0 \times c_0 = 456 \times 10^{-24}$  cm<sup>3</sup>.

Crystallographic density:  $1265 \times 10^{-24}/456 \times 10^{-24} = 2.774$  g/cm<sup>3</sup>, or 2.803 g/cm<sup>3</sup> based on 4 F.

#### *Sodium Llano Vermiculite*

Chemical analysis:  $\text{SiO}_2$ , 38.30 percent;  $\text{Al}_2\text{O}_3$ , 24.84 percent;  $\text{MgO}$ , 22.35 percent.

Cation-exchange capacity: 195 meq/100 g.

Formula:  $(\text{Si}_{5.28}\text{Al}_{2.72})^{\text{IV}}(\text{Al}_{1.32}\text{Mg}_{4.58})^{\text{VI}}\text{O}_{20}(\text{OH})_4, \text{Na}_{1.6}$ .

Unit cell weight:  $793.6 \times 1.660 \times 10^{-24} = 1317 \times 10^{-24}$  g.

Unit cell dimensions from X-ray analysis of dry clay:  $a_0 = 5.21 \text{ \AA}$ ,  $b_0 = 9.18 \text{ \AA}$ ,  $c_0 = 9.82 \text{ \AA}$ ,  $\beta = 97^\circ$ .

Unit cell volume:  $a_0 \times b_0 \times c_0 \times \sin \beta = 465.9 \times 10^{-24}$  cm<sup>3</sup>.

Crystallographic density:  $1317 \times 10^{-24}/465.9 \times 10^{-24} = 2.827$  g/cm<sup>3</sup>.

#### *Potassium Llano Vermiculite*

Unit cell weight:  $819.2 \times 1.66 \times 10^{-24} = 1360 \times 10^{-24}$  g.

Unit cell dimensions: Same as for sodium clay, except that the *c* spacing is 10.17  $\text{\AA}$ .

Unit cell volume:  $482.5 \times 10^{-24}$  cm<sup>3</sup>.

Crystallographic density:  $1360 \times 10^{-24}/482.5 \times 10^{-24} = 2.816$  g/cm<sup>3</sup>.

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