SEPARATION OF SWELLING CLAY MINERALS BY A CENTRIFUGAL METHOD

by

DARRELL C. BUSH, RALPH E. JENKINS

Core Laboratories, Inc., Dallas, Texas

and

STANLEY B. MCCALEB

Sun Oil Company, Richardson, Texas

ABSTRACT

TOTAL, slightly, and highly swelling clay minerals can be separated and measured by the test procedure described. Separations of synthetic mixtures of essentially pure natural sediments indicate that the measurements are accurate within $\pm$ 1% of the true values for samples containing $<$ 20% swelling clays, and that $<$ 1% quantities can be detected. Test results using $<$ 5 micron material show that small grain size is not a problem in effective separation.

The test procedure is primarily a centrifuge separation based on the hydrated grain densities of the swelling clay minerals. The sample grains are pretreated with silicone (Dow 1107). The swelling clays are separated from rock and soil samples by centrifuging the sample-water slurry over a non-water-miscible heavy liquid. The sample is stirred violently at and above the water–heavy liquid interface during this centrifuging. The desired swelling clay fraction is recovered in the water medium and the denser minerals are collected in the heavy liquid. Water-soluble minerals are removed by filtering. Quantitative measurements are based on dry weights.

Application of this method to petroleum engineering and geology is stressed, but other disciplines will have use for the described procedure.

INTRODUCTION

FOR some petroleum reservoir engineering and geology purposes, it is more important to know the swelling capacity and amount of swelling clay minerals present in a reservoir than it is to know the crystal structures and names of these minerals. This is particularly true in petroleum engineering work involving drilling, well completion and secondary recovery techniques where there is danger of deflocculating, dispersing, and expanding the swelling clays in the production interval, and thereby reducing the effective permeability. Also, it is desirable to detect small amounts of these clays. A small amount of swelling clay, especially in a low permeability reservoir, can reduce the effective reservoir permeability to a fraction of what it was before the reservoir was disturbed by undesirable drilling, completion and secondary recovery procedures. The test procedure described here was designed to fulfill the needs of petroleum reservoir engineers and geologists. This test has been

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primarily evaluated in the 0 to 20% swelling clay range since most hydrocarbon reservoirs of economic value do not contain swelling clays in quantities above 20%. However, results of separations of Fithian Illite and Yazoo Clay are presented as a matter of interest in Table 2 along with the X-ray evaluations. Also, a synthetic mixture with 70% swelling clays and a synthetic sample containing 75% kaolinite and 25% montmorillonite have been analyzed and the results tabulated in Table 1.

The total, highly, and slightly swelling clay mineral categories, as measured by this test are here defined: total swelling clays include all clay minerals which swell as much as or more than Ca-montmorillonite; highly swelling clays include montmorillonites which swell as much as or more than Na-montmorillonite; slightly swelling clays include clay minerals which swell less than Na-montmorillonite, but as much as or more than Ca-montmorillonite.

The test procedure is primarily a centrifuge separation of minerals according to their hydrated grain densities. The hydrated grain densities of swelling clay particles are relatively low.

During the development of this procedure, it was observed that Ca-montmorillonite apparently has a hydrated grain density of < 1.85 g/cc, and that Na-montmorillonite apparently has a hydrated grain density of < 1.59 g/cc. All non-swelling, water-insoluble minerals have grain densities of 1.90 or greater. For these reasons, it is practical to separate soil and rock samples into five categories:

1. Non-swelling, water-insoluble minerals
2. Water-soluble minerals
3. Total swelling clay minerals
   (a) Slightly swelling clay minerals
   (b) Highly swelling clay minerals

These separations are accomplished by centrifuging while violently stirring the pretreated (with Dow 1107 silicone) and hydrated samples in a water medium over a 1.85 g/cc or 1.59 g/cc density non-water-miscible heavy liquid, and subsequently removing the soluble minerals by washing through filter paper.

The total swelling clay minerals are separated by centrifuging the pretreated and hydrated sample in a water medium over a 1.85 g/cc mixture of carbon tetrachloride and tetrabromoethane. The total swelling clays fraction is recovered in the water medium along with any water-soluble minerals that survived the pretest cleaning, while the non-swelling minerals are centrifuged into the heavy liquid.

The highly swelling clay minerals are separated by centrifuging the pretreated and hydrated sample in the water medium over carbon tetrachloride (1.59 g/cc). DuPont "Freon-TF" may be a non-toxic substitute for carbon tetrachloride, but has not been thoroughly investigated. The highly swelling clay minerals are recovered in the water medium along with any water-soluble minerals that survived the pretest cleaning, while the slightly swelling clay minerals and the non-swelling minerals are centrifuged into the CCl_4.

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TABLE 1.—STANDARD MIXTURES

Sample identification: Constituents in known mixtures, %*						Swelling clay recovered by testing, per cent of sample*			Error† as indicated by X-ray check
(1) Ca mont.	(2) Na mont.	(3) Kaolinite	(4) < 5 mic Quartz	(5) Diatm earth	100–mesh Ottawa sand	Total	Slightly	Highly	
	17.0		83.0			16.9	0.0	16.9	+1%
	9.7		73.9	16.4		9.7	0.0	9.7	+0.5%
	4.3		95.7			5.0	0.0	5.0	
	1.0		99.0			0.5	0.0	0.5	
	0.5		99.5			0.4	0.0	0.4	
	0.5		99.5			0.2	0.0	0.2	
	0.3		24.3		75.4	0.1	0.0	0.1	
20.3						21.0	21.0	0.0	
8.6			91.4			7.7	7.7	0.0	
5.1			94.9			6.1	6.1	0.0	
1.0			99.0			1.2	1.2	0.0	
0.3			32.5		67.2	0.3	0.3	0.0	
		8.5	76.2	15.3		0.0	0.0	0.0	
		10.9	74.0	15.1		0.0	0.0	0.0	
70.5			29.5			75.3	75.3		
	25.0	75.0				30.0	30.0		

* Per cent of sample or mixture by dry weight.

† Deviation from true per cent based on contamination found in clay fraction. Contamination in the non-swelling fraction was found to be minor in both cases.

(1) X-ray purification check = 100% montmorillonite
(2) X-ray purification check = 100% montmorillonite
(3) X-ray purification check = 2.5% illite, 5.0% quartz, 92.5% kaolinite.
(4) X-ray purification check = 2.8% illite, 95.4% quartz, 1.8% kaolinite.
(5) X-ray and petrographic purification check = 40–50% opal, 25–35% cristobalite, 10% kaolinite, 5% illite.

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TABLE 2.—X-RAY MINERAL DETERMINATIONS ON SEPARATED FRACTIONS OF NATURAL SEDIMENTS

Sample identification	Per cent of sample*	X-ray determinations of each fraction									Centrifuge test error†
		Mont.	Mixed layer	Illite	Kaol.	Chlor	Quartz	Feld.	Calc.	Misc.	
Sample no. 15, Table 3											
Highly swelling clay fraction	0.0										
Slightly swelling clay fraction	12.5	14	21	11	7	12	21	13			+5.1%
Non-swelling clay fraction	87.5	0	2	1	5	3	86	4			+1.7%
Sample no. 19, Table 3											
Highly swelling clay fraction	0.0										
Slightly swelling clay fraction	1.8	2	39	27	7	4	14	7			+0.5%
Non-swelling mineral fraction	98.2	0	0	1	3	0	91	5			none
Fithian illite											
Highly swelling clay fraction	35.0	5	43	34	5	5	3	5			+4.5%
Slightly swelling clay and non-swelling mineral fraction	65.0	7	18	30	4	4	29	8			?
Yazoo clay											
Highly swelling clay fraction	88.0	66	7	4	18		5				+20%
Slightly swelling clay fraction	3.0	46	12	4	17		7	8	6		+1.0%
Non-swelling mineral fraction	9.0	7	2	2	1		79	6	1	2‡	+0.8%

* Per cent of sample by weight as determined by centrifuge test.

† Centrifuge test deviations based on contamination found in each fraction by X-ray determinations. Montmorillonite and mixed-layer clays are considered contamination in the non-swelling fractions, and kaolinite, quartz, feldspar, and carbonate are considered contamination in the swelling fractions.

‡ Analcime.

The sample fraction collected in the CCl_4 can be separated into slightly swelling clay minerals and non-swelling minerals by a secondary centrifuging of this fraction in water over the 1.85 g/cc heavy liquid.

In all three tests, any water-soluble minerals which survive the pretest sample preparation are separated from the desired swelling clay fraction by washing through filter paper.

The quantitative measurements are based on weights after drying at 180°F. The dry densities of swelling clay minerals and their associated sediments usually lie within the same range; therefore dry weight measurements approximate volume quantitative determinations in most cases.

In designing the test, Ca-montmorillonite and Na-montmorillonite were selected to govern the empirically derived hydrated density boundaries for slightly and highly swelling clay minerals, respectively, because (1) they are the most common swelling clay minerals, (2) they differ widely in the degree of swelling in an *abundance* of water, (Foster, 1955, p. 206; Grim, 1953, p. 180), and (3) they are available in essentially pure deposits.

The analytical techniques which are primarily responsible for the success of this test are:

1. The dry sample is treated with silicone which places a permanent preferentially oil-wet film around the sample grains, but this film does not prevent the transmission of water vapor during the hydrating procedure, nor are the clay minerals irreversibly dehydrated during the oil-wet sample treatment.

The entire sample is made oil-wet primarily for the purpose of facilitating the passage of grains (having hydrated densities greater than the oil-miscible heavy liquid) through the sample-water slurry–heavy liquid interface and into the heavy liquid. However, most minerals orient sorbed water directly on their surfaces, This surface sorption of water causes a reduction in the hydrated grain densities by virtue of the oriented water acting as a part of the grain and increasing the grain volume without adding much weight. Possibly the oil-wet film may also be important in preventing or retarding this phenomenon from occurring on the non-swelling clay minerals such as kaolinite, as well as other non-swelling minerals.

2. The interfacial tension between the water slurry and heavy liquid is reduced to about 5 dynes/cm for the 1.85 density heavy liquids, and 0.5 dynes/cm for the 1.59 density heavy liquids by the use of Dowell M-38 and Dowell F-33.

3. The sample-water medium is stirred continuously during centrifuging at and above the interface with the heavy liquid, in order to keep the grains dispersed and give the individual sample grains ample opportunity to segregate themselves by density, aided by preferential wettability.

PROCEDURE

Photographs of the equipment used are presented in Plates 1 to 4. A cutaway drawing of the assembled centrifuge cup is shown in Fig. 1. All

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equipment in contact with the heavy liquid is stainless steel. Identification of the equipment parts are noted in the plates and figure; discussion of their use is included in the detailed procedure.

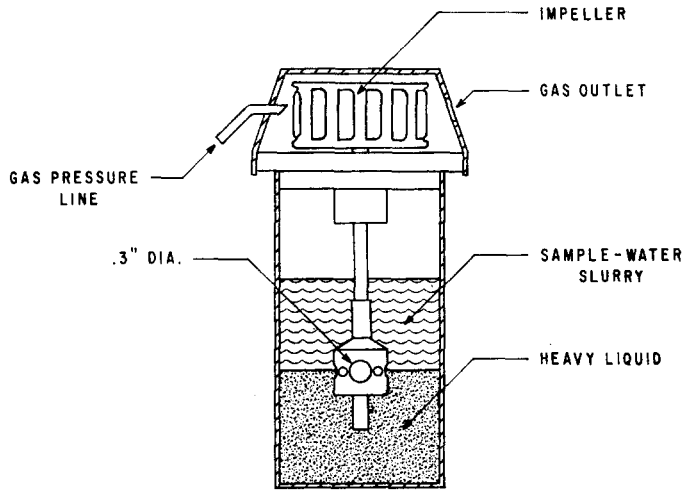


FIG. 1. Sample cup and stirring assembly.

Test Procedure Summary

1. Clean samples free of hydrocarbons, organic residues, and water-soluble salts. Then dry at 180°F.
2. Pulverize to chip clay coatings from grains.
3. Dry at 180°F to a constant weight and record sample weight.
4. Make grains of entire sample water-repellent with silicone which does not impair water vapor transmission.
5. Hydrate sample, causing swelling clay particles to expand and lower their densities.
6. Centrifuge sample-water slurry over non-water-miscible heavy liquid while stirring continuously to keep the grains dispersed and allow individual sample grains ample opportunity to segregate by density, aided by preferential wettability. The slurry–heavy liquid interfacial tension has been minimized by the use of surfactants added to the water during hydrating.
7. Filter swelling clays from the water medium and dry to a constant weight at 180°F.
8. Calculate swelling clay fraction in per cent of sample dry weight.
9. The separated fractions can then be stored for future reference.

Detailed Procedure

1. For best results, the amount of sample used is roughly based on the per cent of swelling clay. Estimate the per cent of swelling clay in the sample with

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benzidine dye. For $<$ 1 per cent, use 20 to 40 g of sample; for 1 to 5 per cent, use about 10 g; for 5 to 20 per cent, use about 4 g.

2. Thoroughly extract the hydrocarbons from consolidated samples with distilled and recycled hot toluene (less than 180°F) and a centrifugal extractor for 2 hr (more time may be required for very heavy crudes and low permeability samples). Dry at 180°F.

3. Disaggregate the sample to grain size or slightly less.

4. Place sample in special centrifuge extracting vial (Plate 1), extract about 2 hr in centrifuge extractor with hot toluene, follow with a few 10 ml slugs of benzene, and centrifuge out as much benzene as possible. Dry at 180°F.

5. Heat for 30 min in 6% hydrogen peroxide or until it appears that the sample is free of organic matter.

6. Filter sample through 2-in. diameter, 0.20-micron pore filter, in the pressure filter apparatus (Plate 1), and wash with distilled water to remove all water-soluble minerals present. Dry at 180°F.

7. Pulverize in pulverizer using two balls for 20 min. This step serves to chip the clay coatings from the grains and to free cemented grains. Grim and Cuthbert (1945) note the common occurrence and difficulty of removing these coatings. Put sample in weighed sample jar (a sidewall core sample jar is suitable).

8. Dry at 180°F and weigh. This weight less sample jar weight gives the sample dry weight. In unusual cases, when it is obvious that a significant amount of water soluble minerals are present in the rock skeleton, the quantity of these minerals can be predetermined and the sample dry weight value increased proportionately.

9. Make grains of entire sample water-repellent and impart oil-wet characteristics with a 1.0 or 2.0% mixture of Dow 1107 silicone in CCl_4. Use just enough CCl_4 to wet the sample well. Use 1% Dow 1107 in CCl_4 for samples containing $<$ 10% swelling clays and 2.0% Dow 1107 for samples containing 10 to 20% swelling clays. The amount of silicone needed may change somewhat with age or from batch to batch. This can be controlled by replacing the silicone annually and separating standard samples with each new batch. A good rule is to use the same number of milliliters of CCl_4 as there are grams in the dry sample. For a completely powdered sample, use 1.3 times this amount of CCl_4. Put a neoprene stopper on the sample jar and blend in the Spex without grinding balls for 1 min. The Dow 1107 does not impair water vapor transmission to the particles during the swelling clay hydrating process (Step 11 below).

10. Evaporate the CCl_4 to dryness in the oven at 180°F overnight. Cool the sample to room temperature and then heat the sample for 5 min at 300°F. This step serves to cure and permanently fix the silicone coatings on the sample particles.

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11. Hydrate the cooled sample after scraping into centrifuge cup, by the following steps:

Add two drops of Dowell F-33 and two drops of Dowell M-38 to the sample. These surfactants aid in wetting the silicone-treated sample particles with water for the purpose of hydrating the swelling clays. The F-33 is a dispersing agent and the M-38 is an emulsion breaker. Add 90 ml of boiling water, stir with spatula briefly, cover and let stand 30 minutes. Stir until grains of sample appear wet with water (about 20 min) with high speed hollowhead stirrer located near the bottom of the cup. Cover the cup and let stand overnight.

12. Put 110 ml of appropriate unused heavy liquid in another centrifuge cup. Re-stir sample in water with high speed stirrer as in step 11 for 20 min and pour into cups with heavy liquid. If the sample has foam, let the foam dissipate before pouring onto heavy liquid. The surfactants used in step 10 serve here to reduce the interfacial tension between the sample-water slurry and heavy liquid to a low value. Raise the hollowhead stirrer to the heavy liquid water interface, place the stirring heads in place, and place sample cups in centrifuge cups. Balance the assembled cups by weight through adding weight as needed to the outside of the centrifuge cups.

13. Hang the assembled samples, cups and stirring apparatus in the centrifuge and stir at a moderate speed for two minutes just before starting the centrifuge. Centrifuge at 1500 rpm for 10 min and 1800 rpm for an additional 20 min (using an International Size 2 Centrifuge, Plate 3); increase stirring velocity after initiation of centrifuging. The stirring velocities have not been quantitatively determined, but is has been observed that optimum stirring during centrifuging with the Core Lab apparatus ($\frac{1}{16}$ in. ID tubing, 36 in. in length) is achieved at a gas power volume of about 4.5 cu. ft./min (425–450 psi line pressure). Stop stirring for 10 min while the sample continues to be centrifuged at 1800 rpm to allow any particles in the heavy liquid near the interface to descend.

14. Stop the centrifuge, and draw off the clay–water slurry with a 20-cc syringe (no needle) and spoon spatula. Restir the clay slurry in preparation for another 30 min of centrifuging. Add a drop of Dowell F-33 to the clay slurry after each centrifuging, but do not add additional M-38. Filter the heavy liquid and re-use for the sample test duration in order to maintain the desired Dowell M-38 concentration in the heavy liquid. Place the sample in the heavy liquid in a flask and save.

15. Put 105 ml of the filtered heavy liquid in a clean cup and add sample slurry as in step 12. Again stir the sample while being centrifuged at 2200 rpm for 30 min. Centrifuge at 1800 rpm with the stirrer stopped for an additional 10 min.

16. Stop the centrifuge, withdraw clay slurry, and if any material is found in the heavy liquid, repeat centrifuging for 30-min intervals at 2200 rpm until

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no more material is collected in the heavy liquid. Add all minerals collected in the heavy liquid to that saved from step 14. Usually two 30-min centrifugings complete the separation of the average oil reservoir rock sample, and the third centrifuging turns out to be a blank run, but a necessary check.

17. Filter each fraction and wash through weighed 2-in. diameter, 0.20-micron pore filters in a pressure filter to remove any water-soluble minerals (which may still be present in spite of step 6) from the swelling clay fraction, and flush samples which have been in contact with tetrabromoethane with CCl_4 to remove any of this heavy liquid from both fractions prior to dry weight determinations. Thus, the dry weights of swelling clay minerals, and non-swelling minerals are determined, from which the per cent of sample by dry weight of each can be calculated.

18. Store the separated fractions in plastic bottles for future reference or testing.

19. The slightly swelling clays and non-swelling minerals collected in the CCl_4 during steps 13, 14, 15 and 16 can be separated from each other. Water-wash these minerals from the filter paper in step 17 before drying, add enough water to make a 90-ml slurry and add one drop of F-33, blend sample and then centrifuge over the 1.85 g/cc heavy liquid by following steps 12 through 18. The heavy liquid used here is made by adding tetrabromoethane to the CCl_4 used previously in analyzing for highly swelling clays, in order to maintain the desired Dowell M-38 concentration in the heavy liquid.

DISCUSSION

Tests performed on quantitatively known mixtures of less than 2-micron Na-montmorillonite, pulverized Ca-montmorillonite, and pulverized kaolinite blended with < 5 micron quartz, diatomaceous earth (40–50% opal), and < 100 mesh quartz indicate the test measurements are accurate to $\pm 1\%$ for samples containing $< 20\%$ swelling clays, and that swelling clay quantities $< 1\%$ of the sample can be detected. The results of these tests are tabulated in Table 1. The results of the opal separations show that even an amorphous mineral with a low grain density (1.90 g/cc) can be successfully separated from the swelling clay minerals. The results of the separations of non-swelling powdered minerals from swelling clays indicate that smallness of grain size is not a problem in effective separation.

In testing the standard mixtures, it would be improbable, but possible, to have cancelling errors due to swelling clay contamination in the non-swelling mineral fraction, and non-swelling mineral contamination in the swelling clay fraction. X-ray diffraction analysis of some of these samples show this was not the case. The quantitative error from the X-ray results are tabulated in Table 1. X-ray data obtained on some natural sediment separations are presented in Table 2.

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Table 3.—Oil Reservoir Rock Samples

Sample identification			Swelling clay recovered by testing, per cent of sample dry weight			Permeability, millidarcies			
							Liquids		
No.	Formation	Depth (feet)	Total	Slightly	Highly	Air	Fresh water	10,000 ppm NaCl brine	kW/kA ratio
1	Triassic sand	3223–24	<0.3			3049	2282		0.748
2	Triassic sand	3219–20			<0.3	2580	1985		0.769
3	Triassic sand	3205–06	0.5			548	225		0.410
4	Triassic sand	3208–09	<0.3			534	372		0.697
5	Oligocene sand	2456–58	1.6			2038		739	0.363
		2284–87	3.2			1609		1295	0.805
6	Oligocene sand	2301–04	2.7	2.7	<0.3	386		213	0.551
7	Oligocene sand	2228–31	0.1			78		67	0.859
8	Oligocene sand	2370–71	20.5			35		0.38	0.011
9	Oligocene sand	2323–26	36.4	36.4	<0.3	0.68		0.023	0.034
10	Unknown sand	5958	1.2			3.3	0.64		0.194
11	Unknown sand	5955	1.7			0.68	0.087		0.128
12	Unknown sand	5962	3.5			0.06	0.006		0.100
13	Unknown sand Australia	6747 (Well A)	6.1						
14	Unknown sand Australia	6753 (Well A)	0.0						
15	Unknown sand Australia	6824 (Well A)	12.5	12.5	0.0				
16	Unknown sand Australia	6190 (Well B)	5.1						
17	Unknown sand Australia	6195 (Well B)	0.0						
18	Unknown sand Australia	6220 (Well B)	0.0						
19	Unknown sand Australia	6831 (Well B)	1.8	1.8	0.0				
20	Unknown sand Australia	6841 (Well B)			0.0				
21	Unknown sand Australia	6851 (Well B)	7.0						

Clay mineral percentages as determined by X-ray diffraction are difficult to estimate in the silicone-treated natural sediment materials. The silicone coating has a tendency to obscure the (001) spacing of the micaceous minerals and difficulty is experienced in water-wetting the materials for dispersion. Comparative X-ray studies of silicone-treated and untreated samples have been made so prismatic spacings can be used for estimating the amounts of clay minerals present semi-quantitatively. Increasing concentrations of silicone apparently increase the amount of error in making estimates of mineral content. It also appears that different batches of silicone, because of age and perhaps quality, have different effects on the clay and the quality of the X-ray diffraction pattern. X-ray patterns of artificial mixtures do not have diffraction problems, except for those which contain mixed-layer clays.

Comparisons of swelling clay measurements made by this procedure with water permeability measurements are useful in determining whether swelling clays or small particle plugging is responsible for permeability damage. Comparisons of such data are presented in Table 3. The swelling clay analysis and water permeability data support each other except for sample number 5. The permeability reduction in this sample is possibly due to a combination of swelling clay and particle plugging. The data indicate, as others have found, that small amounts of swelling clay, either alone or combined with small mobile non-swelling particles, can cause severe reservoir permeability damage, especially in low permeability rock. Also, the data from samples numbered 6 and 9 show that the slightly swelling clays can cause extensive permeability damage.

H. van Olphen (1964) noted the importance of differentiating between osmotic swelling (greater than 10 Å) and crystalline swelling (less than 10 Å) when considering clay swelling under confining pressures such as exist in an oil reservoir. Osmotic swelling would not be anticipated in most oil reservoirs because of normal confining pressures. For this reason the present test procedure tends to approximate clay swelling under reservoir conditions since the separation is accomplished at about 40 psi centrifuge pressure.

CONCLUSIONS

For samples with $< 20\%$ swelling clays, the amount of total, slightly and highly swelling clay minerals in a rock or soil sample can be determined within $\pm 1\%$ of the true value by the described method; quantities $< 1\%$ can be detected.

The test has the following advantages over other clay mineral analytical procedures:

1. A relatively large sample is used (4 to 40 g).
2. Tests of known mixtures of natural sediments indicate the good quantitative accuracy shown in Table 1.
3. Ca-montmorillonite (as well as other slightly swelling clay minerals) are

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differentiated from Na-montmorillonite (and other highly swelling montmorillonites).

4. The separations are made under about 40 psi centrifuge pressure, which tends to approximate clay swelling under confining reservoir pressures.

5. The separated fractions can be stored for further testing

6. Relatively inexpensive laboratory procedures and equipment are required.

The test results are useful in detecting water-sensitive petroleum reservoirs. It is probable that this test, or a modification of it, has application in the fields of construction engineering, agriculture, stratigraphy, and as an aid to clay analysis by other procedures as well as further application to petroleum reservoir engineering and geology.

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