

CLAY MINERALS IN PETROLEUM RESERVOIR SANDS AND WATER SENSITIVITY EFFECTS

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ABSTRACT

The ability of some petroleum reservoir sands to conduct oil is decreased by interaction of the porous rock with water, usually water fresher than that coexisting with oil in rock interstices. Shales penetrated by drilling operations may swell upon interaction with relatively fresh water drilling liquids. The question of the relation of specific clay mineral content to reservoir sand water sensitivity has not been investigated in detail by other workers, although bentonitic clays often have been considered responsible.

A selection of 90 core samples from widely scattered American oil fields has been analyzed for clay mineral content. Reservoirs of known water sensitivity history and others where no such problem exists are represented by the samples. Modern X-ray diffraction techniques were employed to determine clay mineral types, lattice expandability, and approximate amounts present. The main purpose was to test the hypothesis that there exists a direct relationship between content of 3-sheet, glycerol-expandable clay minerals and water-sensitive behavior.

It was found that water sensitivity can be predicted with surprising accuracy by measuring the intensity of the X-ray diffraction peak of the glycerol-expanded basal plane spacing. Samples producing "moderate" or greater intensities of the glycerol-expanded peak were taken from sands that exhibited economically serious water-sensitive behavior. Large concentrations of nonexpandable kaolin, chlorite, and mica clay minerals did not produce serious water sensitivity effects in the absence of expandable minerals.

A selection of samples from West Texas sands of Permian age were the only samples older than the Mesozoic found to contain expandable clay minerals. These expanded anomalously, possibly as a result of interstratification. The characteristic clay mineral suite might be employed as a geological marker to identify the Yates and Queen sands over a wide geographical area in Pecos, Ward, and Winkler counties of West Texas.

A possible mechanism of the swelling of clay particles lining reservoir rock pores is discussed in terms of osmotic and Donnan membrane effects as applied to *intraparticle* swelling. The swelling of expandable clay mineral particles upon contact with relatively fresh water is postulated as the most general cause of water sensitivity difficulties encountered in petroleum production operations. Swollen particles restrict flow in rock pores, and minute, expanded lamellae break away to be dispersed in water within a pore and restrict flow further when they lodge in pore constrictions. Non-expandable clay mineral grains do interact specifically with water but are incapable of swelling and disintegrating to the same degree as those grains containing expandable minerals.

INTRODUCTION

Any discussion of water sensitivity effects in petroleum reservoir sands encounters immediately a major difficulty in defining the problem precisely. In order to examine the role of clay minerals, let us propose two limitations.

First, let us confine our attention to sandy sediments such as sandstones, shaly sands, shales, conglomerates, and poorly consolidated sands, but eliminate all types of relatively massive calcareous rocks such as dolomites and limestones. Next, let us differentiate between phenomena of a more physical or mechanical nature such as "relative permeability" water blocks caused by high water saturations that result in low permeability to oil. The water sensitivity problems remaining generally are believed to be the result of the specific interaction of water, usually relatively fresh water, with components of the sandy sediments. Most workers in the field blame "clays" for the difficulties, but efforts to relate water sensitivity effects to specific clay minerals have been few and not too successful. One of the reasons for the confusion that exists is the development only very recently of more reliable means of identifying small concentrations of clay minerals in complex natural sediments, usually of marine origin. Identification procedures are still being improved, especially for minerals such as chlorites and vermiculites that have received less attention in the past. It is our purpose to determine if currently available identification methods permit us to predict the water sensitivity tendencies of reservoir rocks. Can we develop relatively simple criteria that will allow us to recognize reservoir sands wherein the degree of water sensitivity will be severe enough to justify, on an economic basis, the application of moderately expensive corrective measures?

In considering this problem, we have attempted to set up some simple assumptions as a basis for experimental study. We assume that water sensitivity in a petroleum reservoir sand, keeping in mind the limitations set forth in the first paragraph, is a function of the concentration of expandable three-sheet clay minerals in the sand. The most common such minerals are members of the montmorillonite group. We propose to determine expandability by X-ray diffraction measurement of the basal plane spacing before and after treatment with glycerol. There is no intention to imply here that whenever a trace of glycerol-expandable three-sheet clay mineral is found in the separated fine fraction of a reservoir sand this formation will demonstrate serious water sensitivity effects. Rather it is our intention to determine a certain critical intensity of the basal plane X-ray diffraction reflection, after treatment of the fine fraction with glycerol, which intensity corresponds to the maximum amount of glycerol-expandable, three-sheet mineral that can be tolerated from an economic point of view. In other words, the *degree* of water sensitivity varies with the concentration of expandable clay minerals.*

In addition to the amount of glycerol-expandable clay mineral present, the location and distribution of such clays in the reservoir rock are of utmost importance with respect to their effect on petroleum production. First

* For purposes of this discussion in which we are dealing with marine sediments, it is permissible to drop the restriction of "three-sheet" expandable clay minerals. The only known expandable two-sheet clay mineral is hydrated halloysite, but its occurrence in marine sediments has not been reported (Grim, 1953, pp. 349 and 357) and is considered unlikely.

it is necessary that the clay particles occur at points along the interconnected rock pore system where they can come in contact with reservoir fluids in order to affect the water-sensitive behavior. Clays held within the nonconnected or impermeable portions of rocks are incapable of interacting with water. Second, it has been found that moderately large amounts of clays may not appreciably affect over-all water sensitivity if located only along shale streaks. Such streaks are more or less impermeable to water, but oil and water can move readily through the surrounding relatively clean sand. These considerations suggest the desirability of critical examination of reservoir rock samples submitted for analysis. Finally, in considering the grosser aspects of clay mineral distribution throughout a petroleum reservoir, it occasionally is noted that the expandable clay minerals are located only in isolated and relatively small volumetric portions of the producing sand. If such is the case, it may be economically expedient to ignore any water sensitivity problems connected only with these portions. These considerations do, nevertheless, emphasize the need for adequate sampling of the entire reservoir volume whenever this is possible.

EXPERIMENTAL

Procedures

All rock samples analyzed were cut from cores, except those obtained from cuttings during drilling operations. Most of the cores were cleaned by extraction with toluene, but this operation did not measurably affect the amounts or distributions of clay minerals found. The samples were crushed gently, to avoid grinding quartz grains, and screened through a 325-mesh screen. The fines were suspended in water and smeared on a three- by one-inch microscope slide to form a thin strip down the center about $\frac{3}{8}$ -inch wide. If the particles were preferentially oil wet, the smear was made with alcohol. The size of the smear was determined by the optimum geometry of the General Electric X-ray spectrogoniometer. Sample smears prepared for heat treatment at 550° C were made on Pyrex glass slides. For such samples, the uniform use of isopropyl alcohol in preparing the smear generally eliminated excessive cracking and flaking of the dried film during heat treatment. All of the smears were prepared from sufficiently dilute suspensions so that marked basal plane orientation of particles in the dried film was obtained. Samples employed for measurement of glycerol expandability were treated with 4 to 5 drops of a 10 percent solution of glycerol in methyl alcohol. X-ray diffraction patterns of the latter samples were made as soon as the surfaces of the smears appeared to be dry. The troublesome background caused by scattering from excess liquid glycerol was avoided. Complete saturation of a smear with glycerol was observed to occur within minutes as judged by uniform attainment of the 17.7 Ångstrom spacing for those samples containing montmorillonoids.

Semiquantitative determinations of clay mineral content of the samples

were obtained by measurements of the heights of selected diffraction peaks. Results were reported in terms of the peak intensities as "trace," "weak," "moderate," "strong," and "very strong," abbreviated as "T," "W," "M," "S," and "VS," respectively. Expandable clay mineral content was determined by the height of the 17.7 Å peak (except for the Permian Basin samples) on samples treated with glycerol. The mica clay mineral content was measured at the 10 Å peak. Chlorite minerals were determined on X-ray patterns of samples previously heated to 550° C for about 4 hours followed by cooling to room temperature in the laboratory atmosphere. The intensity of the peak at 13.6 to 14.0 Å was measured. Clay minerals of the kaolin group were determined by the intensity of the diffraction peak at 7 Å together with observation of the obliteration of this peak by heat treatment.† A 7 Å reflection that persisted after heat treatment was attributed to chlorites, but estimation of the chlorite content was made only at the 14 Å peak (Brindley and Robinson, 1951, p. 188). In addition to the above minerals, the presence of hydrobiotites, as indicated by a basal spacing of 11.4 to 12.1 Å (Walker, 1951, pp. 212-215), was noted in some samples; but no measurements were reported.

In order to make an approximate conversion of X-ray diffraction peak intensities to content of specific clay minerals, a series of known mixtures of Wyoming "bentonite" (montmorillonite), Florida kaolin, and illite from a Pennsylvanian shale, together with finely divided quartz and calcite were mixed by grinding in a mortar and tumbling on a set of ball-mill rollers. X-ray diffraction patterns were determined in the same manner as for the unknowns. Results of the calibration experiments in terms of percentage content of clay mineral versus observed diffraction intensity are presented in Table I. It is of interest to note that a rated "moderate" content of expandable clay mineral was obtained with only 5 percent of Wyoming montmorillonite, whereas 5 percent of illite produced only a "weak" rating of mica clay mineral content and 5 percent of kaolin only a "trace" rating. Calibrations such as these are presented only to indicate approximate concentrations of clay minerals. Variations in the degree of crystallinity, kind of isomorphous substitution, degree of hydration, and peak shape would alter appreciably the quantitative relationship between clay mineral content and observed X-ray intensity. No calibrations were made for the content of chlorite clay minerals because identified samples were not available.

Water-sensitive behavior of the reservoir samples was measured in the laboratory by comparing the air and (distilled, sterilized, and filtered) water permeabilities of laboratory test plugs cut from core samples at points adjacent to those from which the clay samples were taken. If the measured water permeability of a plug was approximately 60 percent or more of the dry air permeability, the sample was not considered to be water sensitive.

† If chlorites and kaolin minerals were present in the same sample, this procedure would lead to slightly high estimations of kaolin content, but the difference would be unimportant for the purpose of this work.

TABLE I.—CALIBRATION OF MEASURED X-RAY DIFFRACTION PEAK INTENSITIES¹

	Intensity of diagnostic X-ray diffraction peak				
	T (Trace)	W (Weak)	M (Moderate)	S (Strong)	VS (Very strong)
Glycerol-expandable minerals Height (mm.) of 17.7 Å peak (with heightened 10 Å peak after heat treatment)	4-6	7-12	13-23	24-45	>45
Concentration of Wyoming montmorillonite in artificial mixture	<5%	<5%	5%	10-15%	>20%
Mica clay minerals Height (mm.) of 10 Å peak	{"Break" at 10 Å}	4-8	9-15	20-25	
Concentration of illite from Pennsylvanian shale in artificial mixture		<5%	5%	10-50%	>50%
Kaolin clay minerals Height (mm.) of 7 Å peak (completely destroyed by heat treatment at 550° C)	4-6	7-11	12-25	26-45	>45
Concentration of Florida kaolin in artificial mixture	5%	5-10%	10-20%	25-50%	>50%
Chlorite clay minerals Height (mm.) of 14 Å peak after heat treatment at 550° C (No standard chlorite clay mineral available for calibration; probably similar to mica clay calibration)	3-4	5-8	9-15	16-22	

¹ X-ray diffraction patterns recorded on General Electric XRD-3 spectrometer using nickel filtered copper radiation, tube operated at 45 KV and 16 ma, 1° beam slit, A-3 time constant; samples smeared on glass microscope slides.

Brine permeabilities invariably were higher than distilled water permeabilities for water-sensitive rocks. In addition to water permeability measurements, a few of the laboratory results were based on observations of the degree of disintegration of the plugs after submersion overnight in a beaker of distilled water.

Results

Determinations of clay mineral content have been completed on samples of about 125 subsurface sediments, of which 90 are reported in Table II. Together with the laboratory code number, the geological age of the formation and the geographical location (usually state) for the well from which the sample was obtained are listed in columns 2 and 3. In columns 4 through 7 are presented the clay mineral contents in terms of the observed intensities of the significant basal plane X-ray diffraction peaks.

In order to test the simple hypothesis that significant water sensitivity is related directly to expandable clay mineral content, it is necessary to compare the clay mineral analyses with independent observations of the water-sensitive behavior of the rock sample or reservoir under study. Information concerning the water sensitivity of the subject formation is summarized in column 8, based either on laboratory or field data, and sometimes on both. These data are expressed in terms of negative, positive, or questionable water sensitivity. Additional information presented in the last column of the table is intended to amplify, for each sample, the abbreviated nature of the results in columns 4 through 8 and especially the nature of field observations of water sensitivity.

Careful study of the results presented in Table II suggests that the concentration of glycerol-expandable three-sheet clay minerals that will not lead to economically serious water-sensitive behavior corresponds to "weak" or lower intensities of the 17.7 Å X-ray diffraction peak obtained with the glycerol-treated samples. This permits us to draw the line between "weak" and "moderate" intensities, or, in other words, to predict that economically serious water-sensitive behavior will be observed in the field if "moderate" or greater intensities of the 17.7 Å line are measured on diffraction patterns of samples prepared and measured in the manner described above. Application of this criterion to the data in Table II yields a surprisingly high percentage of correct predictions. Of the 90 samples, predicted water-sensitive behavior is in complete agreement with that observed for 77. Of the other 13 samples, indicated by question marks in column 8 of Table II, the extent of disagreement between prediction and observation is generally slight and only a matter of degree. In some cases, it may be explained on the basis of inadequate sampling. In other cases, the clay was present only in shale streaks but not disseminated throughout the rock sufficiently to affect field performance. In general, the results amply justify the assumption that glycerol-expandable clay minerals are responsible for water sensitivity effects if the limitations outlined in the Introduction are kept in mind.

TABLE II. — CLAY MINERAL CONTENT AND WATER-SENSITIVE BEHAVIOR OF ROCK SAMPLES

Code	Sample description		Geological epoch and/or period ¹	State ²	Clay mineral content ³				Observed water sensitivity ⁴	Notes
	Sand and/or formation				Glycerol-expandable	Mica clay	Chlorite clays	Kaolin group		
BAW16	Humphrey	Sp., I. Pa.	OK	W	—	W	S	—	Laboratory water perm. 70% of air	
APH20	Massive Wilcox	EO., I. Te.	TX	T	M	M	M	—	Not water sensitive in field	
P398	Massive Wilcox	EO., I. Te.	TX	—	M	M	M	—	Lab. water permeability 66% of air	
P3918	Massive Wilcox	EO., I. Te.	TX	—	M	M	M	—	Lab. water permeability 45% of air	
ABY15	Slick Wilcox	EO., I. Te.	TX	W	W	W	VS	—	Lab. water permeability 82% of air	
ZX11	Slick Wilcox	EO., I. Te.	TX	T	M	W	VS	—?	Lab. water permeability 31% of air	
P193	Slick Wilcox	EO., I. Te.	TX	—	—	W	VS	—?	Lab. water permeability 20-50% of air	
P1911	Slick Wilcox	EO., I. Te.	TX	W	M	M	M	+	Water loss from mud damages cores; water floodable with brines; poorly consolidated, nonhomogeneous formation requires extensive sampling	
NP29	2nd Grubb, Repetto	I. Pl., u. Te.	CA	M	M	S	W	+	Successful water flood	
WW14	3rd Grubb, Repetto	I. Pl., u. Te.	CA	M	M	S	W	+	Not water sensitive in field	
GK13	3rd Grubb, Repetto	I. Pl., u. Te.	CA	T	M	M	M	?	Cores from offset wells not water sensitive by laboratory test; wells come in flush but die soon because of fracture porosity	
EAR1	Senora, Des Moines	Ds., Pa.	OK	—	S	S	S	—	Marked field water-sensitive history.	
AB4	Bend Conglomerate	Ds., Pa.	TX	—	M	S	VS	—	See Collingwood and Bethancourt (1953). Difficult completions; unable to core with water. Successful brine water flood	
AB16	Bend Conglomerate	Ds., Pa.	TX	—	S	M	S	—		
AB24	Bend Conglomerate	Ds., Pa.	TX	W	T	M	VS	—		
BKW10	Muddy	u. Cr.	CO	T	T	T	M	—		
BKWXY1	Muddy	u. Cr.	CO	W	T	W	M	—		
BKWXY2	Muddy	u. Cr.	CO	T	W	M	M	—		
BKWXY3	Muddy	u. Cr.	CO	—	S	M	S	—		
C15	Government Wells, Jackson	EO., I. Te.	TX	VS	W	W	—	+		

TABLE II. — Continued

Code	Sample description		Geological epoch and/or period ¹	State ²	Clay mineral content ³				Observed water sensitivity ⁴	Notes
	Sand and/or formation	Shannon, Steele			Expandable	Mica clays	Chlorite clays	Kaolin group		
BJW20	Shannon, Steele		u. Cr.	WY	S	S	S	M	+	Permeability blocks observed in field. Extremely water sensitive by laboratory test
BJW25	Shannon, Steele		u. Cr.	WY	S	S	S	M	+	
A128	Sussex, Steele		u. Cr.	WY	M	M	M	M	+	Cores completely disintegrated in water
M214	Sussex, Steele		u. Cr.	WY	—	M	M	M	+	
M226	Sussex, Steele		u. Cr.	WY	T	M	M	M	—	No water sensitivity by laboratory test
VS7	Sussex, Steele		u. Cr.	WY	T	S	S	M	?	
VS17	Sussex, Steele		u. Cr.	WY	—	M	M	M	?	Clay in shale streaks. Cores disintegrated in water along shale streaks. Cores from just above Morrison shale
NN37	Lakota		1. Cr.	WY	W	—	T	S	—	
JR15	Lakota		1. Cr.	WY	—	W	M	S	—	No water sensitivity by laboratory test
JR23	Lakota		1. Cr.	WY	—	W	M	S	—	
AWN9	Sundance		Ju.	WY	W	—	S	M	—	No water sensitivity by laboratory test
FD3	Frio		1. O1., Te.	TX	VS	T	—	—	+	
FD11	Frio		1. O1., Te.	TX	VS	T	—	—	+	Zero permeability to water
FD43	Frio		1. O1., Te.	TX	W	W	W	S	?	
PT5	Frio		1. O1., Te.	TX	T	W	M	M	?	All samples from same field
GR2	Frio		1. O1., Te.	TX	W	W	S	M	?	
GR28	Frio		1. O1., Te.	TX	M	T	M	M	+	Overall behavior is markedly water sensitive; wells die when water production starts
JN7	Frio		1. O1., Te.	TX	S	M	S	M	+	
IK21	Frio		1. O1., Te.	TX	W	W	W	T	?	Isolated sand lens
ALJ4	Frio		1. O1., Te.	TX	S	T	T	—	+	
JAI	Frio		1. O1., Te.	TX	—	—	—	—	?	Isolated sand lens

BLB21	Parkman, Mesa Verde	u. Cr.	WY	W	M	S	S	—	No water sensitivity by laboratory test	
YT109	Tensleep	u. Pa.	WY	—	W	T	—	—	No water sensitivity by laboratory test	
AYF43	Amsden	l. Pa.	WY	—	W	—	—	—	No water sensitivity by laboratory test	
HBE1	Unknown		CAN	M	S	S	+	+	Heaving shale penetrated during drilling	
C57	Gunsight	u. Pa.	TX	W	M	S	?	?	Generally not water sensitive in field although drilling mud filtrate has disintegrated some cores	
PD5	Vicksburg	l. Ol., Te.	TX	T	M	S	—	—	All samples from same field. Cores not water sensitive by laboratory tests; oil productivity in field declines after wells are worked over; but this apparently is caused by saturation blocks and precipitation of scale and not by clays as was first assumed.	
PD40	Vicksburg	l. Ol., Te.	TX	—	T	T	—	—		
PUI1	Vicksburg	l. Ol., Te.	TX	T	W	M	—	—		
PU30	Vicksburg	l. Ol., Te.	TX	—	M	S	—	—		
RP39	Vicksburg	l. Ol., Te.	TX	—	M	M	—	—		
TJ12	Vicksburg	l. Ol., Te.	TX	T	W	M	—	—		
TJ89	Vicksburg	l. Ol., Te.	TX	—	T	S	—	—		
TR8	Vicksburg	l. Ol., Te.	TX	—	T	W	—	—		
TR35	Vicksburg	l. Ol., Te.	TX	—	T	W	—	—		
ADK10	Vicksburg	l. Ol., Te.	TX	—	W	M	—	—		
NC24	Vicksburg	l. Ol., Te.	TX	—	W	S	—	—		
NC35	Vicksburg	l. Ol., Te.	TX	—	W	M	—	—		
NC41	Vicksburg	l. Ol., Te.	TX	W	M	M	—	—		
PZ20	Vicksburg	l. Ol., Te.	TX	—	W	M	—	—		
RR8	Vicksburg	l. Ol., Te.	TX	T	M	S	—	—		
RR31	Vicksburg	l. Ol., Te.	TX	W	W	W	—	—		
SRBM1	Stevens, Monterey	u. Mi., Te.	CA	S	M	—	+	+		From S. Coles Levee Field. Stevens sand in adjacent Paloma Field markedly water sensitive (Nahin <i>et al.</i> , 1951, pp. 156-157)
C72	120 Foot, Cisco	u. Pa.	TX	—	M	M	—?	—?		High laboratory water permeability. Mud filtrate caused some core disintegration
C192	500 Foot, Cisco	u. Pa.	TX	—	M	S ^s	—	—		High laboratory water permeability
C88	750 Foot, Cisco	u. Pa.	TX	—	M	W ^s	—	—		High laboratory water permeability
C202	800 Foot, Cisco	u. Pa.	TX	—	M	M ^s	—?	—?	High laboratory water permeability. Mud filtrate caused some core disintegration	

TABLE II. — *Continued*

Code	Sample description		Geological epoch and/or period ¹	State ²	Clay mineral content ³					Observed water sensitivity ⁴	Notes
	Sand and/or formation				Glycerol-expandable	Mica clays	Chlorite	Kaolin			
C147	1,300 Foot, Cisco		u. Pa.	TX	—	M	W ⁵	S	—	—	High laboratory water permeability
C149	1,300 Foot, Cisco		u. Pa.	TX	—	M	M	S	—	—	High laboratory water permeability
BLJ1	Frio		Ol., Te.	TX	S	M	W	—	+	+	Dry hole; difficult completion with water base mud; no oil on drill stem test; cores showed no water permeability in laboratory test
BNC2	Sespe		Ol., Te.	CA	S	—	W	M	+	+	Dry hole; difficult completion with water base mud; no oil on drill stem test; cores oil saturated; high pressure reservoir; apparent water block Many successful water floods
BNC26	Sespe		Ol., Te.	CA	VS	—	M	W	+	+	
BNC50	Sespe		Ol., Te.	CA	S	W	M	W	+	+	
BFRG	Bradford 3rd		Ca., De.	PA	—	W	M	—	—	—	Low laboratory water permeability, about 10-20 percent of air; wells difficult to complete with water base mud; can be water flooded with brines
C12	Yates (Pecos County)		u. Pe.	TX	S ⁶	M	M	M	+	+	
C111	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	W	+	+	
C318	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	W	W	+	+	
C334	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	—	+	+	
C1822	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	—	+	+	
C1729	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	—	+	+	
C1730	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	W	+	+	
AZZ65	Yates (Pecos County)		u. Pe.	TX	M ⁶	M	M	M	+	+	
C957	Yates (Pecos County)		u. Pe.	TX	S ⁶	W	W	—	+	+	
C1673	Yates (Pecos County)		u. Pe.	TX	S ⁶	M	W	W	+	+	
C1227	Yates (Winkler Cty.)		u. Pe.	TX	M ⁶	M	M	W	+	+	
C1112	Yates (Ward County)		u. Pe.	TX	M ⁶	M	M	—	+	+	
C1138	Yates (Ward County)		u. Pe.	TX	M ⁶	W	W	—	+	+	
C419	Yates (Ward County)		u. Pe.	TX	M ⁶	M	M	—	+	+	
C429	Yates (Ward County)		u. Pe.	TX	S ⁶	M	M	—	+	+	

C108 Queen (Pecos County) u. Pe. TX .M⁶ M M — + Low field water intake rates in water floods; wells blow in but decline rapidly

¹ Abbreviations used for geological epochs, Sp.—Springer; Eo.—Eocene; Pl.—Pliocene; Ds.—Deese; Ol.—Oligocene; Mi—Miocene; Ca.—Canadaway; for geological periods, Pa.—Pennsylvanian, Te.—Tertiary, Cr.—Cretaceous, Ju.—Jurassic, De.—Devonian, Pe.—Permian; u.—upper, l.—lower.

² Abbreviations used for states, OK—Oklahoma, TX—Texas, CA—California, CO—Colorado, WY—Wyoming, PA—Pennsylvania, and CAN—Canada.

³ Clay mineral content recorded as described in Table I and text.

⁴ Code used for recording water sensitivity on basis of field and/or laboratory observations, + = positive water-sensitive behavior, — = negative, ? = borderline case and indicates disagreements with predictions.

⁵ Hydrobiotite may be present.

⁶ Expanded to about 16 rather than 17.7 Å; also see text, "Experimental Results."

An unexpected result of this study was the behavior upon glycerol treatment of clays from all of the reservoir rock samples from the Yates and Queen sands of Permian age from Pecos, Ward, and Winkler counties in West Texas. Before treatment with glycerol or heat, the clay minerals in these Permian sediments exhibited strong basal plane spacings of 13.4 to 14.5 Å with a generally diffuse background. After heat treatment at 550° C followed by cooling to room temperature, spacings of 11.8 to 12.2 Å, often with an 8.5 Å peak and less frequently with a more or less diffuse 14 Å spacing, were observed. On a few samples the 12 Å peak was weak or very diffuse. After glycerol treatment, all the samples exhibited sharpened diffraction maxima at 15.8 to 16.2 Å together with other peaks at about 12.7, 11.2, 9.0, 8.0, and 7.0 Å. In addition, all diffraction patterns had 10 Å peaks regardless of pretreatment. Clay minerals having these properties may not be unique, but they have not been specifically reported in the literature, to our knowledge.

It is of interest to note that these samples of Permian age were the oldest sediments tested that contained glycerol-expandable clay minerals. The fact that expansion did occur upon treatment with glycerol was considered evidence that water-sensitive behavior should occur in the field, as, indeed, it does.

DISCUSSION

Water Sensitivity Predictions Based on Glycerol Expandability

The surprising accuracy of water sensitivity predictions made on the basis of glycerol-expandable clay mineral content supports the generally accepted concept that "bentonites" are responsible for water sensitivity problems (bentonite rocks usually contain expandable montmorillonoid minerals). Other workers (Fancher, Lewis, and Barnes, 1933; p. 141; Johnston and Beeson, 1945; Hughes and Pfister, 1947; Nahin *et al.*, 1951, pp. 155-157; Nowak and Krueger, 1951, pp. 165-168; and Muskat, 1949, pp. 139-142) have emphasized the importance of using brines rather than fresh water in waterflooding operations. These investigators imply that the swelling and hydration of clays are responsible for most of the difficulties involved in producing water-sensitive pay zones, although Bertness (1953) considers other factors more important. No other workers have stated specifically which clay minerals in a given formation are responsible for the observed water sensitivity. Cardwell (1954) has stated that it is impossible to state whether or not a given clay will "swell" short of making an actual swelling test. He stated, furthermore, that, "lattice expanding ability as observed in the usual X-ray test is not directly related to macroscopic swelling ability; and swelling ability cannot be predicted from such an X-ray test" (1954, Abstract). He implied that these conclusions applied to water sensitivity properties of clays in reservoir rocks also. The results obtained in our work are in complete disagreement with Cardwell's implications, as applied to reservoir problems. Inasmuch as he was concerned only

with interparticle but not intraparticle swelling, it is our belief that his conclusions should be limited to evaluations of clays for use in drilling muds and the like.

There are very few published data with which to compare the present results. A comparison of laboratory measurements of air, water, and brine permeabilities with bentonite contents of Wyoming reservoir rock core samples (Baptist *et al.*, 1952, Tables III and IV) is in general agreement with our results if we assume the bentonites to be glycerol-expandable clay minerals. In a later paper, Baptist and Sweeney (1954) presented comparisons of air and water permeabilities for reservoir rock samples from three fields in Wyoming. All of Baptist and Sweeney's data were consistent with those presented in this paper, when considered from the standpoint of *degree* of serious economic water sensitivity. They emphasized one additional point concerning the importance of the absolute permeability of a reservoir rock, *i.e.*, the lower this permeability the greater the effect of contained clay minerals on water sensitivity (aside from gas slippage effects). Rocks characterized by low fluid permeabilities generally possess a fine pore structure that can be more or less completely plugged by swollen clay particles. Rocks of higher permeabilities can tolerate higher concentrations of expandable clays before exhibiting serious water-sensitive behavior.

Mechanism of Clay Swelling in Reservoir Rocks

It is important to differentiate between interparticle and intraparticle effects in this discussion. In general it is the interparticle phenomena such as those observed when a semipermeable membrane, impermeable to suspended clay particles, is interposed between a clay sol and aqueous solution, that are referred to when osmotic pressures, Donnan membrane effects, membrane potentials, and swelling pressures are discussed. It is also correct to consider that Donnan membrane effects occur in other systems that do not include a semipermeable membrane as such but do consist of colloidal particles or a gel that restrains the diffusion of anions or cations to the outer solution (Marshall, 1949, pp. 133-134 and 162). Interstitial, expandable clay particles consisting of negatively charged layer lattice units of molecular thickness constitute such a system. The expandable layers permit entrance of water and exchange of cations with the solution, but solution anions are repelled. In view of the remarkable correlation we have found between water sensitivity effects and expandable clay mineral content, it appears reasonable to postulate that the swelling of such particles upon contact with fresh water is the most general cause of water sensitivity difficulties encountered in petroleum production operations. If the particles swell sufficiently so that portions break away and actually are dispersed in the water within a pore, flow of fluids through the pore is reduced further whenever the dispersed portions lodge in pore constrictions.

We have found that the nonexpandable clay minerals such as kaolins,

chlorites, and micas do not exhibit water-sensitive behavior to the extent the expandable minerals do. These results are more reasonable in terms of the concept discussed above. First, the nonexpandable clay particles do not swell so as to restrict rock pores. Second, although the nonexpandable clays can be dispersed in water to form stable suspensions or sols, smaller portions of the particles lining pore walls are not separated as readily as in the case of expandable minerals. Thus, fewer dispersed particles are available to plug pore constrictions. Finally, we have found, and other workers have reported, that reduced permeabilities of reservoir rock caused by flowing fresh water can be reversibly increased by flowing brines; and the cycle can be repeated many times. Experiments of this sort have been performed both in the laboratory (Muskat, 1949, pp. 141-142) and in the field (Hughes and Pfister, 1947, pp. 194-196). Such reversibility would not be expected if dispersed clay particles rather than swollen grains lining pores were largely responsible for the reduced permeability to fresh water.

Glycerol Expandability of Clays in West Texas Permian Sediments

With the exception of reservoir rock samples from the Yates and Queen sands of Permian age in West Texas, all the clay samples that expanded measurably upon treatment with glycerol expanded to 17.7 Å, within the experimental error of the diffraction data. We experienced no apparent difficulty in attaining such expansions within a few minutes after treatment according to the procedure outlined in the experimental section. Other laboratory studies did show some inconsistencies in the glycerol expansion of specially prepared monoionic-saturated (particularly potassium-saturated) montmorillonites, but we found no evidence of such behavior in the marine sediments in reservoir rock. On the other hand, the X-ray diffraction patterns (described above) of the Yates sand samples and one sample from the Queen sand, were unique, reproducible on different portions of the same sample, and uniform over a wide geographical area of West Texas embracing Pecos, Ward, and Winkler counties.

Analysis of the diffraction data obtained with untreated, heat-treated, and glycerol-treated samples of clays from the Yates and Queen sands indicates the possibility of interstratification of montmorillonoid and chlorite layers and, to a lesser extent, of montmorillonoid and illite layers. Possibly interstratification of all three types of layers occurs. Although Grim (1953, p. 28) has stated that the chlorites are the only known examples of clay minerals with regular ordered interstratification, we have found that the observed diffraction effects of the Yates and Queen samples can be explained on the basis of a regular interstratification (Brown and MacEwan, 1951, pp. 266 and 267) of montmorillonoid and chlorite layers in proportions of from 3:2 to 1:1. Additional diffraction peaks would be accounted for by the presence of micas or hydrous micas mixed with the interstratified material. The degree of regularity of interstratification and the kinds of interstratified layers appear to vary somewhat with the different samples,

but the essential nature of the clay mineral suite appears quite uniform. This explanation would require the presence of montmorillonoids in sediments older than the Mesozoic, although Grim (1953, p. 356) has found montmorillonite generally absent in older rocks.

An alternative but less tenable explanation of the unusual 16 Å diffraction peaks observed with the glycerol-treated samples requires the simultaneous presence of water and glycerol layers in a vermiculite having somewhat different isomorphous lattice substitutions and expansion properties than the vermiculite samples described by Walker (1951, p. 204) and Barshad (1950, p. 231). A layer of glycerol molecules having a thickness of 4.15 Å (MacEwan, 1948, p. 363) added to the interlayer space of partially dehydrated vermiculite (Walker, 1951, pp. 205-208) would increase the basal plane spacing from 11.8 to 16.0 Å. A recent determination of the structure of partially dehydrated magnesium vermiculite (Mathieson and Walker, 1954) reveals the sole interlayer sheet of water molecules to be bound more tightly to one silicate layer than the opposite; thus a glycerol layer interposed between the water and the more weakly bound silicate layer is not unreasonable. On the other hand, the supplemental observation that the samples heated to 550° C exhibited basal plane spacings of 11.8 to 12.2 Å would indicate a type of vermiculite to be present that would not lose its last layer of water at this temperature. The magnesium vermiculite studied by Barshad (1952, p. 177) was collapsed to an interlayer spacing of 10.0 Å by dehydration of 410° C and to 9.4 Å at 610° C. Possibly a more telling argument against the vermiculite explanation is the difficulty of accounting for the additional diffraction peaks observed with the glycerol-treated samples.

Occurrence of Montmorillonoids in Ancient Sediments

Grim (1953, pp. 356-357 and 361-362) has emphasized the general lack of occurrence of montmorillonite in sediments older than the Mesozoic. A review of our results given in Table II confirms the general absence of "moderate" concentrations of expandable minerals in Paleozoic rocks with the exception of the Permian Yates and Queen sands. It would not be surprising if further investigations reveal that all expandable, three-sheet clay minerals in Paleozoic rocks have undergone some type of compaction, dehydration, or interstratification. The Ordovician metabentonites of Pennsylvania and Illinois are examples of this trend. Whether or not partially compacted montmorillonoids would be responsible for water sensitivity difficulties in petroleum reservoir rocks would depend on the amounts present and the remaining expandability following alteration, as well as the factors discussed in the Introduction.

The wide occurrence of the same types of clay minerals in the Yates sands over wide geographical areas of three West Texas counties is a good example of the potential usefulness of clays as geological markers for

purposes of stratigraphic correlation. X-ray diffraction analytical techniques might profitably be applied more widely in mineral exploration programs.

CONCLUSIONS

The results of 90 X-ray diffraction analyses of clay samples from petroleum reservoir sands have confirmed the assumption that there exists a relation between the concentration of expandable three-sheet clay minerals in sandy sediments and the degree of water-sensitive behavior exhibited by the sands during petroleum production operations. (Water sensitivity effects for the purposes of this paper have been limited to those phenomena in sandy sediments that are the result of the specific interaction of water with rock material.) We have found with few exceptions that serious water-sensitive behavior in a given sand, from an economic point of view, occurs whenever the standardized X-ray diffraction peak intensity of the basal plane spacing after treatment with glycerol exhibits a "moderate" rating or higher. Thus, a comparatively simple criterion is available for predicting water-sensitive behavior in a reservoir sand.

In the absence of glycerol-expandable, three-sheet clay minerals, it has been found that large concentrations of nonexpandable kaolin, chlorite, and mica clay minerals in reservoir sands do not lead to economically serious water sensitivity effects. These nonexpandable clay minerals do interact specifically with water, but the degree of the observed effects is appreciably less than that observed when expandable minerals are present in "moderate" or greater concentrations. The results of this paper are in disagreement with those of Cardwell (1954), who concludes that X-ray and other physical tests are of no utility for predicting water sensitivity effects.

We have found that certain Permian sediments occurring over a wide geographical area of West Texas in Pecos, Ward, and Winkler counties contain a similar clay mineral suite, among which are minerals that exhibit somewhat anomalous expansion of the basal plane spacing to about 16 Å after treatment with glycerol. We think that these clays contain interstratified montmorillonoid and chlorite layers, or, less likely, an unusual type of vermiculite. These minerals should be useful as geological markers and suggest the more general application of clay mineral analyses in mineral exploration. In general, the expandable clay minerals found in subsurface sediments occur in formations younger than those of the Paleozoic era. Those found in Permian rocks may be somewhat compacted and partially dehydrated.

The difference between *interparticle* and *intraparticle* swelling phenomena in clay mineral-water systems has been emphasized. We have postulated that the water-sensitive behavior of reservoir rocks is generally related to intraparticle osmotic and Donnan membrane effects in clay mineral grains lining reservoir rock pores. The ultimate crystallite lamellae act as semi-permeable membranes that repel anions and restrict water entry between

layers. Nonexpandable clay mineral grains are incapable of swelling to the extent that particles containing expandable minerals do. Neither are minute portions of the layers of nonexpandable grains dispersed as readily in the water within rock pores, but grain swelling apparently is more important because flow restriction is reversible with change in the salt content of the flowing water. The basal plane expandability of glycerol-saturated clay mineral crystals may not be a completely satisfactory measure of the water sensitivity tendencies of reservoir rock, but it appears to be the best tool we have at this time.

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