CLAY IN PETROLEUM-RESERVOIR ROCKS:
ITS EFFECT ON PERMEABILITY, WITH PARTICULAR REFERENCE TO TEJON-GRAPEVINE AREA, KERN COUNTY, CALIF.

BY FRANK C. MORRIS, QUINTIN A. AUNE, AND GEORGE L. GATES

United States Department of the Interior—1959
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* * * * * * * * * * Report of Investigations 5425

1959
Morris, Frank C

iii, 66 p. diagrs., tables. 27 cm. (U. S. Bureau of Mines. Report of investigations, 5425)

Bibliographical footnotes.

TN23.U43 no. 5425 553.282 59-60194

Library of Congress
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CLAY IN PETROLEUM-RESERVOIR ROCKS

Its Effect on Permeability, With Particular Reference
to Tejon-Grapevine Area, Kern County, Calif. 1/

by

Frank C. Morris, 2/ Quintin A. Aune, 3/ and George L. Gates 2/

SUMMARY AND INTRODUCTION

This report presents the results of a Bureau of Mines study to identify clays found in several petroleum-reservoir rocks in the Tejon-Grapevine area, Kern County, Calif., and to determine the effect of water sensitivity of the clays on the permeability of the reservoir rocks. The clays in the porous rocks were examined in detail, and the clay-mineral types were identified by differential thermal analysis, X-ray diffraction, and optical and dye-staining methods. Fresh-water damage to the permeability of the oil-reservoir rocks was indicated by a study of 125 core samples from productive formations. The study indicated that, although clays were generally less than 5 percent of the reservoir rocks, they swelled in water, particularly fresh water, and nearly blocked the flow channels through which oil flows to the well, effectively reducing the permeability of the formations. The average permeability of rock decreased from 1,600 millidarcys in air to 620 millidarcys in salt water and 120 millidarcys in fresh water.

The dominant clays in the oil-bearing sandstones were members of the montmorillonite group. They were associated with smaller quantities of clays found to be in the mica or illite group. None of the cores appeared to contain clays of the kaolinite group. In the lower section of the J.V. sandstone indications of what appeared to be the mineral sepiolite were noted.

When the liquid-permeability measurements were obtained, it was noticed that some cores swelled so much that their cementing material was ruptured, the structure of the sandstones was broken, and the core was literally pushed outward from the material in which it was mounted for the permeability measurements. The greatest swelling occurred in fresh water.

The results of these tests indicate damage to the flow capacity of the reservoir rocks caused by water reacting with the clays in the formation. Therefore the results suggest the advisability of using a nonaqueous drilling

1/ Work on manuscript completed January 1958.
fluid, such as oil or dry gas, to prevent swelling of the clays. The results of the study show that other California reservoir rocks may be expected to contain swelling clays because of their proximity to the source of these materials. These fields should be studied to ascertain their susceptibility to damage by water. As a part of this study, the clay minerals native to these formations should be identified, and their influence on the productivity of wells in the field should be evaluated.

Differential thermal analysis results and optical methods showed that the clays in the oil-reservoir rocks were not free of oil, even though they had been extracted with toluene. Because enough organic material remained on the clay to burn and affect the thermogram, the differential thermal analyses of the core samples were determined in a nonoxidizing atmosphere of nitrogen.

Reservoir rocks are an accumulation of materials deposited under water. Consequently, contaminants are common in an oil sand. The mineral composition and minerals associated with these "oil sands" have not been studied to any extent. The behavior of certain minerals associated with an oil-reservoir rock, such as the cementation materials composing perhaps no more than 2 or 3 percent of the whole body, may control the physical character so critically that little or no oil may be recovered from the rock. Certain clay types prevail among these minerals in many California oil sands.

ACKNOWLEDGMENTS

The cooperation of the Reserve Oil and Gas Company in making the oil-well cores available for this investigation and supplying related information is gratefully acknowledged. Special thanks are extended to M. C. Eastman, executive vice president, Reserve Oil and Gas Company, for permission to publish the data in this report.

PART I. CLAY MINERALS IDENTIFIED IN CORE SAMPLES FROM TEJON-GRAPEVINE AREA

History and Field Characteristics

Oilfields of the Tejon-Grapevine area are about 26 miles south of Bakersfield and east of California State Highway 99 near the southern border of the San Joaquin Valley in Kern County, Calif. The location map (fig. 1) illustrates the position of the fields in relation to others in the immediate area.

Exploration of this area was begun as early as 1923. Following a number of exploratory disappointments, some production was obtained in the central area of the Tejon-Grapevine field in 1936. The eastern and western areas of this field were proved in 1943 and 1945. Commercial production was obtained from the Tejon Hills field in 1948. These two distinct proved fields constitute the areas from which the principal current production is obtained in the geologic feature now recognized as the Tejon embayment.4/

FIGURE 1. - Location Map of Tejon-Grapevine Area, Kern County, Calif.
Each of the proved areas produces oil from multiple zones. The producing zones found are closely related stratigraphically to prolific producing horizons in other fields in the southern San Joaquin Valley. The depth of the producing horizons varies greatly from one area to another; however, the geological factors governing development of the reservoirs are similar. During development it was found, in most instances, virtually impossible to anticipate the thickness of an oil sand or the potential of any well in advance of completion, owing to extreme structural complication, lenticular overlapping of the producing sands, and changes in lithology.

Current production from the western and eastern areas is from the Transition zone, lying at the base of the Chanac and overlying the Santa Margarita. Well depths in the western area range between 2,500 to 2,600 feet, and the producing interval ranges in thickness from 50 to 125 feet. Production from the eastern area is from wells 1,860 to 2,700 feet in depth, with producing intervals 40 to 265 feet thick.

Six major producing zones have been developed in the central area — the Transition, Santa Margarita, Pulv., Valv., Olcese, and J.V. sands. Several producing zones receive their names from fossils that have been found in the formations. The Pulv. zone was named from the fossil "pulvinulinella gyridinaformis"; the Valv. zone was named from the fossil "valvulineria californica." These sands are found at depths ranging from 2,700 to 4,700 feet.

The Tejon Hills field produces oil from four major zones — the Santa Margarita, Valv., D.K., and L.O. Shallow production from the Santa Margarita is found at a depth range of 365 to 550 feet. The L.O. zone produces at a depth of about 2,150 feet, and 1 well has logged this zone at 3,700 feet.

During March 1957 there were 424 active wells in this area, producing an average daily total of 6,875 barrels of oil. As of June 30, 1956, the cumulative production from the Tejon-Grapevine field had exceeded 12,700,000 barrels of oil from a proved area approximating 1,700 acres; the cumulative production from the Tejon Hills field had exceeded 7,900,000 barrels of oil from a proved area of about 900 acres.

Geology

Structural Relations

The Tejon-Grapevine field and the Tejon Hills field lie in the Tejon embayment, a structural basin in the extreme southeasterly portion of the San Joaquin Valley, Kern County, Calif. This basin lies on the northwest flank of the Tehachapi Mountains and on the west flank of the southernmost part of the Sierra Nevadas. The mountainous areas consist of Jurassic and older basement rocks with a border of Pleistocene to Eocene sediments exposed between the basement rocks and the valley of alluvium.

The Tejon embayment is structurally isolated from the rest of the San Joaquin Valley by the White Wolf fault zone, a major and still active fault zone that borders the embayment on the northwest and is parallel to and structurally similar to the Garlock fault zone to the southeast, as indicated in figure 2.
The movement along the White Wolf fault opposite the embayment has been in part vertical and of the thrust type. The Tejon embayment is on the upthrust block, the main San Joaquin Valley to the north on the downthrust block. The above-defined differential movement is relative. The actual absolute vertical movement along the fault in this area has been a downthrust of the Northern San Joaquin Valley block. This is indicated in figure 2. The top of the Lower Pliocene surface, for example, shown by structural contours in figure 2, has subsided from 0 to 4,000 feet on the embayment side of the fault, whereas on the Northern San Joaquin Valley side this structural subsidence has been on the order of 6,000 - 10,000 feet opposite the embayment.

The lesser subsidence on the embayment side of the White Wolf fault, coupled with structural movement resulting from forces acting along major fault systems adjoining the Tejon embayment, has created numerous domes, flexures, and stratigraphic unconformities. Strata are broken further by short tensional faults crossing the embayment. Oil reservoirs in the Tejon embayment are therefore formed along stratigraphic and structural traps, often with the aid of faulting. Figure 3 shows the relation of producing sands in the Tejon area to those of other areas in the San Joaquin Valley.

Paleogeography and Sedimentation

In discussing the paleogeography of the San Joaquin Valley, Hoots, Bear, and Kleinpell\(^5\) have shown in illustrations that from upper Eocene through upper Miocene time the Tejon-Grapevine and Tejon Hills fields lay at the head of an embayment in which marine sediments were deposited. Since during much of this time there was nonmarine sedimentary deposition in the Coast Ranges west of the Tejon embayment, with marine sediments again farther to the west, it would appear that sediments deposited in the Tejon embayment during much of Tertiary time must have come from land masses to the south and/or the east.

There was some contribution from volcanism, in the form of lava flows and ash, in the Tejon embayment during Oligocene and lower Miocene time. Volcanism in the Coast Range to the west and possibly from the Transverse Ranges to the south and from the Tehachapi Mountains\(^6\) to the southeast undoubtedly contributed considerable ash to sediments deposited in the Tejon embayment during middle and upper Miocene time.

Because of the close proximity of these areas to the San Joaquin and the Ventura Basin, it may be expected that the clay minerals associated with the sediments found in these two basins will have similar characteristics. It is recognized that swelling clays of the montmorillonite group are formed from diagenesis of materials of volcanic origin; consequently, it is reasonable to believe that the occurrence of these swelling clays is not peculiar to the southern San Joaquin and Ventura basins but also may occur in sediments found in other oil-producing areas on the Pacific coast.


FIGURE 3. - Stratigraphic Section of Southern San Joaquin Basin.
Correlations

The stratigraphic cross section in figure 3 shows the relation between producing sands in the Tejon Hills and Tejon-Grapevine fields and those in other San Joaquin Valley producing areas.

Noteworthy are the correlation between Santa Margarita sands in the Tejon embayment and the Stevens sands in the center of the valley and the age correlation of the Valv. sands to Temblor sands on the west side of the valley. The cross section does not show the age relationship of the sands examined in the Tejon area to diatomaceous shales of the Monterey formation, to the west of the valley. This relationship will be considered under the discussion of clay types and volcanism.

Santa Margarita production and that from sands of equivalent age have been obtained from the Mountain View, Paloma, Coles Levee, Wheeler Ridge, Buena Vista, and Midway-Sunset fields in the southern San Joaquin Valley.

Sands of the Pulv., Valv., and Olcese zones also produce in Mountain View and Wheeler Ridge fields but generally are too impermeable for production in the south central and southwest portions of the San Joaquin Valley.

Cementation and Clay Content

The high permeability values obtained for the Santa Margarita, Pulv., Reserve, and Valv. zones probably are due to the low degree of compaction and cementation in these zones. Carbonate cementing material apparently has reduced the permeability of the Olcese and J.V. sands. Only six samples of the L.O. zone were tested, and the observed permeability values may be too high to be representative of the zone as a whole.

Montmorillonite was present in all zones and was the dominant clay in all except the Valv. and the lower part of the Reserve, where submicas predominated, and in some marly beds in the J.V. zone sepiolitelike clays appeared dominant. There appears to be no apparent distinction between dominant clay type and permeability reduction by clay-water reaction in the zones tested. However, in some cores, particularly in the Reserve sand where there was an apparent change in mineralogy of the dominant clay type near the middle of the sand, too few samples were tested for water permeability to indicate a relationship between permeability and clay type.

Geologic Clay-Mineral Distribution

The primary factors controlling clay mineralogy appear to be (1) the association with other rock-forming minerals and solutions in the environment of deposition and (2) the degree of lithification, compaction, and alteration after burial.
Grim\(^{7/}\) has pointed out that the alkaline marine environment tends to bar formation of kaolin in favor of the other clay minerals and that in ancient sediments all the clay-mineral types tend to alter to submicas and the montmorillonites undergo this change the most rapidly. The changes in chlorite clay minerals are less clear. It would appear, then, that in many Mesozoic rocks and in nearly all Paleozoic marine rocks submicas are by far the dominant clay type.

There appears to be considerable variation in clays with respect to environment relationships, with clays listed in the order of probable relative importance for each environment.

**TABLE 1. - Marine clay environments**

**Shelf associations:**
Stable - submica (glauconitic).
Unstable - submica, montmorillonite, kaolin.

**Interior basin associations:**
Normal open marine - submica.
"Wedge" arkosa - kaolin, submica.
Arid restricted (includes playa deposits) - sepiolite.
Black shale restricted - submica.

**Geosynclinal associations:**
Without volcanics - submica, kaolin.
With volcanics - montmorillonite, submica.

The environments are those enumerated by Krumbein and Sloss,\(^{8/}\) and the clay-mineral associations are compiled largely from Grim.\(^{9/}\)

Because California oil sands exclude ancient sediments and are wholly contained within the Pacific coastal belt of Tertiary volcanism, it is to be expected that montmorillonites will make up the predominant clay type associated with these sediments. As shown in table 9 (appendix), montmorillonite was found to be the dominant clay in each sand in the Tejon-Grapevine and Tejon Hills areas, except the Valv. (another possible exception is marls in the J.V. sand). Likewise Quaide\(^{10/}\) found that this condition existed in a study of clays in formations in the Ventura Basin area.

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\(^{9/}\) Work cited in footnote 7, pp. 348-366.

There is no reason to conclude that the Tejon and Ventura areas are unique in California with respect to oil-sand clay mineralogy. The same general environmental conditions prevailed in the sands of most other oil-producing areas within the State.

There is reason to believe that California oil sands are unique among those of North America in that harmful, swelling-type clays are so predominant. A clay-mineralogy and clay-oil-production problem of comparable magnitude appears common in only one other oil-producing area in the United States, that is, in certain oil sands in the Gulf Coast area. The study of clay-distribution types in that area is rather different, as the swelling montmorillonites were probably largely transported from midcontinent bentonite areas and their distribution was controlled by sedimentation patterns rather than by direct association with bentonites or volcanic ash and detritus.

**Clay Minerals Identified**

Montmorillonite, submicas, and a clay mineral thought to be sepiolite were found in the clay-size fractions of the cores recovered from the oil-producing zones of the Tejon-Grapevine field. The clay minerals were identified from differential thermal patterns, optical and dye-staining techniques, and X-ray diffraction patterns of a representative sample. Semiquantitative results reported are based upon a comparison of the amplitude of the peaks of DTA (Differential Thermal Analysis) curves of clay references with the peak amplitude of DTA patterns of the clay-size fractions from cores, figures 21-25 (appendix).

Montmorillonite was found to be the predominant clay mineral associated with the cores studied; in most cores it was associated with submicas. The identifications apply to the characteristics of the individual clays and not to clay complexes; no attempt was made to distinguish mixed-layer clays. Identification of the clay mineral reported as sepiolite \( \text{Mg}_3\text{Si}_{40}_{11} \cdot n\text{H}_2\text{O} \) may be questionable; the sharp exothermic peak at approximately 830° C. is characteristic of this clay (see figs. 24 and 25, J.V. sand, 7,088.5, 7,100.5, and 7,249 feet). It is also found in DTA patterns of other magnesium silicates,\(^{11}\) such as serpentine and possible chlorite-type clay minerals. Core samples where sepiolite was found were from the J.V. zone at depths greater than 7,000 feet and associated with carbonates. According to Winchell and Winchell,\(^{12}\) the occurrence of sepiolite with carbonates is common.

The DTA patterns of the clay-size materials from the deep cores approximated curves of clay references more closely than the DTA patterns from the shallow cores, indicating that there might be a greater clay content in the

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minus-12- to 14-micron-size fraction from the deeper cores, or perhaps the clays are formed more completely in the deeper sediments and exhibit better crystallinity.

Kaolinite was not found in the clay-size material from any of the cores examined by either of the three identification methods used. However, this does not absolutely preclude the presence of kaolinite in the zones sampled.

The clay minerals found in this investigation agree with those identified by Quaide, who examined 65 sandstone samples and a large number of shale samples from the Ventura Basin in southern California. Clay-mineral identification was determined, using X-ray diffraction on clay-size fractions of surface-outcrop samples and oil-well core samples. Semiquantitative estimates of the clay content of the X-rayed sample was made using a procedure developed by Johns and modified by Quaide. The method is based on a comparison of ratios of intensities of particular X-ray reflections from components of natural mixtures with experimentally determined values of ratios of the same reflections.

The clay-mineral groups montmorillonite, mica (the term "mica" used by Quaide corresponds with the term "submica" used in this report), and chlorite were found in nearly all of the samples analyzed. Kaolinite was not identified in any samples. A correlation of the stratigraphic depth below horizon A and the ratio of mica to montmorillonite noted in shales of the Ventura Avenue field is illustrated in figure 4.

Montmorillonite clays predominate over mica by a ratio of 3:1 by weight in the upper part of the section. This relationship appears to hold to a depth of about 4,000 feet. The ratio changes gradually with depth, and at 6,000 feet the 2 clay minerals are present in approximately equal weights.

In the interval between 6,000 and 8,000 feet the data are badly scattered; however, the mica clays appear to be more abundant. From 8,000 feet to the Pliocene-Miocene contact, montmorillonite again becomes the more abundant mineral present. It predominaates over mica by approximately 2:1 by weight. In the Miocene shales the ratios are again scattered; however, there is an indication that the mica clays predominate. The Miocene shales received limited study; only 10 samples were available.

Calculated percentages of the mica, montmorillonite, and chlorite clay minerals present in the sandstones of the Ventura Avenue field have been plotted against the stratigraphic depth below horizon A in figure 5. The occurrence of clay minerals in the sandstones appears to be regular through the sampled interval for micas and montmorillonite. Little variation is noted with depth. The chlorites become more abundant at greater depths, until they make up 80 percent or more of the clay-size fractions.

13/ Work cited in footnote 10 (p. 8).
FIGURE 4. - Ratio of Mica to Montmorillonite in Shales Plotted Against Stratigraphic Depth of Samples Below Horizon A of Ventura Avenue Field.
FIGURE 5. - Percentages Determined for Mica, Montmorillonoids, and Chlorite Constituents of Clay Fraction of Sandstones, Ventura Avenue Field.
Permeability of Core Samples

The permeability of a porous medium to liquids may be calculated from laboratory measurements from Darcy's equation, \( K = \frac{u Q L}{A(P_1 - P_2)} \), where \( K \) is the permeability, in darcys; \( u \), the viscosity, in centipoises; \( Q \), the rate of liquid flow, in cubic centimeters per second; \( L \), the length of the porous medium, in centimeters; \( A \), the cross-sectional area, in square centimeters; and \( P_1 - P_2 \), the pressure differential, in atmospheres. In deriving this equation the assumption is made that there is no reaction between the flowing fluid and the porous medium; under these conditions, the permeability of the porous sample will be a constant independent of the fluid phase flowing through it.

Comparison of the liquid permeability with dry-air permeability of many core samples showed broad divergence; the dry-air-permeability values are consistently higher than the liquid-permeability values. This indicates that the assumption has not been satisfied; the liquid has reacted with the core sample, causing a physical change decreasing the permeability of the core to the liquid phase.

A measure of the permeability of a core in equilibrium with water of various salines may be used as a measure of the effective swelling of the clays in the liquids. Also, changes in permeability are a measure of the damage that may be done to a reservoir sandstone when water enters the formation.

To measure the permeability of the Tejon-Grapevine cores, they were cast in sealing wax within glass cylinders. The equipment for measuring liquid permeability was made of plastics or glass to eliminate corrosion of metal and subsequent plugging of the core sample by the corrosion products. An important part of the liquid permeameter is a filter immediately ahead of the core sample. The filter removes suspended material from the liquid before it enters the core. The filter was removed and cleaned when necessary.

The permeability of the cores to the flow of dry air, a sodium chloride brine containing 2,000 grains of sodium chloride per gallon, and fresh water was measured.

After the core samples were cleaned with toluene and dried at 105° C., the permeability to air was measured; then the cores were evacuated, and the brine was added to the cores. To assure complete hydration of the clays, the cores, saturated with brine, were set aside with tygon tubing as a bactericide. Tygon tubing was found to inhibit growth of organisms in water.

After a minimum of 2 weeks the permeability to brine was measured. The core samples were then placed in distilled water with tygon tubing as a bactericide, and the water was changed frequently until no more chloride diffused from the samples. The permeability was then measured with distilled water. The permeability of the core samples to these fluids is listed in table 9 (appendix).
The permeability of a few samples was measured with a sodium carbonate solution having a pH of about 10. This solution was prepared to simulate the high-pH filtrate from a water-base drilling mud. Although it is known that many clays swell and are dispersed in high-pH solutions, the results of these tests indicated that the permeability to this solution was less than but did not differ greatly from that measured with distilled water. Consequently, the remaining permeability determinations with the high-pH solutions were not measured.

The average permeability to air for all 125 core samples was 1,600 millidarcys. The average permeability of the same samples to brine (2,000 grains of sodium chloride per gallon) was 620 millidarcys. In contrast, the permeability to fresh water was only 120 millidarcys. Thus, the permeability to fresh water is only 7-1/2 percent of the permeability to air.

Comparison of the permeability to air, brine, and fresh water of cores from all eight productive zones is shown graphically in figure 6. The effect of air, brine, and fresh water on the average permeability of all samples is shown in figure 7. The results are summarized in table 2.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Number of samples</th>
<th>Clay-mineral content</th>
<th>K_a, dry air</th>
<th>K_b, brine</th>
<th>K_w, fresh water</th>
<th>K_w/K_a percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santa Margarita</td>
<td>3</td>
<td>Montmorillonite</td>
<td>2,100</td>
<td>730</td>
<td>430</td>
<td>20.5</td>
</tr>
<tr>
<td>Pulv. ..........</td>
<td>6</td>
<td>do. Montmorillonite</td>
<td>3,100</td>
<td>1,700</td>
<td>1,000</td>
<td>33.</td>
</tr>
<tr>
<td>Reserve ........</td>
<td>10</td>
<td>do. Submiccas</td>
<td>1,900</td>
<td>650</td>
<td>78</td>
<td>4.</td>
</tr>
<tr>
<td>Valv. ..........</td>
<td>10</td>
<td>Submiccas Montmorillonite</td>
<td>13,000</td>
<td>6,300</td>
<td>1,100</td>
<td>8.4</td>
</tr>
<tr>
<td>Olcese ........</td>
<td>9</td>
<td>Montmorillonite</td>
<td>620</td>
<td>320</td>
<td>17</td>
<td>2.7</td>
</tr>
<tr>
<td>J.V. (13-33)...</td>
<td>34</td>
<td>do. Submiccas</td>
<td>110</td>
<td>44</td>
<td>3.1</td>
<td>2.8</td>
</tr>
<tr>
<td>D.K. ...........</td>
<td>31</td>
<td>do. Submiccas</td>
<td>530</td>
<td>170</td>
<td>6.3</td>
<td>1.2</td>
</tr>
<tr>
<td>L.O. ...........</td>
<td>6</td>
<td>do. Montmorillonite</td>
<td>1,500</td>
<td>540</td>
<td>10</td>
<td>.7</td>
</tr>
<tr>
<td>Average of all samples</td>
<td>-</td>
<td>-</td>
<td>1,600</td>
<td>620</td>
<td>120</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The results of the permeability tests show that all formations were susceptible to damage by water, particularly fresh water. The permeability of the L.O. zone decreased from an average of 1,500 millidarcys to 10. Thus, the permeability to fresh water is 0.67 percent of the permeability to dry air. The permeability of the Pulv. zone (the least damaged of the 8 producing zones tested) decreased from an average of 3,000 millidarcys to 1,000.

These tests show that fresh water greatly reduced the permeability of the oil-reservoir core samples. The large reductions in permeability observed may be expected from formations in which montmorillonite predominates.
FIGURE 6 - Average Permeability of All Samples From Tejon-Grapevine Area to Flow of (1) Air, (2) Brine, and (3) Fresh Water.
FIGURE 7. - Air, Brine, and Fresh-Water Permeability of Cores From Eight Producing Formations in Tejon-Grapevine Area.
Visible Swelling of Cores in Fresh Water

The addition of fresh water to the cores in preparation for determining the fresh-water permeability showed that many cores swelled appreciably.

Figure 8 is a sketch showing the physical change of a core in fresh water. In figure 9 are photographs of cores illustrating this physical change. Although swelling of a sample portion of the reservoir rock may be observed in the laboratory as it expands in length, breadth, and depth, the formation in the earth must swell into the pore space, thereby restricting the size of the pore channels required for the flow of oil to the well bore.

Some cores swelled until the bond between the sand grains was broken and the rock disintegrated. To show this visible change with time, photographs were taken at different intervals after contact with fresh water. Figure 10 shows how the core sample from a depth of 2,785 feet in the Santa Margarita sandstone increased in volume as the clays hydrated and swelled. This sample had a permeability of 3,100 millidarcys to dry air, 170 millidarcys to brine, and zero to fresh water until the sample disintegrated. As may be seen in figure 10c, the clay pushed outward from the core holder, tipping it to one side.

FIGURE 8. - Sketch of Core Sample From an Oil-Reservoir Rock, Before and After Swelling in Fresh Water, Tejon-Grapevine Area.
The formation photographed is from the Santa Margarita formation, which is correlated (in other parts of the San Joaquin Valley) with the Stevens sandstone. The Stevens sandstone is one of the important oil-reservoir rocks in California.

Figure 11 is a sketch showing distribution of clay in the pore space of reservoir rocks. This sketch is based on a study of thin sections, such as shown in the photomicrograph, figure 12. Shown also is a sketch indicating how the clay may plug the flow channels by swelling and holding water from flowing, except when subjected to very large pressure differentials. This figure illustrates how clay that is only a small part of the reservoir rock may swell in fresh water and effectively block the tiny pores through which oil and gas must pass to reach the well bore.

Extensive swelling of these cores may reasonably be expected, because previously reported studies show that clays containing some montmorillonites swell appreciably. Mielenz and King report "free swelling" of clays ranging from a maximum of 2,000 percent for hectorite from California to a minimum of 5 percent for a New Mexico kaolinite. Wyoming bentonite, which is used in many water-base drilling muds, is reported to have a "free swell" ranging from 1,400 to 1,600 percent.

Although all cores did not show visible swelling, there was large reduction in the permeability of these cores. Apparently, the degree of swelling in these cores sufficed to cause a large reduction in permeability but not to break the visible structure of the rock.

(a) Zero hours; no evidence of clays swelling.

(b) 22 hours; clays have begun to swell, and clay particles can be seen on top and at side of mounted sample.

(c) 23 hours; clays have swelled enough to raise mounted sample in a tilted position.

(d) 168 hours; clays have expanded out of core, covering top of it, and at base of sample. Comparison with (a) shows volume of hydrated material that has migrated out of core.

FIGURE 10. - Swelling of Core From Santa Margarita Sandstone (2,785 Feet) in Fresh Water. Time of Hydration Is Indicated.

**Determination of Particle Size**

In the study of clays in petroleum-bearing rocks the question arises, How much of the reservoir rock is clay? Clay can be defined from several points of view. Grim\(^{16}\) states that: "Clay is used as a rock term and also, as a particle-size term in the mechanical analysis of sedimentary rocks, soils, etc." Clay, as a rock term, is a natural material, very fine grained

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and essentially composed of silicate minerals - the clay minerals. As a particle-size term, the clay fraction, according to the Wentworth scale, is all material smaller than 4 microns. In soils the fraction smaller than 2 microns is often defined as the clay-size fraction. However, Miezenz and King state that clays are composed predominantly of particles less than 20 microns in diameter; but sand, silt, gravel, and organic materials are present. Crystals of clay minerals commonly occur in sizes larger than 5 microns and at least as large as 100 microns in undisturbed materials.

To define clay by means of particle size only is inadequate, because many materials (such as quartz and feldspar) may be smaller than 4 microns in size but do not have many of the other properties associated with clays and clay minerals. Many larger particles have the other properties of clays, such as plasticity in water and an affinity for it. However, the particle-size fraction below about 4 microns generally has a higher concentration of clay minerals of interest to petroleum engineers, because the minute quantity of these particles in reservoir rocks may be affected by their ionic environment (interstitial water, whether introduced or naturally occurring); and they may swell, closing the pore channels required for the flow of petroleum to the well bore.

To measure the portion of the Tejon sandstone cores that is smaller than 4 microns, 3 core samples were crushed lightly and analyzed for particle-size distribution, using the method described by Gates.

18/ Work cited in footnote 15 (p. 18), p. 213.
This method utilizes the hydrometer to measure the quantity of particles in suspension, and the results are expressed as percentage of material related to an equivalent spherical diameter of particles. No dispersing agent other than distilled water was used, because any method for determining particle-size distribution shows the distribution resulting from the mechanical and chemical process instead of the particle-size distribution of the original core materials.

The results of tests for 3 cores shows that none of these cores had more than 8 percent of the solids that may be classified as the clay-size fraction - smaller than 4 microns.

Cores that contained only a small quantity of material in the clay-size fraction were susceptible to large reduction in permeability when fresh water entered the cores. The results are listed in table 3.

### TABLE 3. - Relation of clay-size particles, clay minerals, and permeability of core samples

<table>
<thead>
<tr>
<th>Well number</th>
<th>Depth, feet</th>
<th>Particles smaller than 4 microns, weight-percent</th>
<th>Clay-mineral content</th>
<th>Permeability, md.</th>
</tr>
</thead>
<tbody>
<tr>
<td>62-33</td>
<td>7,113.5</td>
<td>0</td>
<td>Montmorillonite Submicras</td>
<td>110</td>
</tr>
<tr>
<td>13-33</td>
<td>7,224</td>
<td>7</td>
<td>do. Submicras</td>
<td>520</td>
</tr>
<tr>
<td>13-33</td>
<td>7,266</td>
<td>8</td>
<td>do. do.</td>
<td>470</td>
</tr>
</tbody>
</table>

The complete particle-size distribution of the particles in the cores from 7,224 feet is shown in figure 13.

When the core particles are dispersed in water, the larger particles settle to the bottom of the container quickly, and the smaller particles settle more slowly, according to Stokes' law. Figure 14 shows the core particles that settled from suspension in water. The white layer at the top of the sediments was a finely divided, gelatinous material that could easily plug the small channels in a reservoir rock. The figure shows that, although particles smaller than 4 microns were only 8 percent by weight of the reservoir sandstone, the volume of the fine material well-hydrated in water is approximately 20 percent of the total volume of the solids. Thus, the finely divided material in the clay-size fraction swells in water so that it becomes a proportionately larger part of the volume of the rock solids.
Additional samples of cores from the J.V. sandstone, well 62-33, were suspended in distilled water, and the portion containing particles below 14 microns equivalent spherical diameter was removed with a pipet, dried, and weighed. These results are listed in table 4.

Thus, the clay-size fraction is only a small part - about 2 weight-percent - of the reservoir rock, but it has a large effect (approximately tenfold) on the flow of liquids through the rock to the well bore.

Although the clay-size materials in sandstone cores are smaller than about 4 microns, they are approximately in the size range of the pore sizes in most reservoir rocks. Muskat\textsuperscript{20} points out that the pore sizes of sandstones generally range from 10 to 100 microns in diameter. The pore-entry radius of a few cores was measured by mercury injection. The average measured pore-entry radius ranged approximately from 2 to 20 microns. Therefore, clay particles are of such dimensions that they may easily fill the pore channels.

FIGURE 14. - Particles of J. V. Sandstone That Settled From Suspension in Fresh Water.

TABLE 4. - Relation of clay-size particles (minus-14-micron), clay minerals, and permeability of core samples

<table>
<thead>
<tr>
<th>Depth, feet</th>
<th>Particles smaller than 14 microns, weight-percent</th>
<th>Clay-mineral content</th>
<th>Permeability, md.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Dominant</td>
<td>Minor</td>
</tr>
<tr>
<td>7,086.5</td>
<td>2.3</td>
<td>Montmorillonite</td>
<td>Submicas and sepiolite</td>
</tr>
<tr>
<td>7,087.5</td>
<td>2.7</td>
<td>Montmorillonite</td>
<td>Submicas</td>
</tr>
<tr>
<td>7,088.5</td>
<td>1.5</td>
<td>do.</td>
<td>do.</td>
</tr>
<tr>
<td>7,089.5</td>
<td>4.0</td>
<td>do.</td>
<td>do.</td>
</tr>
<tr>
<td>7,091.5</td>
<td>4.2</td>
<td>do.</td>
<td>-</td>
</tr>
<tr>
<td>7,092.5</td>
<td>4.8</td>
<td>do.</td>
<td>Submicas</td>
</tr>
<tr>
<td>7,100.5</td>
<td>4.8</td>
<td>do.</td>
<td>-</td>
</tr>
<tr>
<td>7,104.5</td>
<td>1.4</td>
<td>Montmorillonite</td>
<td>-</td>
</tr>
<tr>
<td>7,105.5</td>
<td>2.0</td>
<td>Montmorillonite and submicas</td>
<td>140</td>
</tr>
<tr>
<td>7,107.5</td>
<td>3.1</td>
<td>Montmorillonite</td>
<td>-</td>
</tr>
<tr>
<td>7,108.5</td>
<td>1.3</td>
<td>do.</td>
<td>-</td>
</tr>
<tr>
<td>7,109.5</td>
<td>2.4</td>
<td>do.</td>
<td>Submicas</td>
</tr>
<tr>
<td>7,110.5</td>
<td>1.7</td>
<td>do.</td>
<td>do.</td>
</tr>
<tr>
<td>7,112.5</td>
<td>1.5</td>
<td>Montmorillonite and sepiolite</td>
<td>150</td>
</tr>
<tr>
<td>7,113.5</td>
<td>1.2</td>
<td>Montmorillonite</td>
<td>do.</td>
</tr>
<tr>
<td>7,114.5</td>
<td>1.5</td>
<td>do.</td>
<td>-</td>
</tr>
<tr>
<td>7,115.5</td>
<td>1.9</td>
<td>do.</td>
<td>Submicas</td>
</tr>
<tr>
<td>7,116.5</td>
<td>0.9</td>
<td>do.</td>
<td>Sepiolite</td>
</tr>
<tr>
<td>7,118.5</td>
<td>1.1</td>
<td>do.</td>
<td>-</td>
</tr>
<tr>
<td>Average</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PART II. DISCUSSION OF CLAYS IN OIL-RESERVOIR FORMATIONS

Clay in Oil Reservoirs

The genesis of reservoir rock predicates the movement of particles, particularly sand grains, that accumulate to form sediment.\(^{21}\) Associated with the sand grains are small particles in the clay-size fraction. The clay-size particles are intermixed with the sand grains and become integral parts of the sandstone when the rock is consolidated.

Most particles transported to form sediments are products of the weathering and erosion of rocks. Pettijohn\(^{22}\) has pointed out that the chief detrital components are quartz, feldspar, and minor amounts of clay materials. Where these particles are deposited with nearly perfect sorting of the grains, the quartz particles form sandstones, and the more finely divided clay particles form shales. However, in natural deposition sorting of the particles is seldom perfect; as a result, the sandstones contain finely divided clay particles. The mixture of visible quantities has led to the use of the term "dirty sandstones."

Pettijohn\(^{23}\) describes the clay minerals in sedimentary rocks as stable secondary minerals formed by chemical decay of the unstable primary minerals in the source rock. Many sediments contain small quantities of materials of volcanic origin that are classified as glass. Volcanic glass generally decomposes to form montmorillonites. The origin of this decomposition product is recognized as volcanic, but in impure sandstones the relationship often is lost due to the intimate mixture of clay with other mineral grains and cement and alteration of the volcanic glass.

The role of clay in oil-reservoir rocks has been clearly discussed by Johnston.\(^{24}\) He points out that, although clays have been studied for years, only recently has the presence of clays in reservoir sands been recognized as an important factor in the production of petroleum from reservoir rocks. Clays are important in oil-bearing sandstones because they occur as small particles in the pore space associated with the formation water and oil. This association is important, because the clays exhibit changes with respect to the water and its dissolved ions. Certain types of clay minerals swell in some water solutions, affecting the flow capacity of the formation.

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\(^{23}\) Work cited in footnote 22, pp. 85-89.

It is known that clays in reservoir sandstones affect the electrical log of the borehole in the reservoir rock. Wylie\(^25\)/ has discussed the role of clay in well-log interpretation.

In 1933 Fancher, Lewis, and Barnes\(^26\)/ stated that the discrepancy between permeability measured with air and with brine largely resulted from hydration of the clays present in the oil sand rather than movement of loose particles within the porous rock. Johnston also observed a similar phenomenon, and he believes that the plugging resulting from movement of fine particles is not of the same order of importance as hydration and swelling of the clay particles.

In 1942 Travers\(^27\)/ mentioned water blocking around a well bore (resulting from water-base mud-filtrate invasion) as a condition that lowered the productivity index and thus the ultimate economic recovery. He did not mention the filtrate invasion as having any effect on the clays but only as occupying space in the pores, thus reducing the permeability to oil.

In 1943 Johnston and Sherborne\(^28\)/ showed the large reduction of well productivity resulting from killing a well with fresh water. They discussed the fact that cores containing drilling-mud filtrate have lower permeability than the same cores after drying. It was also stated that excessive deviations of well productivity from theoretical values resulted more from interaction between the interstitial water and certain constituents of the rock than from blocking caused only by the presence of water.

In 1945 Johnston and Beeson\(^29\)/ discussed in detail permeability of more than 1,200 samples of oil sandstones from 107 wells in 43 zones in 23 fields, mostly in California. This survey showed that about 70 percent of the sandstones studied showed distinct and serious damage to permeability caused by the influx of fresh water.

In figure 15, Johnston\(^30\)/ shows the drastic effect on well productivity of severe hydration plugging of an oil-producing formation for only a short radial distance into the zone and, conversely, the relative difficulty of improving well productivity by increasing sand permeability, even tenfold, for a considerable distance from the well bore.


\(^{30}\) Work cited in footnote 27.
FIGURE 15. - Effect of Reduction of Permeability at Various Radial Distances From Well Bore on Well Productivity (After Johnston).

In 1946 Kersten\(^{31}\) reported a 2:1 improvement in initial productivity of wells completed with oil-base muds compared with fresh-water clay-base mud. In the same year Kelley, Ham, and Dooley recommended several means for obtaining maximum well productivity, including: (1) Minimizing entry of water into the sand; (2) adding salt to whatever water may be allowed to enter; (3) keeping the time of contact of drilling muds on the oil-bearing sandstone to a minimum; (4) using minimum safe low-density mud; and (5) selecting mud-treating chemicals that will have a minimum effect on hydration of clays in oil-bearing formations.

\(^{31}\) Kersten, Glenn W., Results and Use of Oil-Base Fluids in Drilling and Completing Wells: API Drilling and Production Practice, 1946, pp. 61-68.
Wade summarized the results of an extensive study of well-completion data from a large number of California wells. He concludes that maximum productivity of wells was obtained in those where exposure of the oil-bearing sandstone to water-base drilling muds was at a minimum. The entrance of water into the formation should be minimized.

In 1946 Bates, Gruver, and Yuster studied the clay content of samples of the Bradford sand in Pennsylvania, using (1) differential thermal analysis, (2) X-ray spectrometer, and (3) the electron microscope. The results indicate that the samples contained primarily the clay mineral illite, with smaller amounts of kaolinite and montmorillonite. They pointed out that some of these clay minerals could be responsible for the reduction of water rates in waterflooding.

In 1946 Miller, Morgan, and Muskat reported results of a series of permeability tests of California cores to the flow of oil, salt water, distilled water, and air. The results of the tests showed that the average effective permeability to oil of the unextracted cores was 43 percent of that to air. It was also found that, after exposure to fresh water, the oil permeability was reduced, on the average, to about 25 percent of its initial value. This means that, if the clay-containing rock had been subjected to an appreciable amount of fresh-water invasion from a drilling fluid, the effective oil permeability about the wellbore may be 10 percent of the air permeability. When account is taken of further reductions in the effective permeability resulting from the free gas content of the sand and the increased flow resistance from perforations in the casing, resultant large reductions in productivity are not unreasonable.

In 1950 Hughes presented a thorough summary of many concepts relating the clay content to the behavior of oil reservoirs. He states that it is advisable to use no waters in a well that would disperse clays during drilling through the reservoir rock, completion, and cleanout or workover operations.

As Johnston recognized, this suggests a paradox in the drilling and production phases of the oil industry. In general, chemicals such as caustic and quebracho are added to drilling fluids to disperse the clay particles in the mud, enhancing the viscosity and filter properties. These same chemicals,

34/ Miller, K. T., Morgan, F., and Muskat, M., Some Permeability Experiments on Cores From the Stevens Sand, Paloma Field, Calif.: Producers Monthly, vol. 11, No. 1, November 1946, pp. 31-34.
36/ Work cited in footnote 24 (p. 24).
entering the reservoir rock in the mud filtrate, will disperse and swell clay particles in the pore space, closing the pore channels to the flow of oil. Thus the functions of the chemicals added to the mud are highly desirable in the mud but entirely undesirable in the oil-bearing formation.

Another apparent inconsistency in drilling and logging operations exists in the effort of the mud engineer to keep the filtrate volume to a minimum. In contrast, filtration of liquid into the porous formation is shown in the self-potential curve of the electrical log and hence is desirable in electrical logging. Also, the permeability of the formation is indicated by mud cake formed on the wall of the hole, and it is detected by the microlog. This effect resulting from filtration is used to indicate a permeable formation in microlog interpretation.

Although the naturally occurring clay minerals in reservoir rocks have been found to swell and to damage the permeability of rock, clay from drilling muds may be filtered into the reservoir rocks, where it may plug the pore channels. Beeson\(^{37/}\) has published laboratory data indicating that whole mud (including clay particles) enters core samples having a permeability of less than 100 millidarcys. Nowak and Krueger\(^{38/}\) found that clay particles from the drilling mud may penetrate porous rocks. Therefore, a sandstone that ordinarily would be considered free of clay may be contaminated by clay particles from the drilling mud during the completion of the well. These particles, which were filtered into the rock, will resist the flow of oil to the well.

In 1951 Nahin\(^{39/}\) and his coworkers used X-ray diffraction, electron microscopy, thin-section petrography, infrared spectroscopy, and cation-exchange analysis to study clay minerals in four California reservoirs. They found that the Stevens sandstone was fresh-water sensitive and contained predominantly illite and montmorillonite clays. In contrast, the Gatchell sandstone, which was relatively insensitive to fresh water, contained predominantly kaolinite clay minerals.

In a study by Von Engelhardt and Tunn\(^{40/}\) the reduction in permeability of artificial mixtures of quartz sand and 4 percent clay was determined; it is plotted in figure 16. The largest reduction of permeability was observed with

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dilute solutions. The reduction of permeability was greatest for the sands containing sodium montmorillonite, but the sands containing sodium kaolinite also had an appreciable reduction in permeability. These researchers state that the results indicate that the reduction in permeability results only in part from intercrystalline swelling. They suggest that the clay minerals attract and strongly hold an appreciable quantity of water on the surface of the clay particles, thus immobilizing a relatively large volume of water in the vicinity of the clay particles. The clay particles can hold a larger volume of fresh than salt water.

Norrish⁴¹/ studied the swelling of montmorillonite and found that the initial stage of swelling is crystalline swelling and that the absorbed water increased to about 0.5 gram of water per gram of clay and interlayer spacing increased from 9.5 Å for the dry material to about 20 Å, corresponding to 4 molecular layers of water. This water causes little visible swelling. In contact with water, sodium montmorillonite takes up 10 grams of water per gram of clay and increases about 20 times in volume. In the third stage of water attraction the clay is dispersed in the water to form a thixotropic gel containing a small quantity of clay and a relatively large volume of water.

Bentonite, which primarily contains the clay mineral montmorillonite, may be dispersed in water to form the thixotropic gels containing less than 1 percent clay.⁴²/

Dodd and others⁴³/ used X-ray diffraction methods to study the clay content of about 90 core samples from petroleum-reservoir sandstones. The results indicate a relationship between concentration of glycerol-expandable three-sheet clay minerals in sandy sediments and degree of water-sensitive behavior exhibited by the sands during petroleum production.

Nahin\textsuperscript{44}/ studied the swelling of clay under pressure.

Cardwell\textsuperscript{45}/ pointed out that swelling of a clay is not easy to predict from data generally used to describe clays. He calls attention to the difference between crystalline or lattice swelling and microscopic swelling.

The Bureau of Mines has published a series of reports that emphasize the importance of clay in the production of petroleum. Loomis\textsuperscript{46}/ has described a unique method of measuring the surface area of clays.

The clay content and the permeability of four Wyoming oil-bearing sandstones have been studied by Baptist and Sweeney,\textsuperscript{47}/ who reported that X-ray diffraction methods of clay-mineral identification indicated that the sand containing kaolins, illites, and mixed-layer montmorillonite-illite was most sensitive to water and the sands containing only kaolins and illites were least sensitive to water.

In a study of properties of the Newcastle oil-reservoir sand, Wyoming,\textsuperscript{48}/ the presence of kaolin and illite types of clay minerals was indicated. A few samples of the reservoir rock were found to contain montmorillonite and mixed-layer montmorillonite-illite minerals. Liquid-permeability tests indicated that the oil-reservoir sandstone had medium water sensitivity.

Morris\textsuperscript{49}/ described the blocking effect caused by water invasion of oil-reservoir rocks during completion of wells in a deep California field. In this report the damage to well productivity was determined by calculating the "skin effect" based on pressure-buildup data. The results of this study indicate that measurable damage was sustained during completion in 5 of 9 wells completed with water-base drilling fluid. Only 1 of 14 wells completed with oil-base drilling fluid was damaged. A detailed study of one well that was drilled with water-base mud, plugged and redrilled with oil-base mud, shows that a large volume of oil was recovered as a result of recompletion without


\textsuperscript{49}/ Morris, Frank C., A Correlation of Pressure Buildup in Oil Wells With Completion Practice for a Deep California Field: Bureau of Mines Rept. of Investigations 5333, 1957, 27 pp.
damage to the formation. The clay minerals in the oil-bearing sandstone of
this field have been identified previously as illite and montmorillonite.

A petrographic study of thin sections of the reservoir rocks shows that
the swelling clays occur in the pore space, apparently attached to the surface
of the sand grains. A sketch of a typical distribution of oil, water, and
clay-size particles in a pore space within the reservoir sandstone is shown in
figure 11 (p. 21). As shown in this figure, the clay particles and held
water have blocked the flow channel required for the flow of oil. A definite
breakthrough or yield pressure must be exceeded before flow may occur through
the pores. If the reservoir pressure does not suffice to overcome the break-
through pressure, the fluids cannot flow, and the well bore is effectively
shut off from the reservoir fluids.

The breakthrough pressure can be very large. This is illustrated by
well K, described by Morris.50/ The well was completed with water-base drill-
ing fluid, and completion required 138 days. Well K had a drawdown due to
skin effect amounting to about 2,700 pounds per square inch when the well was
producing at a rate of 200 barrels of oil a day. Even this large pressure
differential did not suffice to clean the water and clay particles from the
flow channels. Consequently, the well was plugged back with cement and re-
drilled with oil-base mud; the latter was on the formation 22 days. The skin
factor of the first completion was +46.6, indicating damage to the formation.
In contrast, the skin effect of the redrilled hole was -1.8, indicating no
damage to the formation. Total drawdown pressure in the redrilled hole was
68 pounds per square inch when the well was producing at a rate of 200 barrels
per day.

The plugging action of clays in reservoir sandstones is particularly im-
portant in waterflooding operations. If the clay in the reservoir rock swells
in contact with the flood water, the pore channels are reduced in size, and
injection pressures become excessively large. By proper control of the injec-
tion water, swelling of clays in the reservoir may be minimized. The results
of this study and many studies previously reported indicate that brines are
preferable to fresh water because the clays tend to swell less in brines than
in fresh water.

The brines produced with oil from the reservoir are generally recommended
for waterflooding because the clays in the reservoir rock have been in contact
with and reached equilibrium with these solutions; therefore no change may be
expected with injection of the same brines.

Hughes and Pfister51/ made a detailed study of the relation of water-in-
jection well indices and laboratory data from core samples. Both the labora-
tory and the field data showed increased injectivity into the sandstone with
use of brine instead of fresh water. Illite was the clay mineral identified
in one of the sandstones studies.

50/ Work cited in footnote 49 (p.30).
51/ Hughes, Richard V., and Pfister, Rudolf J., Advantages of Brines in Sec-
All previous work points to reduction of the permeability of the oil-bearing sandstone near the well bore by fresh water; the damage was greater as more water invaded the zone. The damage increases with time, pressure difference, mud-cake permeability, filter properties of the fluid in the hole, and characteristics of the clay in the oil-bearing formation. The work indicates the need, both in well-completion operations and in waterflooding, for complete knowledge of the clays in all reservoir rocks and the changes that occur when the water solutions contact the clays in the reservoir rock. The results indicate further that the plugging action may result either from natural occurring clay in the sandstone or clay filtered into the sandstone from the drilling mud. Part of the reduction in permeability to oil results from the decreased pore space available for flow of oil when water enters the reservoir rock.

Characteristics of Clay

Structure of Clay

There has been a great deal of speculation concerning the nature of clay. Through the use of X-ray and thermal analysis equipment, it has been determined that clays, even in their finest fractions, are crystalline plates of minerals and not, as at one time assumed, an amorphous mixture of metal oxides and hydroxides. Furthermore, it has been shown that clays consist of few and relatively simple building units.

One unit is composed of closely packed oxygen or hydroxyls (depending on the electron balance of the combination), in which aluminum, iron, or magnesium ions are oriented in octahedral positions, so that they are equally spaced from the six oxygens or hydroxyls. Where aluminum is present, it combines with six oxygens or hydroxyls to form an aluminum-oxygen octahedron structure known as gibbsite, $\text{Al}_2(\text{OH})_6$. Magnesium combines with oxygen or hydroxyls to form an octahedron structure known as brucite, $\text{Mg}_3(\text{OH})_6$.

The other building unit common to clays is a silicon atom binding four oxygens or hydroxyls together in the form of a tetrahedron, with the silicon atom at the center of the structure. The clay minerals occur as hydrous aluminum silicates, iron and magnesium often replacing aluminum to some degree. Grim has reported extensively on the character of clay materials. A schematic diagram showing the structure of the clay minerals kaolinite, montmorillonite, and submicas or illite, as discussed by Grim, is reproduced in figure 17.

Kaolinite group. - Kaolinite, the principal member of this group, has the composition $(\text{OH})_8\text{Al}_4\text{Si}_4\text{O}_{10}$. The structure of this clay mineral was first worked out in detail by Gruner (1932). It is composed of 1 tetrahedral Si - O sheet and 1 somewhat distorted octahedral Al - OH sheet (gibbsite). This

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FIGURE 17. - Schematic Crystal Structure of Clay Minerals Kaolinite, Montmorillonite, and Submicas.
structure is usually referred to as the 1:1 lattice type. The lattice structure does not expand with varying water content. Replacement of aluminum by iron or magnesium has not been reported within the structure of this clay mineral.

A differential thermal curve of a typical kaolinite is shown in figure 20 (appendix). The curve is characterized by an endothermic reaction at approximately 610° C. and an exothermic reaction at approximately 980° C. For large, well-crystallized particles this latter peak is exceptionally sharp; a more rounded peak is obtained from finer grained, poorly crystallized samples. These thermal peaks render a distinctive pattern to the curve, from which this clay can be identified. X-ray diffraction patterns of kaolinite have a reflection at 12.3°, 2θ angle which give it a d spacing of about 7.2Å.; this reflection is not picked up from a sample that has been ashed at 600° C. for 1 hour.

Montmorillonite group (OH)4Al4Si8O20.nH2O. - These clay minerals are referred to as the 2:1 lattice type, consisting of 1 uniform Al – OH octahedral sheet (gibbsite) between 2 Si – O tetrahedral sheets. The clay members of this group absorb planar water within their structure between the successive silicon-oxygen tetrahedral sheets. The amount of water in the structure causes a variation of the c dimension, so that this mineral is said to have an expanding lattice. This interplanar water can be driven off at about 200° C. X-ray diffraction studies have revealed that without water between the structural units the height of a unit cell is 9.6 Å., and the distance between the oxygens of the silicon-oxygen tetrahedra sheets is 3.0 Å. When the mineral is treated with glycerin or ethylene glycol a c dimension of 17.1 Å. is obtained. Partial or complete replacement of aluminum in the gibbsite layer by magnesium and ferric iron will result in the clay minerals saponite and nontronite. Beidellite has been described as a montmorillonite with a low silica:alumina ratio; apparently one of the silicas in the tetrahedra sheet has been replaced by alumina. Properties, such as an expanding lattice, high base exchange, and plasticity, characterize this clay mineral.

The differential thermal curve shown in figure 20 (appendix) is typical of montmorillonite. The reactions occur quite rapidly; hence the peaks are sharp. A curve consisting of endothermic peaks at 175° to 200° C., 670° to 725° C., and approximately 900° C., followed by an exothermic reaction at about 960° C., is representative of this clay. This combination of three endothermic reactions, followed by an exothermic, characterizes the 2:1 lattice type of clays. Changes in peak size and the temperature at which the thermal reactions take place occur with a change in composition. For example, nontronite, a high-iron oxide-content member of the montmorillonite group, has endothermic peaks at 200° and 530° C.; a small exothermic peak is apparent near 870° C. This thermal pattern is distinctive and unlike thermal curves of other montmorillonites.

Submica group $(\text{OH})_6\text{K}y(\text{Al}_4 \cdot \text{Fe}_4 \cdot \text{Mg}_4 \cdot \text{Mg}_6) (\text{Si}_{18-y}\text{Al}_y)\text{O}_{20}$. This group of clay minerals has been referred to as illites by Grim.\textsuperscript{55} Some investigators use the terms "hydrous micas" or "hydro micas" to designate this group of minerals. Many investigators, including Brindley, Barshad, Dodd, Yoder, and Eugster, use the term "mica group" or "micalike materials." Yoder and Eugster\textsuperscript{56} state:

It is concluded therefore that the term illite should be used only as a field term, as Grim et al., originally proposed. When identification is made of the material or materials, the polymorph of the mica should be specified, and note made of the clay material with which it may have formed mixed layers. Proof has yet to be obtained that the materials now called illite are not all mixed layer structure.

Consequently, in this report clay minerals in this group will be referred to as micas or submicas.

The basic structure of this group is similar to that of montmorillonite. It is also classified as a 2:1 lattice-type structure and is made up of an octahedron Al-OH (gibbsite) sheet between two tetrahedra Si-O sheets. The structure is held together by sharing oxygen between the alumina and silica sheets. The schematic sketch, figure 17, illustrates this arrangement.

Aluminum (Al\textsuperscript{+++}) replaces about 15 percent of the silicon (Si\textsuperscript{+++}) positions. The loss of the positive charge is balanced by the intake of potassium (K\textsuperscript{+}) ions between layers. Furthermore, substitution of Fe\textsuperscript{+++}, Fe\textsuperscript{+++}, and Mg\textsuperscript{+++} may occur for Al\textsuperscript{+++} in the octahedral layer; with addition of Mg\textsuperscript{++} for Al\textsuperscript{+++}, the structure of this sheet is altered to that of brucite. The K\textsuperscript{+} ion has been described as a tie holding the unit clay layers together so that they do not expand in the presence of water. In industrial use of submicas, the swelling characteristics of the clay may become apparent with the addition of water. Since the submicas and montmorillonite are known to occur as an interlayer complex, the degree of purity of the material may be questioned; the observed swelling nature of the material in use may be due in part to the presence of a small amount of montmorillonite associated or interlayered with the submica clay.

Differential thermal curves of the submicas (fig. 20, appendix), endothermic peaks at approximately 140° C., 580° C., and 870° C., and a small exothermic reaction at about 985° C. complete the pattern; each of these peaks occurs over a broad temperature increment and is less sharp than those described for kaolinite and montmorillonite. X-ray diffraction studies show that this clay has a strong reflection at 8.8°, 2θ angle; the d spacing is approximately 10.0 Å. Glycerin or ethylene glycol does not expand this clay. However, the X-ray diffraction pattern of a sample ashed at 600° C. will have a much stronger reflection at 8.8°, 2θ angle.

\textsuperscript{55} Work cited in footnote 53 (p. 32).
Base Exchange

Base exchange has been described by Pettijohn as the exchange of ions in solution for those of a solid. Clays that have an expandable lattice, such as members of the montmorillonite group, seem to have a greater capacity for exchanging ions than nonexpandable-type clays, such as kaolinite. The submicaceous clays exhibit exchange characteristics somewhat intermediate between montmorillonite and kaolinite. Since some of the exchangeable cations serve as bonds that hold the lattice structure together similar to K⁺ in the submicaceous lattice, their presence affects clay-swelling character, hence their importance. It is significant that, in ion-exchange process, the structure of the clay is not altered; it is thought that ions are acquired at the surface of the lattice layers. Grim, in a review of the work of other investigators, points out that particle size has little effect on the exchange capacity of montmorillonite clays; however, the exchange capacity of kaolinite increases with decreasing particle size. It appears that ion exchange is influenced by physical change of the clay crystal; that is, broken bonds within the structure of kaolinite caused by a change in particle size would require addition of ions to restore a balanced structure. From observed changes in particle size, it follows that broken bonds are responsible for only a small part of cation-exchange capacity of montmorillonite.

Unsatisfied bonds occur in the lattice structure when an ion of lower valence (Si⁴⁺ Al⁺³, Al⁺³ Mg⁺²) takes the place of one of higher valence. Unbalanced charges in the structural units of clay may be balanced by other lattice charges, such as OH⁻ for O²⁻, often the balance is restored by absorbed cations. Substitution within the lattice structure probably is responsible for the high cation-exchange capacity of montmorillonite.

The rate of reaction of cation exchange has been found to be quite rapid. Kelley points out that reaction rate has been studied by mixing a known weight of soil (chernozem, characterized by its high calcium content) with a solution of known concentration of sodium or ammonium chloride. The mixtures were filtered, and calcium was determined in the filtrate. The results of these experiments show that contact between the soil and the sodium chloride solution for the short period of 5 seconds, plus filtering time, was long enough for exchange to take place and equilibrium to be established. The ammonium chloride solution and the soil were in contact 3 minutes before equilibrium was established. It may be concluded that the exchange-reaction rate takes place almost as soon as contact is established between the soil and the solution. These rate-of-reaction studies also show that cation exchange may not necessarily be confined to clay-size particles of colloidal dimensions.

58/ Work cited in footnote 53 (p. 32).
Identification of Clay Minerals

Differential Thermal Analysis

The differential thermal method of analysis measures the thermal reactions that occur when a material is heated. The clay sample selected for analysis is placed adjacent to a sample of thermally inert reference material, such as calcined alumina. Then the system is heated at a constant rate of increasing temperature. The rate of temperature rise of the sample may be less, be equal to, or exceed the heating rate of the reference standard. When heat is absorbed by the sample, in addition to that needed to maintain a constant rate of temperature rise, the temperature of the sample will be lower than that of the reference material. This absorption of heat by the sample is called an endothermic effect.

If the rate of temperature rise in the sample is greater than that of the reference material, it is apparent that heat is generated in the sample, in addition to that absorbed to maintain the constant heating rate; generation of heat by the sample is termed an exothermic effect. Differential thermal analysis measures these heating characteristics. The measurement is obtained by means of a differential thermocouple circuit, a pair of thermocouples connected in series opposition. The potential available at the terminals of the differential thermocouple is the difference of the potentials obtained from the unknown sample and the thermally inert standard.

This potential difference is plotted on the X axis of an X-Y electronic recorder against the temperature of the sample block plotted along the Y axis to obtain thermograms which indicate the differential temperature at any point along the heating curve. Such a curve characterizes the clay minerals present in the sample being analyzed. DTA's of samples containing a mixture of clay minerals will have the characteristic effects of the individual components superimposed on each other.

Each of the clay minerals montmorillonite, kaolinite, and the submica or illite group has a different enough DTA pattern so that the method can be used as a means of identification. Very good results can be obtained when a relatively pure sample is obtained for analysis. Examples of differential thermal curves obtained for API clay reference minerals are shown in figure 20 (appendix). When a sample is contaminated with organic matter or other thermally active minerals the DTA pattern may be rendered indeterminate.

Indeterminate patterns may be simplified to some extent by carefully selecting the size fraction to be examined, pretreating carbonates from the sample with several dilute hydrochloric acid washes, and controlling the atmosphere in which the DTA is performed.

When used in conjunction with other methods, identification of otherwise indeterminate mixtures can often be positive. X-ray-diffraction, optical, and dye-staining procedures also were used to identify clay minerals in the cores examined in this investigation.
The arrangement of equipment used to obtain the DTA curves for the report is similar to that described in literature.\(^{61}\) The heating rate of the furnace was held constant at 10° C., per minute by a commercial electronic temperature controller. The potential differential between the alumina and the unknown was passed through a chopper-type, d.c., microvolt preamplifier before it was received by the X-Y recording potentiometer. A scale multiplier is incorporated in the electrical circuit of the d.c. preamplifier, so that maximum sensitivity can be obtained.

The pure-nickel sample holder used was made from a design recommended by Pask;\(^{62}\) approximately 0.8 gm. of sample is required for each analysis. Platinum and platinum-10 percent rhodium 32-gage wire was used in all thermocouple circuits.

**Preparing Samples**

The cores, where scraped clean of the mud cake from the drilling fluid and samples, were selected from adjacent parts of the core along a bedding plane for identification of clay and determination of permeability. The samples for clay identification were crushed and extracted with toluene. A water suspension was made with the extracted sample; then it was set aside to hydrate a minimum of 3 days. No deflocculents were used. The suspension was stirred vigorously and allowed to settle 10 minutes; then the liquid and suspended particles were removed by siphoning to a depth of 8.5 cm. from the surface. Gates\(^{63}\) has shown that the particles in the removed suspension have an equivalent spherical diameter of 13.7 microns or smaller. By repeated fraction of suspended particles an adequate quantity of free particles was separated from the extracted crushed core sample. It is recognized that all the particles separated from the core were not of the clay-size material in the core. Consequently the term "free particles" is used to distinguish the particles separated from the core sample from those of the same size that are plastered on the coarser material in the core. Much of the clay adheres firmly to the sand, so that ordinary methods of mechanical analysis may determine less clay than is actually present.

The quantity of clay-size material reported should be considered minimum, or the lower limit of fine material composing the core samples, rather than an accurate measure of the amount of small particles present. After the suspension containing 13.7-micron and smaller particles was removed, the liquid was evaporated and the residue ground with a mortar and pestle in preparation for

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differential thermal analysis. When enough minus-13.7-micron material was available, it was used for X-ray diffraction studies.

Although the core samples were extracted with toluene (in some instances an additional extraction with dioxane was tried), it was found that enough oil or other carbonaceous material adhered to the clay-size particles to distort the DTA pattern, so that it could not be used for purposes of identification. Carbonaceous matter usually begins to oxidize at relatively low temperatures and continues over a wide range of temperature, producing a broad exothermic peak. Consequently, this organic material must be removed by treating the sample with some oxidizing agent, or the DTA must be obtained in a controlled atmosphere. Since the oxidizing agents, such as nitric acid or peroxides, may alter the clay, all of the DTA's obtained in this investigation were obtained in a nitrogen atmosphere to prevent oxidation during the heating period. Use of an inert atmosphere eliminated the broad exothermic peak between about 250° and 450° C. caused by heat released by burning of organic matter. The DTA equipment was so sensitive that a trace of organic matter affected the result-ant thermogram. Most clay-size samples from oil-reservoir rocks contain or-ganic matter that cannot be completely extracted from the fine particles. Hence all samples were run in an atmosphere of nitrogen.

Estimating Clay Content From Thermal Patterns

Estimates of the percentage composition of the clay minerals in a powder mixture are based on the amplitude of characteristic endothermic and exothermic reactions observed in the DTA pattern with respect to the temperature at which they occur and for a comparison of the area between the DTA curve and the neutral axis with reference clays. It is important to be aware of the individual clay characteristics that affect the amplitude of the DTA peaks and the area under the curve, such as the size of the particles, development of clay structure, and the degree of purity of the sample. Impurities often will cause a peak shift, so that distinctive endothermic or exothermic reactions do not occur at their characteristic temperatures. This increases the problem of interpretation. From the DTA patterns of the reference clay minerals (figure 20, appendix), it is apparent that the peak amplitude for a relatively pure kaolin at 605°-610° C. is much greater than the peak amplitude for a pure montmorillonite at 710°-720° C. or a submica at 570°-580° C. In all figures shown, the endothermic reactions are plotted below, and the exothermic reactions are plotted above the neutral axis. It is widely accepted that the clay minerals have different crystallites sizes. Kaolin particles usually are larger than the submicas, which are larger than the montmorillonoid minerals. These clay features cast considerable doubt on percentage estimates taken from DTA patterns that are beyond a semiquantitative order.

A small size range should be used for the best results in semiquantitative estimates - perhaps less than 4 microns. However, the results obtained apply to the size range examined and not to the entire range of clay-size particles. The size range of less than 13.7 microns was selected to obtain the DTA and

X-ray patterns, because fractionation to a smaller size required lengthy settling periods. Many particles larger than 4 microns but smaller than 13.7 microns were found to be clay minerals.

When a given clay mineral was estimated to compose 30 percent or more of a powder sample, it was reported as a dominant type; if a clay mineral was estimated to be present in quantities less than 10 percent, it was reported as a minor constituent of the size fraction analyzed.

X-Ray Diffraction Analysis

X-ray diffraction patterns of the clay-size fractions removed from the oil-well cores were obtained with diffractometer unit equipped with a recording goniometer. Copper Kα radiation at 45 kv. and 16 ma. was used, with a nickel filter attachment. Other settings were a 3° takeoff angle, a 1° beam soller slit, a high-resolution (HR) vertical divergence soller slit, and a 0.1° receiver slit. The logarithmic intensity response was recorded on a strip chart operated at 2°, 2 θ angle per minute. The powder samples were mounted in a plastic or phenolic holder, so that a flat, smooth surface was exposed to the X-radiation. Clay-size material from approximately one-fourth of the cores was examined by X-ray diffraction.

Dye-Staining Methods

Dyestuffs and other reagents that exhibit characteristic colors when adsorbed on clay granules frequently have been used as aids in identifying clays. Certain aniline dyes, solutions of which vary in color according to their hydrogen-ion concentration, may be used to indicate the relative acidity of clay surfaces. When a clay sample has been pretreated with acid, the colors assumed by the adsorbed dye depend on the characteristic base-exchange capacities of the various clay-mineral groups present.

Aside from economy, dye staining has one marked advantage over other methods of identification. Small amounts of clay minerals may be identified and the relations of these minerals to other mineral constituents of the rock and to cementing materials may be determined simultaneously by petrographic examination. In oil sands preferential adsorption of oil by montmorillonite clays and lack of similar adsorption by other clay minerals present have been observed.

Mielenz and King have recently developed dye tests employing acid-base reactions using safranine Y and malachite green. A modification of this procedure was used for the dye-stain identification work reported in this paper.

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65/ In using X-ray diffraction methods for clay-mineral identification the authors were assisted by H. H. Heady, supervisory chemist, and Farrel W. Lytle, chemist, Region II, Bureau of Mines, Reno, Nev.


Much of the work on dye-stain techniques is empirical. Investigation of theoretical relations was beyond the scope of this study, and the reader is referred to the above source for information on theoretical implications. Use of the dye-stain method of clay-mineral identification is relatively new, and it seems to hold much promise in the light of progress made to date.

Dye-stain tests used to identify the Tejon-Grapevine oil-sand clays were essentially those described by Mielenz and King, using safranine Y and malachite green, with two exceptions:

(1) Safranine O was used rather than safranine Y, because the latter was not readily available. As far as known, the characteristics of the two dyes are identical as regards this test.

(2) While experimenting with these dyes it was found that the concentrations advocated by Mielenz and King were six times too strong to obtain reliable, diagnostic results for clay-mineral types in California oil sands. Instead of using 339 mg. of safranine O or Y per liter in the solution, approximately 56 mg. should be used; and instead of 1,935 mg. per liter of malachite green, approximately 323 mg. should be used. The resultant colors, using the weaker solutions, are more reddish in the case of the safranine test and more greenish in the case of the malachite-green test; color contrasts between minerals are therefore less prominent. The color contrasts, nevertheless, are readily distinguishable. The results of clay-mineral identification using dye-staining methods agreed well with those obtained from DTA and X-ray methods. This was considered conclusive identification of the sub-mica and montmorillonite clay minerals in the cores studied.

Preparation and Acid Treatment of Samples

Staining tests may be applied to an entire core sample or to size fractions obtained by using sieves. When the entire core sample is used, it is preferable to grind it to minus-100-mesh or finer to facilitate microscopic examination. Limiting studies to size fractions has the disadvantage that, unless all fractions are studied, it is impossible to find percentage relationships of the mineral types in the original core.

If excessive amounts of iron oxides are present, they should be removed to facilitate microscopic examination.68/ Hydrocarbons are a much commoner bothersome impurity in a study of oil-well cores, and these should be extracted using toluene or dioxane before treatment.69/

Extraction will not be complete (particularly of oil-sand hydrocarbons associated with montmorillonites), but it will normally suffice to permit optical examination of the dye-stained sample.

Tejon core samples were not examined microscopically before acid treat-
ment. Instead, carbonates were detected by effervescence during acid treat-
ment and confirmed by DTA analysis of non-acid-treated material. Some acid-
soluble zeolites undoubtedly were lost in acid treatment, inasmuch as an
acid-resistant heulandite-type zeolite mineral was rather commonly present;
and some samples, particularly of the J.V. sand, carried a mineral suite
typically associated with volcanics, with which zeolites are commonly
associated.

Procedure. - To acid-treat the sample or selected fractions, place ap-
proximately 20 grams of the material in a beaker, and add 200 ml. of dilute
hydrochloric acid (1 part concentrated acid to 25 parts of distilled water).
If the sample is a rather clean, well-sorted sand, the proportion of sample
to solution may be larger.

Leave the sample in the solution about one-half hour, stirring once or
twice, or several times if the material settles out rapidly. Centrifuge if
necessary, and pour off the supernatant solution. Repeat the acid treatment
of the sample, using an additional 200-ml. charge of dilute hydrochloric acid.

If carbonates are present, either a stronger concentration of acid must
be used (which may damage the clays), or the acid-treatment procedure must be
repeated until effervescence has ceased; the 1:25 hydrochloric-acid solution
will destroy hectorite, some nontronites, and some montmorillonites. Where
one of these minerals may be expected but a negative dye-stain reaction is
obtained, comparison with DTA or X-ray-identification studies will reveal
whether the clay structure has been destroyed by acid treatment.

After acid treatment wash the sample repeatedly, using about 500 ml. of
distilled water for each washing. Continue washing until no silver chloride
precipitate is observed in the supernatant wash water upon addition of silver
nitrate solution. For most core samples 5 or 6 washings will be necessary.

For precise work the fines in the supernatant liquid may be collected in
a filter paper, when decanting, and may be added afterward to the washed sam-
ple. Since the fines must also be washed until free of acid, this operation
is time consuming and usually may be dispensed with unless a large proportion
of fines remains in suspension. The fines, however, do tend to have greater
concentrations of montmorillonoid clays than the coarse fraction.

Dry the sample and the filter paper with retained fines at 105° C. 25
hours or to constant weight.

It is best to weigh the fines and sample to establish relative proportions
and to examine each separately, since some samples of montmorillonites tend
to concentrate in the fines and the submicas, to settle out and remain with
the coarser material.
Application of Safranine-O and Malachite-Green Dyes

Mielenz and King\textsuperscript{70} report that best clay-mineral identification results are obtained with safranine Y and malachite green in nitrobenzine solution for acid-base reactions. Modifications of this method gave results comparable in accuracy with those described, using the somewhat more complicated and time-consuming water solution of benzidine oxidation-reduction method of clay identification, so the latter method was omitted.

Reagents used for the identification tests in this study were nitrobenzine, malachite-green oxalate, and safranine O (a red dye), which gave color reactions identical with those described by Mielenz and King for safranine Y. A set of refractive index oils was used for complementary optical studies.

The cost of the minimum reagents necessary for the current study (which would include a bottle of Shillaber's index-of-refraction liquid, preferably with a refractive index in the 1.532-1.544 range to differentiate submica from sepiolite, 25 grams of safranine 0 (or safranine Y), 25 grams of malachite-green oxalate, and 1 kilogram of nitrobenzine) would approximate $10.00.

One major departure from the Mielenz and King procedure was found desirable in preparing dye solutions. They state that saturated nitrobenzine solutions of the dyes should be used; however, they add that using saturated solutions of dye readily produces oversaturation of color on the clay sample, yielding an anomalous result if care is not taken. They state further that when malachite green in nitrobenzine is used, twice the volume of dye solution is required to produce oversaturation in a clay sample containing 15 percent by weight of acid-treated Wyoming bentonite as was required of a similarly prepared solution of safranine 0. The acid-treated clay is much more sensitive to the safranine 0 than to the malachite-green dye. Consequently, a complete examination requires that the clay be treated with both dyes.

In preliminary clay-mineral-identification tests, where the primary object was to differentiate submicas from montmorillonites (these being the principal clays present in most of the California oil-sand core samples treated), the saturated dye solutions were found to be much stronger than necessary. As a result of these observations, dilute dye solutions were prepared containing one-sixth the concentration of the saturated solution. These dilute nitrobenzine solutions contained 57 mg. per liter of safranine 0 and 323 mg. per liter of malachite green.

Use of these dilute dye solutions offered two important advantages over saturated solutions for differentiation of submicas from montmorillonites:

1) With the dilute solutions, saturation of the clay by excessive dye coloration was not a problem, and only a minimum of care in preparation was required to obtain reproducible results.

\textsuperscript{70} Work cited in footnote 67 (p. 40).
(2) With the dilute solutions saturation of dye coloration on small amounts of montmorillonite in a sample in which another clay type was dominant was avoided. It is estimated that amounts of montmorillonite making up less than 10 percent of the clay present could be detected in a random oil-sand core sample.

The mount used for studying the unknown was a standard microscope glass slide and coverglass. The flattened end of a paper clip was found suitable for applying the desirable quantity of unknown clay, and just 1 or 2 drops of dye was applied. The determining factor was that enough dye is needed to fill the space around the mineral grains under the coverglass, but not so much that the dye would be squeezed out from under the glass. All samples were prepared on 3 slides, 1 with malachite green, 1 with safranine O, and a third with a colorless index oil, so that original clay color and possible influence of this on dye reaction could be judged.

Many clays were yellowish, usually from staining by oil in the formation. These natural colors gave noticeable interference in the malachite-green test for montmorillonite, since the original clay color sometimes very nearly matched the expected dye-reaction color for this test. This could usually be confirmed by applying the safranine-0 test, since the yellow clay color did not greatly interfere with the purple-blue reaction color to this dye.

Because dilute dye solutions were used compared with the saturated ones recommended by Mielenz and King, the resulting color reactions were of different magnitude, as shown in table 5. Although the color reactions differed from those that resulted when the saturated solution was used, they were found to be consistent throughout the investigation.

### TABLE 5. - Relative color reactions of clay upon addition of organic dyes

<table>
<thead>
<tr>
<th></th>
<th>Montmorillonite</th>
<th>Illite</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Malachite</td>
<td>Safra-</td>
<td>Malachite</td>
</tr>
<tr>
<td>Mielenz and King</td>
<td>5YR-10YR</td>
<td>5PB-10PB</td>
<td>8YR-5BG</td>
</tr>
<tr>
<td>Bureau 1/6 conc.</td>
<td>5Y-7.5Y</td>
<td>2.5P-</td>
<td>2.5BG-</td>
</tr>
<tr>
<td>dye-stain sol.</td>
<td>7.5P</td>
<td>7.5BG</td>
<td>7.5R</td>
</tr>
</tbody>
</table>

The data in table 5 show that the color of the adsorbed dye is almost the same tone for submica and kaolinite clays (and also sepiolite clays) when the dilute dye-stain solutions are used. Consequently, these clays cannot be readily differentiated from one another by dye-stain tests; however, Mielenz and King have shown a clear color distinction between kaolinite and the submicas when saturated dye solutions are used. They suggest that the dye-stain
tests on sepiolite approximate the results obtained for kaolinite. This characteristic lack of distinction by dye staining requires that identification of sepiolite be substantiated through optical studies.

The color nomenclature in table 5 is that defined using the Munsell system. The Munsell Book of Color\(^\text{71}\) was used to describe all the samples studied in the current investigation.

The term "dye stain" is employed in this report to describe the color reaction of acid-treated clays to these dyes. This term is somewhat misleading, since the dye solutions act as dyes or stains only when the solution is adsorbed without color change. In clays, particularly the montmorillonites, where a color change does occur, the resulting color differs from both the original clay color and original dye color, tending toward an extreme of yellow-red for white montmorillonites immersed in blue-green-color-saturated malachite-green dye solution, and purple-blue for white montmorillonites immersed in red-color-saturated safranine-O dye solution.

Color descriptions of some of the clay samples studied using the Munsell system of color description are listed in table 6. These descriptions are of acid-treated clay samples and describe the color reaction of the clay to dye adsorption, using dilute safranine-O or malachite-green dyes.

DTA and X-ray identification data for some of these clay samples are given in figures 20 to 25 (appendix) and confirm the identities based on dye-staining tests.

The results of clay-mineral identification by the use of dyes are listed in table 9 (appendix). The samples from the Santa Margarita, Pulv., Reserve, and Valv. sands were selected at random from the core samples but were taken from a different size fraction than those run on the DTA. Furthermore the core samples were large; the DTA and dye samples from certain cores might have been from different laminae. This may account for the few apparent discrepancies indicated in table 9, comparing quantitative clay-mineral identification with DTA and dye-stain tests for these sands.

In the other sands tested - the Olcese, D.K., J.V., and L.O. - the dye-stain samples were taken from the coarser sample fraction and the DTA from the finer sample fraction. This seemed to have the effect of isolating the sub-mica clays in the dye-stain samples (coarse fraction) and the montmorillonites in the DTA samples (fine fraction). The clay mineralogy tended to differ between size fractions; this tendency was particularly noticeable in the D.K. zone, as may be seen by comparing the DTA and dye-stain results for this zone in table 9.

<table>
<thead>
<tr>
<th>Clay sample</th>
<th>Original color</th>
<th>Safranine-O final color</th>
<th>Malachite-green final color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite (API 9a)</td>
<td>7/4 5.0 Y</td>
<td>5/10 7.5 R</td>
<td>5-6/6 2.5 BG</td>
</tr>
<tr>
<td>Buckhorn P-34</td>
<td>7/5 5.0 Y</td>
<td>5/10 5.0 R, 5/10 2.5 YR</td>
<td>5/6 10.0 G, 6/6 5.0 BG</td>
</tr>
<tr>
<td>Montmorillonite (API 26)</td>
<td>8/8 5.0 Y</td>
<td>6/8 2.5 P</td>
<td>8/2 5.0 Y</td>
</tr>
<tr>
<td>Sepiolite (?), Dry Lake, Nev.</td>
<td>8/2 5.0 Y</td>
<td>6/10 2.5 R</td>
<td>6/6 10 BG</td>
</tr>
<tr>
<td>J.V. sand, well 62-33: 7,086.5'</td>
<td>6/6 2.5 Y</td>
<td>6/10 5.0 R, 5/10 7.5 RP</td>
<td>7/6 5.0 G, 6/6 7.5 Y</td>
</tr>
<tr>
<td>Santa Margarita, Bright #3, 2,785'</td>
<td>8/8 5.0 Y</td>
<td>5/8 7.5 P, 5/10 2.5 R</td>
<td>7/6 7.5 GY, 7/6 7.5 G,</td>
</tr>
<tr>
<td>Valv. well 58-33, 4,863'</td>
<td>8/6 5.0 Y</td>
<td>6/10 5.0 R, 5/10 2.5 P</td>
<td>5/6 5.0 BG, 7/10 7.5 Y</td>
</tr>
<tr>
<td>Olcese, well 34-34, 5,672'</td>
<td>8/4 5.0 Y</td>
<td>5/8 2.5 P, 6/10 2.5 R</td>
<td>8/8 5.0 Y, 6/6 2.5 BG</td>
</tr>
</tbody>
</table>

Y = Yellow.
R = Red.
P = Purple.
B = Blue.
G = Green.
Because of the shortage of core material for some samples and operational
difficulties that made it difficult at other times to coordinate selection of
dye-stain samples with DTA samples, the results in the tables are not meant to
directly compare identification methods. However, there is no indication of
anomalies in the results of either method. Some apparent anomalies, such as
might be caused by destruction of the clay during acid treatment of the sam-
ple (no such example was observed in Tejon cores, although it has been noticed
in a study of a bentonite sample from Tecopa, Calif.), may result.

In summary, dye staining, as used in the present study, offers a rapid,\textsuperscript{72}/
economical, dependable means of identification of clay-mineral groups.

Optical Studies

Optical studies of the Tejon core samples were limited to observation of
textural and mineral associates and relationships within the cores, except
that some complementary mineral-identification work was done, particularly
with the low-refractive-index sepiolitelike clays.

Clay-Sand Relationships

No set rule can be made concerning the relation of clays to other minerals
within the rock. In general, however, where a distinction between clays in a
sample was observed, the finer material consisted of predominantly montmoril-
lonite clays, whereas the coarser fraction contained submicas. The submicas
might have been secondary or authigenic clays intergrown in place into other
mineral crystals, but this was not proved.

Clays, predominantly submicas, in the Reserve and Valv. sands, clung tena-
coolly to the other mineral grains, and in many samples over 90 percent of the
clay remained so attached even after the fine grinding, stirring, and centri-
fuging attendant upon the acid-treatment process. It is assumed that these
were, in part, secondary authigenic clays. On the other hand, in some of the
J.V. sands the finest size fractions contained nearly all the clay and the
coarser size fractions virtually none.

It seems probable that authigenic clays also served as cementing agents
to a large extent; however, such clays, of the submica type, may tend to grow
between grains and lock them together fairly well after clay-water reactions
take place. The montmorillonite clays of the poorly cemented Pulv. sands, on
the other hand, appear to have no such binding power. Swelling of these clays
upon water contact breaks such poor cementing bonds as are present, resulting
in running sands.

\textsuperscript{72}/ "Rapid" does not give enough emphasis to the time required to acid-treat
the samples, though for a large number of samples, treatment and wash-
ing procedures may be "streamlined" to reduce this time appreciably.
Further simplification of the acid-treatment process is a problem des-
erving further research. The term "clay group" might better be used
here than "clay mineral," since it is the submica and montmorillonite
groups rather than submica and montmorillonite minerals that are
differentiated.
Zeolites

Zeolites have previously been reported from the Tejon area,\textsuperscript{73} and a zeolite similar to heulandite was very common in Valv. and Olcese sands and was also present in Pulv. sands of the Tejon-Grapevine field and in the Valv. sand in the Tejon Hills field.

Figure 18 shows the commonly developed faces of authigenic heulandite. Measured optical data were limited to measurement of the angle between the 001 and 201 faces and that between the 001 and 20\(\bar{1}\) faces, and measurement of the refractive indices. The optical angles were measured on crystals lying on the 010 face. Comparative optical data are given in table 7 and are compared with equivalent measurements obtained by Dana,\textsuperscript{74} Winchell,\textsuperscript{75} and Gilbert and McAndrews.\textsuperscript{76} This heulandite-like zeolite occurs in well-shaped secondary or authigenic crystals, commonly 5 to 25 microns long. Two such crystals are shown in figure 19.

![Figure 18. Crystal Habit of Authigenic Heulandite.](image)

The Santa Cruz occurrence reported by Gilbert and McAndrews is the only previous report of authigenic zeolites in sediments. Previously, crystalline zeolites had been reported only in volcanic rocks. It is believed that the occurrence of zeolites in sands indicates genetic relationship of the sand to volcanic source areas or suggests bentonitic sands. If this is true, the presence of authigenic zeolites may be related to swelling-type clays and would suggest the need for caution in introducing water into a sand containing zeolites.

Authigenic crystals grow in place in the formation, and it has been postulated that they may have a preferred orientation, possibly with their \(c\) axis paralleling the flow of water. If their axis should be related to the direction of motion of formation water, this information might be useful to a petroleum engineer in planning development of a field. Further study is necessary to establish this relationship.

TABLE 7. - Optical properties of heulandite

<table>
<thead>
<tr>
<th></th>
<th>Dana</th>
<th>Winchell</th>
<th>Gilbert-McAndries Santa Cruz heulandite (average)</th>
<th>Tejon heulandite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(001) ( \wedge ) (201)</td>
<td>114°</td>
<td></td>
<td>113° 30'</td>
<td>113° 15'</td>
</tr>
<tr>
<td>(001) ( \wedge ) (201)</td>
<td>63° 40'</td>
<td></td>
<td>63° 30'</td>
<td>63° 40'</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.500</td>
<td>1.488 (Si-rich)</td>
<td>1.480</td>
<td>1.481</td>
</tr>
<tr>
<td>Birefringence</td>
<td>.007</td>
<td>.001 (Si-rich)</td>
<td>.007 approx.</td>
<td>.003 approx.</td>
</tr>
</tbody>
</table>

J.V. Sand - Marl Gradation

The J.V. sand was studied from cores taken from two holes, one in the northeast corner of sec. 33, near the middle of the central area of the Tejon-Grapevine field, and the other in the east center of sec. 33, in the south-west part of the central area. Cores from both holes suggested the presence of evaporite marls, similar to those forming today in playa lakebeds in the Great Basin area. In the more northerly hole they interfingered with the sands; in the southerly hole they completely dominated the section, thereby reducing permeability almost to zero, as carbonate cement in the marl filled most of the pore space.

The amount of carbonate present, indicated in table 9, is based upon visual observation of effervescence caused by the action of dilute hydrochloric acid upon finely ground core samples and is therefore only an estimate. Enough carbonate appears to be present to warrant an attempt at acid-treating this formation. The J.V. sand, which overlies volcanics, contains a wide variety of minerals, including both volcanic and playa-lake types. One oddity is the presence of euhedral arsenopyrite in some of the marl zones. The crystals are believed to have been inclusions in another mineral, perhaps chlorite, and to have weathered out. Such quantities of "ore" might tend to give anomalous results in electric log studies.
The montmorillonite and sepiolite clays would reflect the association with volcanics and the playa-lake association, respectively. Sepiolite-like clays, probably somewhat younger in age, are also common in the McKittrick and Vallecitos areas along the west side of the San Joaquin Valley, where they also occur in playa-type marls.

**Clay-Mineral Lithology**

The clay-mineral types frequently have a distinctive appearance under the microscope that aid in identifying them. Thus, aggregates of montmorillonite crystals often appear as a large, rather nebulous, single crystal that has been stained. Sepiolite may appear in a similar manner, but both its reaction to dye stains and its mineral associations (especially with large quantities of carbonates) readily distinguish it from montmorillonite.

Aggregates of other clay minerals appear as discrete particles, often of uniform orientation. The submicras commonly occur in clusters of small, round, flat particles. Under favorable conditions, crystal faces may be seen on kaolin-type crystals, which may be joined in a vermicularlike manner.

Birefringence, or difference in crystal indices of refraction as observed in polarized light, was not found particularly useful in distinguishing clays of the Tejon area, since low-birefringence kaolin types were wholly absent and the presence of other minerals tends to hamper measurement of true birefringence in many instances. In some samples sepiolite types could be distinguished by their low birefringence. Some submicras and montmorillonites appeared to have abnormally low birefringence, perhaps due to poor crystallization.

Dye-staining tests revealed an interesting relation, especially in Pulv.-Reserve and Valv. sands. It was noted that some of the clay grains appeared oil-saturated to opaqueness, whereas others were not. In samples where this occurred, it was found, in every instance, by dye-stain tests that the opaque grains were montmorillonite and the clear grains submicras.

**Estimating Clay-Mineral Content**

Numerous workers have estimated the clay content of given rock samples; usually this is done for a particle-size fraction rather than for a pure clay-mineral fraction of the rock.

Clay-mineral content may be determined accurately in thin sections, provided that, during impregnation and cutting of the thin section, no swelling occurs to create a secondary lineation parallel to the section. Such lineation might sharply increase the apparent clay content of the rock.

It is suggested that, where a large number of samples is to be studied optically, a number of known mixtures, by weight, of clay and nonclay materials be selected for comparative studies. In studying oil sands, for example, mixtures containing 1, 2, 3, 4, 5, 7, and 10 percent clay and the remainder pure quartz and/or feldspar would be helpful in orienting the worker, so that
he might be able to judge within 1 or 2 percent, say, the clay-mineral content of an unknown.

Need for Multiple Identification Methods

Several methods of analysis are necessary for identifying clays because each method yields data that are not available from other analyses. Barshad\textsuperscript{77} points out that, although the X-ray is indispensable for crystal-structure analysis, DTA are needed to record changes that occur in a mineral during heating. He states furthermore:

It would be practically impossible to identify and estimate amounts of various clay minerals in a clay sample derived from a soil unless various methods of analysis are used.

Recently apparatus\textsuperscript{78} has been developed for obtaining X-ray diffraction data for a powdered sample while it is being heated at constant rate. When such equipment has received further development, close coordination may be expected from the results of DTA and X-ray analysis.

To illustrate the confusion that may exist due to limited analysis, Brindley\textsuperscript{79} has reviewed the work of others who have reported that a montmorillonite X-ray pattern was obtained from an illite treated with MgCl\textsubscript{2}; other investigators have shown that biotite leached with MgCl\textsubscript{2} over a long period is converted to an expandible vermiculite. Brindley concludes from these observations that the change from a swelling to a nonswelling mineral and return is rather easy; the swelling property is connected primarily with chemical composition. These "minerals" should be regarded as essentially different chemical species rather than different structural arrangements. It is apparent that X-ray patterns cannot be expected to reveal chemical changes in clays.

A number of chemical analyses of samples of kaolinites, montmorillonites, and illites have been published.\textsuperscript{80} The SiO\textsubscript{2}:Al\textsubscript{2}O\textsubscript{3} ratio calculated from these analyses for kaolinite seldom exceeds 2, and as a rule the ratio is of the order of 1.25 ± 0.1; for montmorillonite the SiO\textsubscript{2}:Al\textsubscript{2}O\textsubscript{3} ranges from about 2.5 up to 3.1; for illites or submica clays the SiO\textsubscript{2}:Al\textsubscript{2}O\textsubscript{3} ratio ranges from 1.47 up to about 2.4. When the ratio is calculated for SiO\textsubscript{2}: (Al\textsubscript{2}O\textsubscript{3} + Fe\textsubscript{2}O\textsubscript{3} + MgO) the values are of the order of those obtained


for kaolinite. However, 3 to 8 percent K₂O usually is associated with the submica clays; less than 1 percent of this oxide is found in most analyses of kaolinite or montmorillonite. Chemical analysis of clays will separate the 2-layer clays (such as members of the kaolinite group) from the 3-layer clays, montmorillonite and the micas. However, individual members of these groups or a specific clay mineral cannot be identified from chemical analysis without the help of some supplementary\(^81\) identifying procedure. Chemical analysis appears to have principal importance to the study of crystalline structure of clays as related to their composition and associated exchangeable ions.

**TABLE 8. - Average ratio SiO₂ : Al₂O₃ of clays from chemical analysis**

<table>
<thead>
<tr>
<th></th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
<th>Submicas or Illites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio SiO₂ : Al₂O₃</td>
<td>1.25 ± 0.1</td>
<td>2.5 to 3.1</td>
<td>1.47 to 2.4</td>
</tr>
</tbody>
</table>

Measurement of the optical characteristics of minerals has been developed on the premise that "seeing is believing." The clay-mineral groups have distinctive optical properties, so that clay-mineral identifications sometimes are possible from optical microscopic examination. Aggregates\(^82\) of clay minerals are equally as difficult to identify by optical procedures as by other means.

Staining clays with dyes or reagents that bring about color change when adsorbed on clay particles has been used as a supplementary aid in identifying clay by optical methods.

The reactions that take place are: Acid-base reactions, in which the stains act as pH indicators; and oxidation-reduction reactions, in which the stains are partly oxidized. Stains involving acid-base reactions require acid treatment of the sample so that an H⁺ clay is available for examination. The acid-treating process should be carried out with considerable care to avoid possible alteration of the clay sample.

Optical methods are limited further in that they do not supply information related to clay-mineral structure. However, these studies are valuable as an auxiliary procedure and as a preliminary method of evaluating and planning the analysis of a sample. The study of thin sections is particularly helpful in showing the relationship between the occurrence of clay in sediments with respect to cementing material, pore space, and rock structure. Considerable work is needed to develop these procedures further.


During the last 20 years electron-microscope\textsuperscript{83} studies have been used as an aid for identifying clays.

Electron micrographs of clays have revealed the shape of particles of various clay minerals and their particle-size range; however, the equipment needed is very expensive, and clay samples require precise preparation and techniques, especially when replica studies are made.

Clays usually occur as complex mineral associations or sometimes as mixed layer aggregations of several minerals. No one method of study will yield enough information for a complete evaluation of a clay and its properties.

Each technique used for studying and identifying clays has been developed to seek out some trait or characteristic that is not obtainable from other methods of study. Use of several complementary techniques will show various characteristics that together may yield enough information for adequate evaluation of a clay and its properties.

APPENDIX

Stratigraphy of Tejon-Grapevine Field and Tejon Hills Field

The following descriptions of oil sands and production data were taken largely from observation by Lavery and Vallely\textsuperscript{84} and from more recent observations by Lavery.\textsuperscript{85} These descriptions are supplemented by results of laboratory determinations of clay content and other significant characteristics of some of the oil sands.

Tejon-Grapevine Field

Figure 3 (p. 6) shows the principal producing formations in the Tejon-Grapevine field. Of these, cores from all but the Transition zone were included in the present study.

The Tejon-Grapevine field is divided into three distinct areas of production: The western, the central, and the eastern. Nearly all current production in the western and eastern areas is from upper Miocene Transition zone sands. This discussion deals mainly with the central area, which now has six major producing zones - the Transition, Santa Margarita, Pulv., Valv., Olcese, and J.V. sands.

Upper Miocene Transition Zone. - The Transition-zone sand ranges in depth from 1,860 to 2,690 feet in the eastern area to 2,600 to 2,800 feet in the


central area of the Tejon-Grapevine field. Effective well depths in the western area range from 2,500 to 2,600 feet. Gravity of the oil is 16° - 18° API.

The productive interval ranges from 50 to 125 feet in the western and central areas and from 40 to 265 feet in the eastern area. Air permeability ranges between 200 to 1,200 millidarcys, and recovery is estimated at 350 barrels per acre-foot.

Trapping is stratigraphic on domelike or monoclinal structures in all three areas, with gradation in permeability the major factor. No core samples from the Transition zone were tested in the present study.

The sand has been described as fine-grained to coarse and pebbly, with a green, clayey matrix. The early wells were drilled in with water-base mud. It soon became apparent that water from the drilling mud was seriously impairing productivity. Running-sand conditions resulted, and the clay matrix in the pay zone swelled, reducing permeability. The running-sand conditions were handled with some success by gravel-pack liners. The use of oil-base drilling fluids in recent five-spot completions has apparently corrected the problem of permeability reduction, and higher productivity indices have resulted. No gas cap is found in the main sand, but upper stringers apparently contain gas over the entire production area.

**Upper Miocene Santa Margarita.** - The Santa Margarita sand ranges in depth from 2,700 to 2,900 feet, with a productive interval of 60 to 150 feet. This is a gray, fine- to medium-grained sand, with a permeability of 600 to 1,500 millidarcys, and yields 18° gravity oil. The estimated recovery is 200 barrels per acre-foot. The trap is partly stratigraphic, with gentle folding and no gas cap.

Clay-identification tests of two core samples of the Santa Margarita sand indicated montmorillonites as the predominant clay type, with traces of submicas.

**Upper Miocene Pulv. Zone.** - The Pulv. zone ranges from 3,000 to 4,600 feet and consists of shale and sand members, the most productive of which is the Reserve sand, at or near the base of the zone. This sand - the first productive sand in the area - is bluish to brownish gray, very fine grained and well-sorted, with a somewhat clayey matrix. The Reserve sand is about 100 feet thick. The structure is a narrow anticline plunging to the west, with the sand shaling out on the south flank and thinning on the north flank. The zone yields 23° API gravity oil, and the recovery is estimated to be approximately 200 barrels per acre-foot. There is an active water drive.

The Pulv. is the most difficult zone to produce from because of the running-sand conditions. It is essential to complete the wells with oil or oil-base mud; then, when the zone becomes depleted, sand troubles begin. The swelling of interstitial clays on contact with water-base mud decreases the permeability drastically.
Clay-identification tests of six core samples taken from the Pulv. zone in sec. 34, T. 11 N., R. 19 W., suggest a strong predominance of montmorillonite characteristics, with minor amounts of submicas present, whereas clays in the lower 75 feet of this Reserve-sand section show strong submica characteristics, with minor amounts of montmorillonites present.

All Pulv.-zone core samples observed under the microscope contained secondary (authigenic) crystals of a zeolite resembling heulandite, although in much smaller quantities than in the Valv. zone discussed below. The presence of zeolites is considered to be indicative of the presence of bentonitic or swelling-type clays in the oil sand.

Middle Miocene Valv. Zone. — The Valv. zone has one major productive sand (Luisian) about 80 feet thick at a depth of 4,700 feet. The sand is light gray, fine- to medium-grained, well-sorted, and clean. Submica is the dominant clay type, with minor amounts of montmorillonite clays. The structure is an east-west-trending fold, with the sand shaling out on the south flank.

The wells have been drilled in with water-base mud, and most of them were completed through gun perforations. An active water drive, as well as an expanding primary gas cap, provides the reservoir energy.

Middle Miocene Olcose Pool. — The Olcose is a basal Relizian sand and conglomerate. The gas cap consists of thinly interbedded sands and shales about 150 feet thick. The oil reservoir consists chiefly of conglomerate, with a medium-grained, well-sorted, clean, oil-sand matrix. It varies from 40 to 170 feet in thickness at an average depth of 5,650 feet. Air permeability varies from 0 to 2,000 millidarcys, and the gravity of the oil is 28° to 30° API.

An expanding gas cap, as well as an active water drive on the north flank, provides the reservoir energy. The Olcose structure is a northeast-southwest-trending anticline, faulted on the south flank. A rapid facies change is exhibited by the Olcose conglomerate, being thickest on the northeast nose, thinning on the north flank, then shaling out on the crest and becoming sandier again to the west.

In cores obtained from sec. 34, T. 11 N., R. 19 W., montmorillonitelike clays tend to predominate, but only slightly less clay of submica type is present, except near the middle of the formation, where submicas dominate. A zeolite resembling heulandite similar to that observed in the Valv. zone is common at the top and middle of the Olcose, associated with both dominant submica and montmorillonite clay types.

Lower Miocene J.V. Sand. — The Saucesian J.V. sand overlies basalt throughout the Tejon-Grapevine field. It is 45 to 100 feet thick at depths of 6,600 to 7,400 feet, with a 15- to 20-foot-thick gas cap covering an area exceeding 100 acres. Air permeability ranges from 3.5 to 5,000 millidarcys, and the gravity of the oil is 35° to 39° API.
The structure, shown in detail by Lavery, is a northeast-southwest-trending anticline. Production appears to be limited on the south by a pre-Oligocene thrust fault. Productive limits to the west had not been established as of 1955.

Mineralogically the J.V. is a very distinctive formation. In the northern part of sec. 33, T. 11 N., R. 19 W., where the J.V. sand is productive, the upper half of the formation is a tight, impermeable marl, containing abundant carbonates, a sepiolitellike clay mineral along with some montmorillonoid clays, and locally abundant quantities of opaline crystals, which appear to be arsenopyrite.

In the middle of sec. 33, the lower 90 feet is composed of tight, impermeable marl containing montmorillonite and sepiolitellike clays, with some zones containing large quantities of arsenopyrite. There are few sand streaks in this section. The upper 20 feet consists of marly, rather permeable sands containing montmorillonite and submica clay-mineral types.

**Deeper Sands.** - The J.V. sand overlies a Saucesian volcanic section 1,400 to 1,800 feet thick, the thickest section reportedly underlying the J.V. and Oligocene fold in the central area. The section consists of basaltic detritus, basalt flows, ash beds, and occasionally sand fingers.

The sediments below the volcanics have not as yet been intensively explored. They are productive in other areas nearby, such as Tejon Hills, Wheeler Ridge, and Edison, and are known to include some sand members in the Tejon-Grapevine area. The basal Eocene beds overlie a basement complex, consisting of schists, phyllites, and granites. The basement rises from a depth of about 15,000 feet in the Tejon-Grapevine field to 3,000 feet in the Tejon Hills, 6 miles eastward.

### Tejon Hills Field

The major productive zones in the Tejon Hills field (as shown in fig. 3, p. 7) are the Santa Margarita, Valv., D.K., and L.O. The Springs fault, surface evidence of which is a line of springs and a small near-vertical escarpment in Pleistocene gravels, limits production to the southeast in most of the sands. A distinguishing feature of the field is the relatively high production of high-gravity oil from shallow depths. Close well spacing, combined with an active water drive and good permeability, would tend to make the ultimate recovery high, probably in the order of 400 barrels per acre-foot.

**Santa Margarita Production.** - The Santa Margarita sands produce in all parts of the field and were the only sands producing in the northeastern half of the field in 1954. The depth ranges from 365 to 550 feet, with a productive interval of 20 to 200 feet. The sand is light gray, coarse-grained, and massive and has been previously reported to be somewhat clayey.

Oil has accumulated in numerous fault blocks and minor folds. The eastern limit of production is controlled by the Springs fault, and closure to the northwest apparently is due to faulting. Daily well production ranges from 20 to 100 barrels of 28° API oil. Air permeability ranges from 170 to 5,600 millidarcys.

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86/ Work cited in footnote 85 (p. 53).
Valv. Zone. - The Valv. zone is productive in as many as 6 sands of limited areal extent at a depth range of 750 to 1,325 feet in secs. 21, 22, and 28 in the southwestern part of the field. These sands are brownish gray, fine-grained, firm, and clean. Clay (which occurs in the 1 sample tested - from 1 of the lower sands in sec. 29) consists mainly of montmorillonites, with some submicas. Significantly, as was the case with the Valv. in the Tejon-Grapevine area, this sample contained zeolite crystals resembling heulandite.

The Valv. zone has a definite facies change along strike from almost all shale in sec. 29 on the southwest to all sand in sec. 21 on the northeast. Farther northeast it laps out against the rising basement complex.

Initial well production is 100 to 200 barrels per day of 29° to 31° API oil. Permeability values range from 120 to 3,200 millidarcys. Accumulation is due to stratigraphic trapping and structural trapping by the Springs fault and minor crossfaults.

D.K. Zone. - The D.K. zone is roughly equivalent in age to the lower Miocene Zemorrian unit regionally known as the Vedder. This zone has several producing sands at a depth range of 1,500 to 2,500 feet in secs. 20, 21, and 29 in the southwest part of the field. The sands are light gray-green, fine-grained, and somewhat ashy. When samples of these sands were ground for clay identification, the sample was separated into a turbid or finely divided portion and a nonturbid portion. Clay-mineral identification tests of the finely divided, turbid portion suggest montmorillonoid, whereas tests of the remaining coarse portion indicate submicas.

Accumulation of oil is due to stratigraphic trapping, folding, and faulting. Initial daily production is 150 to 300 barrels of 33° to 34° oil. Air permeability ranges from 40 to 8,000 millidarcys.

Oligocene L.O. Zone. - L.O.-zone production, as of 1954, was limited to a few wells in sec. 29, at a depth of about 2,150 feet, and 1 well in sec. 20, at 3,700 feet. The sand ranges from 20 to 75 feet in thickness and is coarse, granitic, ill-sorted, and dirty, with relatively low permeability. The predominant clay minerals in the sample tested in most instances resemble montmorillonite. One dolomitic sample near the center of the zone contained a montmorillonoid clay giving thermal reactions similar to nontronite. Initial daily well production is 80 to 125 barrels of 33° oil. This reservoir accumulation appears to be largely stratigraphic.

**Laboratory Data**

The laboratory data on which the discussion and conclusions of this report are based are given in the following tables. Differential thermal curves of clay references and typical differential thermal curves of the clay-size fractions from oil-bearing formations in the Tejon-Grapevine and Tejon Hills fields (figs. 20-25), Kern County, Calif., are also shown.
FIGURE 20. - Thermal Curves of Reference Clays.
FIGURE 22. - Typical Thermal Curves of Clay-Size Fractions From Oil-Bearing Formations in Tejon-Grapevine Area.
FIGURE 23. - Typical Thermal Curves of Clay-Size Fractions From Oil-Bearing Formations in Tejon-Grapevine Area.
FIGURE 24. - Typical Thermal Curves of Clay-Size Fractions From Oil-Bearing Formations in Tejon-Grapevine Area.
FIGURE 25. - Typical Thermal Curves of Clay-Size Fractions From Oil-Bearing Formations in Tejon-Grapevine Area.
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<th>Clay minerals identified by dye staining</th>
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1/ M indicates montmorillonite.  2/ S indicates submic.  3/ Indicates carbonate.  4/ Sep indicates sepiolite.  
5/ I indicates indeterminate.