Electrical Conductivities in Oil-Bearing Shaly Sands

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ABSTRACT

A simple physical model was used to develop an equation that relates the electrical conductivity of a water-saturated shaly sand to the water conductivity and the cation-exchange capacity per unit pore volume of the rock. This equation fits both the experimental data of Hill and Milburn and data obtained recently on selected shaly sands with a wide range of cation-exchange capacities.

This model was extended to cases where both oil and water are present in the shaly sand. This results in an additional expression, relating the resistivity ratio to water saturation, water conductivity and cation-exchange capacity per unit pore volume. The effect of shale content on the resistivity index—water saturation function is demonstrated by several numerical examples.

INTRODUCTION

A principal aim of well logging is to provide quantitative information concerning porosity and oil saturation of the permeable formations penetrated by the borehole.

For clean sands, the relationships between measured physical quantities and porosity or saturation are well known. However, the presence of clay minerals greatly complicates log interpretation, particularly the electrical resistivity and SP logs, and considerably affects evaluation of hydrocarbon-bearing formations. The conductance and electrochemical behavior of shaly sands and their relation to log interpretation have been studied by many workers. Willie and Lynch reviewed this work in some detail.

Virtually all laboratory measurements of electrical resistivity and electrochemical potential of shaly sands published to date are the work of Hill and Milburn. Their measurements were made on about 300 cores covering a large variety of sedimentary rocks, and a wide range of equilibrating NaCl solution concentrations. Hill and Milburn described their conductivity data by an empirical equation in which the shaly sand conductivity $C_w$ was expressed as a function of the solution conductivity $C_{sol}$ and two parameters $b$ and $F_01$. The quantity $b$ was shown to be a measure of the effective clay content of the rock, being approximately proportional to the cation-exchange capacity of the rock divided by its pore volume. The latter ratio is designated as $Q_v$ in this paper and has the dimensions meq/ml or equiv/liter. $Q_v$ is identical with the term representing the concentration of fixed charges in the Meyer-Sievers and Teorell theory of permeable membrane behavior. $F_01$ is a formation resistivity factor referred to a hypothetical equilibrating solution resistivity of 0.01 ohm m at 25°C, where clay effects presumably are minimized. $F_01$ was correlated to porosity by an Archie-type equation.

The Hill-Milburn equation describes their data with a standard deviation of approximately 1 percent and a maximum deviation of ±10 percent.

Shaly sands behave as permeselective cation-exchange membranes, their electrochemical efficiencies increasing with increasing clay content. The electrochemical potential data of Hill and Milburn were expressed graphically, and demonstrate that the membrane efficiency (or cation transport number) of these sands is a function only of the $b$ value (i.e., $Q_v$) and the respective salt concentrations of the two solutions forming the liquid junction in the sand. The diffusion potentials are not dependent on $F_01$ or any parameter relating to the porosity or pore geometry of the rock.

The Hill-Milburn resistivity equation correctly predicts a decreasing sand conductivity $C_w$ with decreasing solution conductivity $C_{sol}$. However, at some low value of $C_{sol}$, the calculated $C_w-C_{sol}$ function goes through a minimum; with further decrease in $C_{sol}$, the predicted sand conductivity increases sharply. As pointed out by Hill and Milburn, an increasing value of $C_w$ with decreasing $C_{sol}$ is physically meaningless. Since this occurs below the range of practical values of $C_{sol}$, the usefulness of the empirical equation is not affected when

*This value is four times less than the resistivity of a saturated NaCl solution at 25°C.
applied to water-saturated sands. However, as will be discussed later, the equation cannot be extended to oil-bearing shaly sands since the minimum in the $C_o - C_w$ curve then is shifted to higher $C_w$ values.

In this paper an equation for shaly sands is developed which relates the resistivity ratio to water saturation, water conductivity and an independently determined shaliness parameter, using a simple physical model and modern concepts of the nature of the electrical charge of clay minerals.

THE MODEL

The essential features of the shaly sand conductivity plots ($C_o$ vs $C_w$) are shown in Fig. 1. In the range of dilute equilibrating electrolyte solutions (from 0, to about 0.1 to 0.5 $m_{NaCl}$), the sand conductivity increases sharply with increasing solution concentration at a greater rate than can be accounted for by the increase in $C_w$. With further increase in equilibrating solution conductivity, the sand conductivity increases linearly.

The model consists of two resistance elements in parallel, one component consisting of the free electrolyte contained in the pore volume of the rock $C_{el}$ and another resulting from the conductance contribution of the exchange cations associated with the clay $C_c$. We can write

$$C_{rock} = C_o + C_{el} \ldots \ldots \ldots (1)$$

and

$$C_o = xC_c + yC_w \ldots \ldots \ldots (2)$$

where $C_o$, $C_c$ and $C_w$ are the specific conductances of core, clay exchange cations and equilibrating salt solution, respectively; and $x$ and $y$ are appropriate geometric constants. We assume that the electrolyte solution in the porous system has the same electrical conductivity as that for the equilibrating solution, i.e., Donnan effects are neglected.

The sharp increase in conductance with increasing concentration of electrolyte in the dilute range is attributed to an increasing exchange-cation mobility. Conductance due to exchange cations can proceed by cation migration in the electric field from one fixed exchange site on the clay particles to another, from assemblages of clay platelets to exchange sites on other assemblages and through the free electrolyte. An increase in clay content and available exchange sites with little or no free electrolyte present should decrease the energy required for electrical conduction and, consequently, result in an increase in exchange-cation mobility. Further, if increasing concentrations of salt solutions were introduced in the pores, there should be another and energetically easier path through the solution, again accompanied by a significant increase in exchange-cation mobility. At some relatively high concentration of equilibrating electrolyte solution, further increase in concentration should make little difference in exchange-ion mobility, i.e., this mobility should then reach a constant and maximum value. At higher electrolyte concentrations, the sand conductivity will increase linearly with increase in solution conductivity.

Various self-diffusion and activation energy measurements of ionic diffusion in three-dimensional matrices having fixed charge sites support these assumptions. Richman and Thomas\(^7\) reported values of the self-diffusion coefficients for Na$^+$ ion in cylindrical rods of a synthetic ion-exchange resin.

The concentration of counter ions $Q_o$ in this material varied from 1.5 to 1.7 equiv/liter. These authors observed that the diffusion coefficient $D$ increased by a factor of about 4.8 as the equilibrating electrolyte solution was varied from deionized water to 0.03 $N$ NaCl, and then remained constant as the concentration was increased further. Activation energies for self-diffusion of the Na$^+$ ion decreased from about 10.3 to about 2.2 kcal mole$^{-1}$ as the external salt concentration was increased from 0.01 to 0.07 $N$.

Similar measurements were made in bentonite-water plugs by Lai and Morton.\(^8\) Their data show a decrease in the activation energy for self-diffusion of the Na$^+$ ion with increasing clay concentrations in salt-free bentonite plugs. Lai and Morton also reported measurements of the self-diffusion of Na$^+$ ion in bentonite plugs (0.5 gm clay/2 ml system) equilibrated with varying concentrations of NaCl solution. The diffusion coefficient increased from about 2.3 to 4.8 $\times 10^{-6}$ sq cm sec$^{-1}$ when the solution concentration in equilibrium with the plug was increased from 0.01 to 1 $N$ NaCl.

Recently, Gast\(^9\) reported measurements of the self-diffusion coefficients of sodium and chloride ions in a 3.75 percent Na-bentonite gel containing increasing amounts of NaCl. The self-diffusion coefficient for sodium ion increased from about 2.3 $\times 10^{-6}$ to 8 $\times 10^{-6}$ sq cm sec$^{-1}$ with increase in NaCl concentration from 0 to about 0.06 $N$; no significant change in $D$ was observed for the chloride ion. Calculated self-diffusion coefficients obtained from conductivity data on the same systems,
the use of a two-component model as in Eq. 1 and
the Nernst-Einstein equation were in excellent
agreement with the observed coefficients.

We assume next that the electric current
transported by the counterions associated with the
clay travels along the same tortuous path as the
current attributed to the ions in the pore water.
Thus, the geometric parameters \( x \) and \( y \) of Eq. 2
are assumed to be equal. By analogy with the idea
of formation resistivity factor for clean sands,

\[
x = y = \frac{1}{F^*} \quad \ldots \ldots \ldots (3)
\]

where \( F^* \) is the shaly sand formation resistivity
factor. We can then write

\[
C_0 = \frac{1}{F^*} (C_a + C_e) \quad \ldots \ldots \ldots (4)
\]

For clean sands, \( C_e = 0 \), and \( F^* \) reduces to \( F \), the
usual formation factor defined as \( C_w/C_0 \). This
assumption is justified since the cation transport
numbers are independent of any parameter relating
to rock porosity or pore geometry, as indicated by
the electrochemical data of Hill and Milburn.\(^3\)

Various expressions for the cation transport
number (and hence, electrochemical potentials) can be
derived from conductivity equations based on a
parallel conductance model, depending on the
number of resistor elements considered.\(^10,11\) Under
these conditions, the resulting cation transport
numbers would not be independent of geometric
"cell constant" parameters such as \( x \), \( y \), and \( F^* \)
unless these parameters are equal.

For the straight-line portion of the conductivity
curve where a constant and maximum exchange-
cation mobility has been assumed, we write

\[
C_a = \frac{\mu_{Na}^a e}{1000} Q_v = \frac{\lambda_{Na}^a}{1000} \quad \ldots \ldots (5)
\]

where \( C_a \) = specific conductance of the clay counter-
ions, mho cm\(^{-1}\)
\( \mathcal{F} \) = faraday
\( \mu_{Na}^a \) = maximum sodium exchange ion mobility,
sq cm vol\(^{-1}\) sec\(^{-1}\)
\( Q_v \) = concentration of sodium exchange ca-
tions associated with the clay, equiv/liter
\( \lambda_{Na}^a \) = maximum equivalent ionic conductance
of the sodium exchange ions, sq cm
equiv\(^{-1}\) ohm\(^{-1}\)

Since \( C_e \) is a constant over this range of \( C_w \)
values, the slope of the straight-line portion of the
conductivity curve is equal to the reciprocal of the
formation factor \( 1/F^* \) (Fig. 1); the intercept \( C_0 \),
obtained by extrapolating the straight-line portion
of the conductivity plot to the \( C_0 \) axis, is equal to
\( C_e/F^* \); and the line segment \( AB \) is equal to \( C_e \) or
\( (\lambda_{Na}^a Q_v)/1000 \).

Required tests of the model are (1) demonstration
of a proportionality between segments \( AB \) obtained
from \( C_w \) plots, and \( Q_v \) values determined
independently by analytical methods for a variety
of shaly sands, and (2) correlation of \( F^* \)’s obtained
from slopes of \( C_w \) plots to porosity and pore
geometry of the rocks.

\( C_e \) is expressed as a volume conductivity in Eq.
5. This model cannot differentiate between a volume
and a surface conductance mechanism for the clay
counterions, since either consideration results in
the volume concentration term \( Q_v \) in Eq. 5. Con-
sidering the exchange ion contributions as a surface
conductance, we obtain

\[
C_a = \mathcal{S} \mu_{Na}^e Q_v \quad \ldots \ldots \ldots \ldots \ldots (6)
\]

where \( C_a \) is the specific surface conductance of
the clay (ohm\(^{-1}\)) and \( Q_v \) is the number of equivalents
of exchange cation per unit of surface area. Further,

\[
C_e = SgC_a = Q_s Sg\lambda_{Na}^e \quad \ldots \ldots \ldots (7)
\]

where \( S \) is the specific surface area of the clay
(sq cm/gm clay) and \( g \) is the weight of clay per
unit of rock pore volume (gm clay/cu cm). Comparing
Eqs. 5 and 7,

\[
Q_s Sg = Q_v /1000 \quad \ldots \ldots \ldots (8)
\]

Clearly the volume concentration term \( Q_v \) and the
associated volume conductivity are simpler to
measure and use than the parameters of Eqs. 7 and
8 which are required to describe the surface
conductivity mechanism, i.e., surface concentration
of fixed charge sites, specific surface area of the
clay, etc.

Returning to the curved portion of the conductivity
curve in the low \( C_w \) region, we assume an
exponential rise of the counterion mobility up to
its constant and maximum mobility at higher
solution conductivities. This assumption is based
on conductivity data for synthetic ion-exchange
resin plugs, e.g., the work of Sauer et al.\(^12\) It may
be tested by comparison with shaly sand conduc-
tivity data, and by extrapolation to \( C_w = 0 \) for
comparison with literature data for clay conduc-
tivities.

The general equation for water-saturated shaly
sands then becomes

\[
C_o = \frac{1}{F^*} (BQ_v + C_e) \quad \ldots \ldots \ldots (9)
\]

with

\[
B = [1 - a \exp (-C_e / \gamma)] 0.001 \lambda_{Na}^a \quad (10)
\]

\( C_o \) and \( C_w \) have the units mho cm\(^{-1}\), \( B \) is introduced
as an equivalent conductance of the
counterions as a function of solution conductivity
\( C_w \) with units in mho sq cm/meq. The value of \( \gamma \) is
determined by the rate of increase of the counterion
mobility from that at zero water conductivity up to
its constant value at the higher water conductivities.
The parameter \( a \) is determined by the mobility of the exchange cations at \( C_w = 0 \),

\[
a = 1 - \frac{\lambda_{Na}^N}{\lambda_{Na}}
\]

where \( \lambda_{Na}^N \) is the equivalent ionic conductance of the exchange cations at \( C_w = 0 \).

**COMPARISON WITH EARLIER WORK**

Similar assumptions as to the equivalence of the cell factors for surface and bulk solution conductivity were made by Creemers and Lauedelout\textsuperscript{13-15} in their work on clay mineral suspensions and gels. Their data indicate that isoconductivity points exist for different clay mineral gel-salt systems. By extrapolating the straight-line portions of the \( C_w \) vs \( C_a \) plots for a series of gels consisting of varying percentages of the identical clay species, a common isoconductivity point is found. Creemers and Lauedelout observed that the conductivity at an isoconductivity point is independent of gel porosity. By comparison, they found that their form of the \( F-\phi \) function is in formal agreement with that derived from theories by Burgez\textsuperscript{16} and Fricke,\textsuperscript{17} relating electrical conductance of stationary particles in dilute suspensions to particle shape factors and porosity. The Creemers-Lauedelout \( F-\phi \) relation clearly is not applicable to shaly sands; moreover, the accuracy of the Creemers-Lauedelout data does not permit calculation of reliable values of exchange-cation mobilities for clay plugs equilibrated at any salt concentration.\textsuperscript{18}

The proposed mechanism differs from that suggested by Wyllie and his co-workers,\textsuperscript{1,10,12} They represented the conduction process by an equivalent resistor model containing three resistance components in parallel instead of two as suggested here. Two resistor elements are common to both models; the third consists of conductive solid and electrolyte solution elements in series. Contributions from this component can account for the sharp increase in the conductivity curves at low \( C_w \) values, rather than an increase in exchange-ion mobility. The Wyllie model requires four geometric parameters, three of which are independent. These can be obtained by appropriate manipulation of the conductivity equation under various limiting conditions.

Some comparison should be made with the work of de Witte.\textsuperscript{19} He concluded from empirical considerations that the conductivity behavior of water-bearing shaly sands could adequately be represented by the equation

\[
C_w = A_D + B_D C_w
\]

where \( A_D \) and \( B_D \) are constants. Eq. 12 is similar to that originally proposed by Patnode and Wyllie,\textsuperscript{20} and neglects the curved portion of the conductivity plots at low \( C_w \)'s. However, de Witte defined a "maximum formation factor", the limiting value of apparent formation factor as \( R_w = 0 \), namely \( F_m = 1/B_D \). \( F_m \) is identical to \( F^* \) of this paper. de Witte also recognized a shaliness factor \( A_P/B_P \), which was "an absolute rock parameter...independent of \( R_w \)". In this paper, \( A_P/B_P \) is equal to the maximum specific conductance of the exchange cations of the clay \( (\lambda_{Na} Q_v)/1,000 \).

**EXPERIMENTAL PROCEDURES AND DATA**

Conductivity data for about 315 shaly sand cores have been published by Hill and Milburn.\textsuperscript{3} These data include independent cation-exchange capacity and \( Q_v \) determinations on 36 samples. Additional unpublished measurements including \( Q_v \) and conductivity data on some 54 cores, together with conductivity data on 167 other samples, were made available to us by H. J. Hill. The conductivity data generally include three to four experimental points in the straight-line portion of the curve \( (C_w > 0.05 \text{ mho cm}^{-1}) \) and one to two points in the curved region, but these usually were obtained at equilibrating solution conductivities greater than 7 m mho cm\textsuperscript{-1} (solution resistivities less than about 1.4 ohm m). Group 1 refers to all the above samples.

While a large variety of rock types is represented in Group 1, the distribution of \( Q_v \) values is weighted heavily in the range 0 \( \leq Q_v \leq 1 \) equiv liter; this group contains about 94 percent of the total number of samples. Another set of shaly sands (Group 2) was selected on the basis of a wider distribution of \( Q_v \) values; with these samples, conductivity measurements at low equilibrating solution conductivities (down to about 2.1 m mho cm\textsuperscript{-1}) were emphasized. Conductivity data for Group 2 cores are probably the most accurate and complete with respect to range of \( Q_v \) and \( C_w \) values examined.

**GROUP 1**

Independent \( Q_v \) determinations, together with \( C_w \) measurements, were described for a selected set of sands by Hill and Milburn.\textsuperscript{3} Petrophysical and conductivity data for this set are presented in Table 1. Similar measurements were carried out on 54 additional cores. A description of these samples is given in Table 2; petrophysical characteristics and conductivity data are summarized in Table 3. Table 4 gives general characteristics and petrophysical data for the remaining samples used in the conductivity studies.

Experimental procedures employed in these conductivity measurements were described by Hill and Milburn.\textsuperscript{3}

**\( Q_v \) Determinations**

Cation-exchange capacities (CEC) as determined by Hill and Milburn (Table 1) were measured chromatographically using ammonium acetate solutions. Further CEC determinations (Table 3) were made using a procedure suggested by Mortland and Mello.\textsuperscript{21} This method requires repeated equilibration of the crushed rock sample with concentrated BaCl\textsubscript{2} solution and washing to remove excess barium ions, followed by conductometric
titration with standard MgSO₄ solution. Results are equivalent to the ammonium acetate method.

Core porosities were calculated from the following measurements made prior to the CEC determinations: (1) bulk volumes measured by mercury displacement and (2) grain volumes determined by buoyancy weighings under brine.

**TABLE 1 — PETROPHYSICAL AND CONDUCTIVITY DATA, SHALY SANDS (HILL AND MILBURN)**

<table>
<thead>
<tr>
<th>Suite</th>
<th>Sample Number</th>
<th>Porosity (%)</th>
<th>Air Permeability (μd)</th>
<th>Q₀ (equiv./liter)</th>
<th>Ψ</th>
<th>k</th>
<th>C₉ (Conductivity Units, nHm cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Clean Sandstone, Mincone, Neches Island</td>
<td>25 20.3 18.9 0.076 16.0 0.650 1.31 3.39 5.62 9.43 13.6</td>
<td>9.00</td>
<td>20.2</td>
<td>33.3</td>
<td>87.7</td>
<td>167.0</td>
<td>247.5</td>
</tr>
<tr>
<td>2 Clean Sandstone, Cretaceous, Paluxy Sand, Quitman, Texas, and Mitchell Creek, Texas</td>
<td>16 11.8 17.5 0.008 5.00 0.400 1.02 1.72 2.19 2.49 2.19</td>
<td>6.00</td>
<td>65.9</td>
<td>90.9</td>
<td>128.0</td>
<td>204.0</td>
<td>0°C</td>
</tr>
<tr>
<td>3 Clean Sandstone, Eocene, Lower Wilcox Sand, Sheridan, Texas</td>
<td>17 13.9 0.5 0.247 31.5 0.480 0.960 1.94 3.06 7.29 7.29</td>
<td>7.33</td>
<td>15.0</td>
<td>32.5</td>
<td>87.9</td>
<td>167.0</td>
<td>249.3</td>
</tr>
<tr>
<td>4, Group 1 Shaly Sandstone, Oligocene, Priro Sand, Seeligson, Texas</td>
<td>19 20.3 0.1 0.293 33.0 0.360 - 1.80 2.92 6.61 6.79</td>
<td>6.60</td>
<td>65.9</td>
<td>90.9</td>
<td>128.0</td>
<td>204.0</td>
<td>0°C</td>
</tr>
<tr>
<td>5, Group 1 Shaly Sandstone, Cretaceous, Paluxy Sand, Sheridan, Texas</td>
<td>22 20.1 44.0 0.327 24.6 0.400 2.22 3.99 5.48 8.68 8.68</td>
<td>5.30</td>
<td>90.1</td>
<td>218.0</td>
<td>0°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Very Shaly Sandstone, Taylor Sand, Big Foot, Texas</td>
<td>25 26.6 1.6 0.887 19.9 2.70 3.94 - 9.03 12.3</td>
<td>15.0</td>
<td>20.0</td>
<td>27.6</td>
<td>92.6</td>
<td>146.0</td>
<td>213.0</td>
</tr>
<tr>
<td>7, Group 2 Cretaceous, Petrict Limestone, Chapel Hill, Texas</td>
<td>21 17.5 1.3 0.064 29.8 0.210 0.820 1.94 5.00 7.20 7.20</td>
<td>6.00</td>
<td>25.0</td>
<td>35.0</td>
<td>148.0</td>
<td>216.0</td>
<td>0°C</td>
</tr>
</tbody>
</table>

**GROUP 2**

Shaly sand samples were selected which varied widely both in CEC and in manner of clay distribution. The range of Q₀ values extended from 0 to 1.5 meq/ml. Cores where 0.3 < Q₀ < 1.5 originated from a lower Tertiary horizon and contained fairly pure montmorillonite as the clay fraction, mainly

**JUNE, 1968**
<table>
<thead>
<tr>
<th>Suite</th>
<th>Sample Number</th>
<th>Permeability (μ)</th>
<th>Air Permeability (md)</th>
<th>Brine Permeability (md)</th>
<th>Gp Exp. (equiv/liter)</th>
<th>Pp</th>
<th>Gp (Conductivity Units, m ma cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Clean</td>
<td>1</td>
<td>21.7</td>
<td>-</td>
<td>68.1</td>
<td>0.093</td>
<td>17.6</td>
<td>1.33 2.16 4.91 13.1</td>
</tr>
<tr>
<td>Sandstone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Very Shaly</td>
<td>1</td>
<td>15.0</td>
<td>-</td>
<td>8.3</td>
<td>2.057</td>
<td>119</td>
<td>0.86 1.05 1.42 2.82</td>
</tr>
<tr>
<td>Sandystone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Brine containing 12 g NaCl per liter.
2. At 300 psi differential pressure.
TABLE 2 — DESCRIPTION OF SAMPLES INVESTIGATED

<table>
<thead>
<tr>
<th>Suite</th>
<th>Type of Formation</th>
<th>Description</th>
<th>Age and Locality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Clean sandstone</td>
<td>Clean, medium to fine grained (340 to 80 μm), friable quartz sand; major cementing material present: calcite and quartz</td>
<td>Miocene, Weeks Island, L.a.</td>
</tr>
<tr>
<td>2</td>
<td>Shaly sandstone</td>
<td>Miocene, shaly, fine grained to silty (100 to 65 μm), hard quartz sand; cementing material: chiefly calcite</td>
<td>Eocene, lower Wilcox sand, Sheridan, Tex.</td>
</tr>
<tr>
<td>3</td>
<td>Shaly sandstone</td>
<td>Highly calcareous, shaly, medium to fine grained (25S to 110 μm) argillic sandstone; cementing material: chiefly calcite</td>
<td>Oligocene, Fri sand, Seeligton, Tex.</td>
</tr>
<tr>
<td>4</td>
<td>Very shaly sandstone</td>
<td>Very shaly, very fine grained to silty (105 to 60 μm), consolidated quartz sand</td>
<td>Cretaceous, Taylor sand, Big Foot, Tex.</td>
</tr>
</tbody>
</table>

surrounding the grains and interstitial. The cores in which 0 < Q<sub>e</sub> < 0.5 came from an Eocene and an Albian horizon and contained mainly kaolinite and illite. In these cores, the clay occurs around the grains, but mainly in thin laminae. The compositions of the clay fractions (<2 μ) of the samples are given in Table 5.

Cylindrical cores 2.54 cm in diameter and 2 to 4 cm long were cut with their axes parallel to the bedding planes. After extraction with chloroform and ether, they were encased in epoxide resin. The cores then were equilibrated with a deaerated, saturated NaCl solution, and stored in this solution for several months before the experiments were started.

**Apparatus**

Electrical conductivities were measured with an accuracy of 0.1 percent using an impedance bridge. The cell was similar to that described by Hill and Milburn, contact between the platinitzied platinum electrodes and the cores was achieved through the equilibrating electrolyte solution in the end compartments of the cell. The measuring frequency was 1,592 cycles/second. Tests indicated that measured conductivities were independent of frequency, at least from 50 to 20,000 cycles/second. Measurements were conducted at a constant temperature of 25 ± 0.05°C.

TABLE 4 — DESCRIPTION AND PETROPHYSICAL CHARACTERISTICS OF ROCKS INVESTIGATED

<table>
<thead>
<tr>
<th>Age, Locality</th>
<th>Number of Samples</th>
<th>Conductivity Points per Sample</th>
<th>Range of Equilibrating NaCl Solutions (Normality)</th>
<th>Porosity Range (percent)</th>
<th>Permeability Range (md)</th>
<th>Range of F&lt;sub&gt;∞&lt;/sub&gt; Values</th>
<th>Range of Q&lt;sub&gt;e&lt;/sub&gt; (equiv/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Cretaceous, Nacatash Field, Bellevue, L.a.</td>
<td>51</td>
<td>4</td>
<td>0.11 -2.5</td>
<td>7-14</td>
<td>&lt;0.1-680</td>
<td>6-56</td>
<td>0.04-0.30</td>
</tr>
<tr>
<td>Pliocene, Ventura Field, Calif.</td>
<td>39</td>
<td>5</td>
<td>0.06 -3.06</td>
<td>4-16</td>
<td>0.13-19</td>
<td>22-120</td>
<td>0.1 -0.45</td>
</tr>
<tr>
<td>Cretaceous, Viking Formation, Alta, Canada</td>
<td>34</td>
<td>4</td>
<td>0.12 -4.79</td>
<td>14-30</td>
<td>0.6 -664</td>
<td>8-28</td>
<td>0.03-0.36</td>
</tr>
<tr>
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<td>27</td>
<td>4</td>
<td>0.048-1.86</td>
<td>5-15</td>
<td>&lt;0.1-1.5</td>
<td>10-146</td>
<td>0.02-0.15</td>
</tr>
<tr>
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<td>5</td>
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<td>8-12</td>
<td>—</td>
<td>30-75</td>
<td>0.02-0.05</td>
</tr>
<tr>
<td>Eocene, Gohke Field, Victoria, Tex.</td>
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<td>5</td>
<td>0.01 -3.25</td>
<td>16-20</td>
<td>—</td>
<td>19-21</td>
<td>0.03-0.05</td>
</tr>
<tr>
<td>Miocene, Weeks Island Field, L.a.</td>
<td>2</td>
<td>5</td>
<td>0.01 -3.25</td>
<td>20-25</td>
<td>—</td>
<td>15-22</td>
<td>0.01-0.02</td>
</tr>
<tr>
<td>Cretaceous, Big Foot Formation, Tex.</td>
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<td>5</td>
<td>0.01 -3.25</td>
<td>3-20</td>
<td>—</td>
<td>10-11</td>
<td>0.2 -0.4</td>
</tr>
<tr>
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<td>5</td>
<td>0.01 -3.25</td>
<td>4-16</td>
<td>—</td>
<td>31-41</td>
<td>0.2 -0.3</td>
</tr>
</tbody>
</table>

JUNE, 1968
The contribution of the electrode compartments was determined by measuring the conductivity of cells with the cores replaced by perspex rings having an internal diameter equal to the nominal diameter of the cores (2.54 cm) and varying in length from 1 to 5 cm. The "cell constant" of the electrode compartments was obtained by extrapolating the conductance data to zero length. The influence of small variations in core diameter on this cell constant was determined by measuring conductivities with perspex rings 3 cm long, but varying in internal diameter from 2.0 to 2.8 cm.

Cores with higher clay content (Qv greater than 0.2 meq/ml) were in danger of falling apart upon flushing with NaCl solutions of a concentration lower than 0.072 molar. To prevent their disintegration, these cores were fitted at each end with a plate of highly permeable, fired Bentheim sandstone. These plates were 2.54 cm in diameter and a few millimeters thick and were cut from a long bar previously mounted in epoxide. They were glued to the cores at the resin rim at each axial end of the cores.

Before mounting, the electrical cell constant of the plates was determined so that appropriate corrections could be made for the electrical conductivity determinations.

**NaCl Solutions**

The salt used was Analar reagent NaCl, fused overnight at 300°C and stored until use in a desiccator in which CaCl2 was the drying agent. Salt solutions were made up by weight.

The concentrations of the salt solutions in use were verified by conductivity measurements at 25°C. The accuracy of these electrical concentration determinations is somewhat better than 0.1 percent, except for concentrations higher than 4 molar. At these higher concentrations, the change of conductivity with concentration becomes increasingly smaller and accurate results cannot be expected. For solutions with concentrations greater than 4 molar, checks were made gravimetrically by evaporation of a known weight of solution.

**Cation-Exchange Capacity Measurements**

The determinations of CEC per unit pore volume of the shaly sand cores were made on pieces of rock adjacent to the places from where the cores had been removed because the method used was destructive. The cores were selected for the investigation from homogeneous portions of rock. Some duplicate determinations of exchange capacities were made at different adjacent pieces of rock, and the measure of agreement can be seen in Table 6. These cores have become valuable as a result of having undergone many electrochemical measurements; in order that they be available for further work, some accuracy in the exchange capacities has been sacrificed. We do not believe, however, that this is a serious disadvantage since no systematic errors are introduced. The Qv values cited in the second sample set of Table 6 were used in further calculations since they were taken closer to the cores of interest.

**Measuring Procedure**

As shaly sands may fall apart when kept in contact with brine of very low salinity, the investigation was started at high NaCl concentrations. At each concentration the cores were equilibrated by repeated flushing and storing in a desiccator filled with the appropriate salt solution. We considered the cores to be at equilibrium with the salt solution when, upon further flushing, the conductivity measurements scattered within the measuring accuracy of about 0.1 percent.

At high salt concentrations, equilibrium is reached very slowly. Equilibrating times of 2 to 3 months frequently were required. Nevertheless, in all cores except those from extremely clean sands, the first two or three conductivity points at descending NaCl concentration were found to be irreproducible. When the measurements were repeated after the cores had been flushed and "equilibrated" again with brines of higher salinity, much higher conductivities were recorded. The shaler the sand, the more pronounced was this effect.

To investigate the phenomenon, a few cores with varying clay content were selected. A typical example is shown in Fig. 2. Here the conductivity of a moderately shaly core is given as a function of saturating brine conductivity for a sequence of

---

**TABLE 6 — MEASUREMENTS OF Qv FOR ADJACENT SAMPLES OF ROCK**

<table>
<thead>
<tr>
<th>Core</th>
<th>First Sample</th>
<th>Second Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.30</td>
<td>0.29</td>
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<tr>
<td>22</td>
<td>0.70</td>
<td>0.72</td>
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<tr>
<td>23</td>
<td>0.78</td>
<td>1.04</td>
</tr>
<tr>
<td>24</td>
<td>0.58</td>
<td>0.81</td>
</tr>
<tr>
<td>25</td>
<td>1.37</td>
<td>1.27</td>
</tr>
<tr>
<td>26</td>
<td>1.62</td>
<td>1.47</td>
</tr>
<tr>
<td>27</td>
<td>1.20</td>
<td>1.48</td>
</tr>
</tbody>
</table>

---

**FIG. 2 — ELECTRICAL CONDUCTIVITY (Cv) OF A SHALY CORE AS A FUNCTION OF THE CONDUCTIVITY OF THE EQUILIBRATING BRINE (Cw).**
observations obtained under equilibrating conditions as previously described. It is seen that reproducible data were obtained only from Point 7 on.

The reproducible data are considered now as equilibrium data. The clay of this particular core occurs mainly in laminae. Effects demonstrated in Fig. 2 are less pronounced when the clay is more homogeneously distributed, and also when the cores are first saturated with an NaCl solution of a concentration lower than about 1 molal. This behavior of the conductivity of shaly sands may be caused primarily by the almost complete dehydration of the clay due to the Soxhlet extraction procedure and the heating during encasing in epoxy resin. It is presumed from the above observations that rehydration of the clay, and therefore reactivation of the clay counterions, is an extremely slow process as far as saturated solutions are concerned because of their lower water activity. Grim\(^2\) reported that completely dehydrated montmorillonite is extremely difficult to re-equilibrate with water.

Results of the equilibrium conductivity measurements made at 25°C on the shaly sands equilibrated with NaCl solutions at 10 different concentrations varying from saturated solutions of 6.144 to 0.018 molal, are given in Table 7. Origin of the samples, their porosities and \(Q_v\) values also are in Table 7. Some representative plots of core conductivity \(C_p\) vs electrolyte solution conductivity \(C_m\) are presented in Fig. 3 for cores with different values of \(Q_v\).

**DISCUSSION OF DATA**

Values of \(F^*\) and \(\lambda_NaQ_v/1,000\) were calculated from the slopes and intercepts \((AB, Fig. 1)\), respectively, of the straight-line portions of the conductivity plots. Extrapolations were made with Eq. 9 and the method of least mean squares. These calculated values of \(\lambda_NaQ_v/1,000\) were plotted against \(Q_v\) to independently determined values of \(Q_v\) for the 90 cores of Group 1 (Fig. 4). The data were fitted by a straight line passing through the origin and a method of reduced regression where both variables are considered subject to error. The correlation coefficient for the resulting relation

\[
\left(10^{-3}\right)\lambda_NaQ_v \text{ cond.} = 0.0383\{Q_v\} \text{ sat.}
\]

was 0.981, with \(\lambda_Na\) or \(\lambda_Na\) equal to 38.3 sq cm equiv\(^{-1}\) ohm\(^{-1}\). Confidence limits of 10 and 90 percent (80 percent of the expected values lie between these limits) for \(\lambda_Na\) were 36.9 and 39.6 sq cm equiv\(^{-1}\) ohm\(^{-1}\).

The method of least mean squares was used to calculate \(F^*\) and intercept \(AB\) values from the conductivity data obtained with Group 2 cores. Values of \(\lambda_Na\) were calculated from the adjacent \(Q_v\) determinations for each of the individual samples (Table 8). The average value of \(\lambda_Na\) for this set was 46.3 sq cm equiv\(^{-1}\) ohm\(^{-1}\), and the standard deviation was 15.8 sq cm equiv\(^{-1}\) ohm\(^{-1}\). The value of \(\lambda_Na\) obtained from cores in Group 1 lies within the above standard deviation.

\(F^*\) values were plotted vs the Hill-Milburn \(F_{01}\) values for the total of 535 cores of Group 1, and it is apparent that the two parameters are equivalent. The data were fitted by a straight line through the origin, and the slope was determined to be 1.031 by reduced regression methods; the 10 and 90 percent confidence limits of the slope were 1.023 and 1.039, respectively. The correlation coefficient for this relation was essentially unity.

The various relations between \(F_{01}\) and porosity found for some four different formations by Hill and Milburn\(^3\) also must hold between \(F^*\) and porosity as well. Similar correlations are shown for Group 2 sands (Fig. 5). For the Eocene sand, \(m = 1.74\); for the lower Tertiary sand, \(m = 2.43\). In both sets, a few cores obviously do not belong to the same group with similar pore geometries. We have no detailed explanation for these deviations.

We conclude that the formation resistivity factor \(F^*\), defined as the reciprocal of the slope of a plot of \(C_p\) vs \(C_m\), is related to porosity according to Archie's\(^6\) first empirical equation

\[
F^* = \varphi^{-n}
\]

Similarly, other forms of Eq. 14, as suggested by

---

**Fig. 3**—ELECTRICAL CONDUCTIVITY \(C_p\) OF THREE SHALY CORES VS EQUILIBRATING BRINE CONDUCTIVITY \(C_m\).

**Fig. 4**—PLOT OF \(\lambda_NaQ_v\) OBTAINED FROM CONDUCTIVITY CURVES VS \(Q_v\) DETERMINED BY DIRECT MEASUREMENT FOR GROUP 1 CORES.
<table>
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<th>Core No.</th>
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<th>Depth</th>
<th>Porosity (%)</th>
<th>Q,250.5</th>
<th>233.5</th>
<th>192.2</th>
<th>160.0</th>
<th>139.8</th>
<th>94.5</th>
<th>52.49</th>
<th>28.22</th>
<th>14.92</th>
<th>7.802</th>
<th>4.049</th>
<th>2.085</th>
<th>C_w^-1</th>
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<td>-</td>
<td>7.50</td>
<td>6.49</td>
<td>-</td>
<td>5.21</td>
<td>4.13</td>
<td>3.14</td>
<td>2.48</td>
<td>2.046</td>
<td>1.826</td>
<td>1.597</td>
<td>1.503</td>
</tr>
<tr>
<td>27</td>
<td>Lower Tertiary</td>
<td>983.4</td>
<td>20.9</td>
<td>1.48</td>
<td>-</td>
<td>7.04</td>
<td>6.10</td>
<td>-</td>
<td>4.90</td>
<td>3.88</td>
<td>2.97</td>
<td>2.41</td>
<td>2.039</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### TABLE 8 — FRACTION (δ) OF MAXIMUM EQUIVALENT CONDUCTANCE (λ̂e) AS A FUNCTION OF WATER CONDUCTIVITY

<table>
<thead>
<tr>
<th>Core No.</th>
<th>Q_v (meq/cm³)</th>
<th>(λ̂e Q_v)/1000</th>
<th>λ̂e/1000 (mho cm²/meq)</th>
<th>The Value of δ for C_w in mho/cm =</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.03249</td>
</tr>
<tr>
<td>1</td>
<td>0.017</td>
<td>0.00232</td>
<td>(0.136)</td>
<td>0.929</td>
</tr>
<tr>
<td>2</td>
<td>0.052</td>
<td>0.00264</td>
<td>0.0507</td>
<td>0.979</td>
</tr>
<tr>
<td>3</td>
<td>0.052</td>
<td>0.00268</td>
<td>0.0515</td>
<td>0.959</td>
</tr>
<tr>
<td>4</td>
<td>0.26</td>
<td>0.00287</td>
<td>0.0110</td>
<td>0.961</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>0.00412</td>
<td>0.0206</td>
<td>1.014</td>
</tr>
<tr>
<td>6</td>
<td>0.095</td>
<td>0.00415</td>
<td>0.0437</td>
<td>1.027</td>
</tr>
<tr>
<td>7</td>
<td>0.053</td>
<td>0.00589</td>
<td>(0.111)</td>
<td>0.921</td>
</tr>
<tr>
<td>8</td>
<td>0.053</td>
<td>0.00584</td>
<td>(0.110)</td>
<td>0.910</td>
</tr>
<tr>
<td>9</td>
<td>0.085</td>
<td>0.00443</td>
<td>0.0521</td>
<td>1.039</td>
</tr>
<tr>
<td>10</td>
<td>0.253</td>
<td>0.01376</td>
<td>0.0544</td>
<td>0.952</td>
</tr>
<tr>
<td>11</td>
<td>0.253</td>
<td>0.00857</td>
<td>0.0339</td>
<td>0.993</td>
</tr>
<tr>
<td>12</td>
<td>0.28</td>
<td>0.01243</td>
<td>0.0444</td>
<td>1.016</td>
</tr>
<tr>
<td>13</td>
<td>0.28</td>
<td>0.01617</td>
<td>0.0578</td>
<td>0.996</td>
</tr>
<tr>
<td>14</td>
<td>0.28</td>
<td>0.01384</td>
<td>0.0494</td>
<td>0.957</td>
</tr>
<tr>
<td>15</td>
<td>0.41</td>
<td>0.02433</td>
<td>0.0593</td>
<td>0.968</td>
</tr>
<tr>
<td>16</td>
<td>0.67</td>
<td>0.02898</td>
<td>0.0433</td>
<td>1.006</td>
</tr>
<tr>
<td>17</td>
<td>0.33</td>
<td>0.02947</td>
<td>0.0893</td>
<td>1.014</td>
</tr>
<tr>
<td>18</td>
<td>0.59</td>
<td>0.02356</td>
<td>0.0399</td>
<td>1.003</td>
</tr>
<tr>
<td>19</td>
<td>0.59</td>
<td>0.01853</td>
<td>0.0314</td>
<td>0.985</td>
</tr>
<tr>
<td>20</td>
<td>0.59</td>
<td>0.01463</td>
<td>0.0248</td>
<td>1.005</td>
</tr>
<tr>
<td>21</td>
<td>0.29</td>
<td>0.00872</td>
<td>0.0301</td>
<td>1.056</td>
</tr>
<tr>
<td>22</td>
<td>0.72</td>
<td>0.02474</td>
<td>0.0444</td>
<td>1.005</td>
</tr>
<tr>
<td>23</td>
<td>1.04</td>
<td>0.03564</td>
<td>0.0437</td>
<td>0.996</td>
</tr>
<tr>
<td>24</td>
<td>0.81</td>
<td>0.0526</td>
<td>0.0649</td>
<td>1.002</td>
</tr>
<tr>
<td>25</td>
<td>1.27</td>
<td>0.0724</td>
<td>0.0570</td>
<td>1.010</td>
</tr>
<tr>
<td>26</td>
<td>1.47</td>
<td>0.0771</td>
<td>0.0524</td>
<td>1.008</td>
</tr>
<tr>
<td>27</td>
<td>1.48</td>
<td>0.0783</td>
<td>0.0529</td>
<td>1.012</td>
</tr>
</tbody>
</table>

Average: 0.0463, 0.990, 0.916, 0.821, 0.690, 0.592, 0.524
Std. dev.: 0.0158, 0.034, 0.082, 0.111, 0.110, 0.130, 0.159

Values between parentheses considered not reliable because of extreme deviation from the rest of the assembly, probably due to Q_v determination. They were not used in calculating the average.

For C_w > 0.060 mho/cm, δ = 1.
Winsauer et al., can be used to relate $F^*$ to porosity.

The two major tests of the proposed conductivity model, as discussed previously, are met.

Conductivity data obtained for Group 2 cores are quite detailed in the curved portion of the $C_0 - C_{\text{w}}$ plots (2.085 < $C_{\text{w}}$ < 52.49 mho cm$^{-1}$) and permit calculation of the increase in counterion mobility with increasing equilibrating electrolyte concentrations within this concentration range. The increase in $\mu_{Na}^{\text{eq}}$ has been represented by a simple empirical relation (Eq. 10) for $B$ as a function of $C_{\text{w}}$ and two constants $a$ and $\gamma$.

$$\delta = [1 - a \exp(-C_{\text{w}}/\gamma)] \ldots (15)$$

$$B = \delta \frac{\lambda_{Na}^{\text{eq}}}{1000} \ldots \ldots \ldots \ldots \ldots (16)$$

The equivalent conductance of the clay counterions is denoted by $B$, with $\lambda_{Na}^{\text{eq}}/1,000$ representing $B$ at its maximum value ($\delta = 1$) in the straight-line portions of the $C_0 - C_{\text{w}}$ curves.

Values of $\delta$, at each value of $C_{\text{w}}$ and for each core, were calculated from the ratio of the measured $C_0$ values to the hypothetical values ($C_0'$) of $C_0$, calculated from the straight-line extrapolation at the same $C_{\text{w}}$ (Fig. 1). Since the same formation factor $F^*$ applies throughout the entire electrolyte concentration range,

$$\frac{C_0}{C_0'} = \frac{C_0 + (\delta \lambda_{Na}^{\text{eq}}Q_{\text{w}})}{C_0 + (\lambda_{Na}^{\text{eq}}Q_{\text{w}})}$$

thus,

$$\delta = (\frac{1000}{C_0} - 1) \frac{1000}{\lambda_{Na}^{\text{eq}}Q_{\text{w}}} + \gamma \ldots \ldots (18)$$

Values of $\delta$, together with their average values and standard deviations, are given as a function of $C_{\text{w}}$ in Table 8.

Values of $B$ as a function of $C_{\text{w}}$ were calculated according to Eq. 16 using average values of $\delta$ and $\lambda_{Na}^{\text{eq}}$ (Fig. 6). The empirical equation representing $B$ as a function of $C_{\text{w}}$ at 25°C is found to be

$$B = [1 - 0.6 \exp(-C_{\text{w}}/0.013)]0.046$$

mho cm$^2$ meq$^{-1}$ \ldots \ldots \ldots \ldots \ldots \ldots (19)

and, as shown in Fig. 6, provides a reasonable fit for these data. Eqs. 9, 10 and 19 describe available shaly sand data about as well as does the Hill-Milburn equation.

Extrapolation to $C_{\text{w}} = 0$ using Eq. 19 results in a calculated value for the equivalent conductance of the sodium exchange ion ($\lambda_{Na}^{\text{eq}}$) of 18.4 sq cm equiv$^{-1}$ omh$^{-1}$ which can be deduced from conductivity measurements of sodium montmorillonite-distilled water gels at 25°C reported by Van Olphen and Waxman. While this agreement is quite comforting, some caution should be observed since the calculated value of ($\lambda_{Na}^{\text{eq}}$)$^2$ is obtained by extrapolating an empirical relation beyond observed data.

The assumption in the model of an exponential increase of counterion mobility with increase in solution conductivity is justified by comparison with shaly sand conductivity data and by the apparent agreement of extrapolated conductivity at $C_{\text{w}} = 0$ with clay gel conductivities.

A further general criterion for the model follows from the thermodynamic relation between electrical transport numbers calculated for conditions of nonzero electric current flux and zero concentration gradient, and diffusion potentials measured under conditions of nonzero concentration gradient and zero electric current flux. It should be possible to

![Graph](image-url)  
**FIG. 5 — SHALY SANDS FORMATION RESISTIVITY FACTOR ($F^*$) VS POROSITY ($\phi$).**

![Graph](image-url)  
**FIG. 6 — EQUIVALENT CONDUCTIVITY ($B$) OF THE COUNTERIONS ASSOCIATED WITH CLAY AS A FUNCTION OF EQUILIBRATING ELECTROLYTE CONDUCTIVITY ($C_{\text{w}}$).**

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obtain expressions for the cation and anion transport numbers from the conductance model. These expressions then can be introduced into the equation for the diffusion potential generated by a liquid junction in the shaly sand. This is discussed by Smiths$^{11}$ who compared experimental diffusion potentials in shaly sands with calculated potentials based on theory, including parameters developed from the conductance model. Excellent agreement was obtained between both sets of potentials.

CONDUCTIVITY EQUATION FOR OIL-BEARING SHALY SANDS

The conductivity equation for water-bearing shaly sands is extended to describe the conductivity of shaly sands containing both oil and brine.

When water saturation $S_w$ is less than unity, the exchange ions associated with the clay become more concentrated in the remaining pore water. This concentration $Q'_c$ is related to $Q_v$ and $S_w$ according to

$$Q'_c = Q_v / S_w \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (20)$$

where $Q'_c$ is the effective concentration of exchange ions at $S_w > 0$. We assume that the mobility of the exchange ions is unaffected by the partial replacement of water. Then the conductivity of the counterions is given by $B Q'_c / S_w$ (mho cm$^{-1}$). This assumption was based initially on field evidence which indicates that the SP deflection opposite oil-bearing rocks is reduced when compared with the SP response opposite water-bearing sections of the same reservoir. Reduction of the total electrical potential is attributed to an increase in permselective membrane efficiency of the oil-bearing sands relative to the efficiency of the same sands at $S_w = 1$. The diffusion potential across these sands comprises one of the components of the total SP response. This increase in the membrane efficiency of the sands is associated with an increased effective clay content which must be due to a decrease in the volume of pore space filled with water. A similar suggestion was made earlier by Hill and Milburn$^3$ and later by de Witte.$^{19}$ The equivalent Hill-Milburn assumption is

$$b' = b / S_w \ldots \ldots \ldots \ldots \ldots \ldots (21)$$

recalling that the $b$ parameter is approximately proportional to $Q_v$.

LABORATORY EVIDENCE FOR $Q'_c$ ASSUMPTION

Laboratory data obtained by McLaughlin$^{25}$ support the assumption stated in Eq. 20. These data consist of diffusion potential measurements using shaly sands at conditions of water saturation equal to and less than unity. The respective membrane efficiencies are interpreted from the measured $em^f$'s using Fig. 13 of Ref. 3, and are expressed in terms of the $b$ and $b'$ parameters.

A group of plugs were cut from cores taken from a formation in the Gohlke field, Texas. Diffusion potentials in the samples were measured using two NaCl solutions having concentrations equal to the original mud filtrate and formation water, respectively. These potentials were measured both at $S_w = 1$ and at residual oil conditions.

As indicated above, values of $b'$ were determined at $S_w$ from the $em^f$ measurements. Similarly, $b$ values were determined for these sands at $S_w = 1$. A plot of $b$ vs $b' S_w$ is given in Fig. 7. Considering the experimental problems inherent in the determination of $S_w$, comparison of $b$ values with values of $b' S_w$ shows remarkably good agreement.

The assumption of Eq. 20 rules out the use of the Hill-Milburn equation to describe the conductance behavior of oil-bearing shaly sands. With decrease in $S_w$ and the accompanying increase in $Q'_c$ or $b'$, the minima in the calculated conductivity curves are shifted to quite high values of $C_w$, well within the range of practical field values. Thus, depending on the original values of $b$ and the particular values of $S_w$, substantial portions of the conductivity curves will indicate increasing sand conductivities with decreasing $C_w$'s (at constant $S_o$ values) and will be physically meaningless.

We further assume that the conductivity of an oil-bearing shaly sand can be described by an equation analogous to Eq. 9 for water-saturated sands,

$$C_i = \frac{1}{G^*} (C_w + B Q'_c / S_w) \ldots \ldots \ldots (22)$$

Here $C_i$ is the specific conductance of a partially water-saturated sand and $G^*$ is a geometric factor, being a function of porosity, water saturation and pore geometry, but independent of clay content ($Q_v$). $G^*$ is expected to increase with decreasing $S_w$ since the water-filled pore space is decreasing apart from complications due to distribution of the two phases in the pore network of the rock.

For clay-free or "clean" sandstones, $F^*$ and $G^*$ reduce to

FIG. 7 — EFFECT OF OIL SATURATION ON DIFFUSION POTENTIALS OF SHALY SANDS.
\[ F = C_w/C_o = R_o/R_w \quad \ldots \ldots \ldots \quad (23) \]

and

\[ G = C_v/C_t = R_t/R_v \quad \ldots \ldots \ldots \quad (24) \]

The resistivity ratio \( I \) is defined as

\[ I = R_t/R_o = C_v/C_t = G/F \quad \ldots \ldots \ldots \quad (25) \]

and according to Archie's second empirical relation,\(^6\)

\[ I = S_w^n \quad (= G/F) \quad \ldots \ldots \ldots \quad (26) \]

The value of \( \pi \) may differ from the value of \( m \) in Eq. 14.

By analogy, we define

\[ G^* / F^* = S_w^{-n^*} \quad \ldots \ldots \ldots \ldots \quad (27) \]

where \( n^* \) is the exponent for a hypothetical rock having the same pore geometry as the shaly sand, but whose clay content is inactive, i.e., \( n^* \) is independent of \( Q_u \). For the limiting cases \( Q_u = 0 \) or \( C_w \rightarrow \infty \), Eq. 27 reduces to Eq. 26.

Combining Eqs. 9, 22, 25 and 27, we obtain for the resistivity ratio

\[ I = S_w^{-n^*} \left[ \frac{C_v + B Q_u}{C_w + B Q_v/S_w} \right] \quad \ldots \ldots \ldots \quad (28) \]

Eq. 28 can be expressed in terms of water resistivity

\[ I = S_w^{-n^*} \left[ \frac{1 + R_w B Q_v}{1 + R_w B Q_v/S_w} \right] \quad \ldots \ldots \ldots \quad (29) \]

where the units of water resistivity \( R_w \) and the term \( B Q_v \) are ohm m and (ohm m)\(^{-1} \), respectively. For \( Q_u \) expressed as meq/ml or equiv/liter, the numerical value of \( B \) in Eq. 28 is

\[ B = [1 - 0.6 \exp (-0.77/R_w)]4.6 \quad \ldots \ldots \ldots \ldots \quad (30) \]

Figs. 8 through 11 demonstrate the effects of variation of clay content, water salinity and pore geometry on the \( I-S_w \) relationship, as predicted by Eq. 29. We observed that even small amounts of clay have a marked effect on the resistivity ratio. Significant departures from the simple \( I-S_w \) relation (Eq. 26) are noted with increasing water resistivity at constant \( Q_u \); further, \( \log S_w \) is nonlinear with respect to \( \log I \).

As a final example, an illustration of the influence of clay in a reservoir sand on electric log interpretation is given. We assume a resistivity ratio of \( I = 4 \) obtained from log readings, and estimate the
value of $n^*$ to be 2. For a clean sand, these values lead to an oil saturation $S_o = 0.50$ by the Archie relation (Eq. 26). The influence of various degrees of shaliness associated with different water resistivities for this example is shown in Fig. 12. Oil-in-place estimates are increased considerably from 33 to 47 percent with increasing values of $Q_o'$ above the clean sand estimate in certain fresh water zones.

CONCLUSIONS

An equation has been developed, based on a physical model, that relates the electrical conductivity of a water-saturated shaly sand to the water conductivity and the clay content of the sand. Clay contents are expressed by the cation-exchange capacities per unit pore volume of the rocks which can be determined by independent analyses. Various criteria established to test the model are satisfied by shaly sand conductivity data. These data further permit determination of sand conductivities and clay counterion mobilities down to very low equilibrating electrolyte solution conductivities.

The model is extended to describe the conductivity of oil-bearing shaly sands. An expression is developed which relates the resistivity ratio to water saturation, water resistivity and CEC per unit pore volume of rock. This equation generally predicts higher oil-in-place estimates than are obtained from the usual clean sand relations.

NOMENCLATURE

$a =$ dimensionless constant, Eqs. 10 and 11
$A_D =$ constant in de Witte's equation$^{19}$ (Eq. 12 in this paper)
$B_D =$ constant in de Witte's equation$^{19}$ (Eq. 12 in this paper)
$b =$ Hill-Milburn parameter$^3$ related to effective clay content of shaly sand at $S_w = 1$
$b' =$ Hill-Milburn parameter$^3$ related to effective clay content in oil-bearing shaly sand
$B =$ equivalent conductance of clay exchange cations (sodium) as a function of $C_w$ at 25C (Eq. 10), mho sq cm meq$^{-1}$
$C_e =$ conductance contribution of clay exchange cations to shaly sand conductivity, ohm$^{-1}$ or mho
$C_e =$ specific conductance of clay exchange cations, mho cm$^{-1}$
$C_{e1} =$ conductance contribution of bulk electrolyte solution to conductivity of shaly sand, ohm$^{-1}$ or mho
$C_o =$ specific conductance of sand, 100 percent saturated with aqueous salt solution, mho cm$^{-1}$
$C_o' =$ hypothetical specific conductance of shaly sand at low values of $C_w$ defined in Eq. 17, mho cm$^{-1}$
$C_s =$ specific surface conductance of clay, ohm$^{-1}$ or mho
$C_t =$ specific conductance of a partially water-saturated sand, mho cm$^{-1}$
$C_w =$ specific conductance of aqueous electrolyte solution, mho cm$^{-1}$
$D =$ self-diffusion coefficient, sq cm sec$^{-1}$
$F_{01} =$ Hill-Milburn formation resistivity factor$^3$
for shaly sands
$F =$ formation resistivity factor for clean sand
$F^* =$ formation resistivity factor for shaly sand (this paper)
$F =$ faraday
$g =$ weight of clay per unit of rock pore volume, gm clay/cu cm
$G =$ formation resistivity factor for partially water-saturated clean sand, Eq. 24
$G^* =$ formation resistivity factor for partially water-saturated shaly sand
$I =$ resistivity index, Eq. 25
$m =$ porosity exponent or lithology factor, Eq. 14
$m_{NaCl} =$ molal concentration of NaCl solution, mol NaCl/1,000 gm water
$N =$ aqueous electrolyte solution concentration, Normality, moles solute/liter solution
$n =$ Archie saturation exponent for clean sands, Eq. 26
$n^*$ =$ saturation exponent for shaly sand
$Q_s =$ surface concentration of clay exchange cations, equiv cm$^{-2}$
$Q_u =$ volume concentration of clay exchange cations, meq ml$^{-1}$ or equiv liter$^{-1}$
$Q'_u =$ volume concentration of clay exchange cations in oil-bearing shaly sand (Eq. 20), meq ml$^{-1}$ or equiv liter$^{-1}$
$r =$ ratio of measured to hypothetical shaly sand conductivities at identical $C_w$'s, Eq. 17
$R_o =$ resistivity of sand 100 percent saturated with aqueous salt solution, ohm m

![Fig. 12 — Oil-in-place estimates as a function of clay content of sand and formation water resistivity (assumed conditions, $I = 4$, $n^* = 2$).](image)

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\[ R_p = \text{resistivity of a partially water-saturated sand, \text{ohm m}} \]
\[ R_u = \text{resistivity of equilibrating aqueous salt solution, \text{ohm m}} \]
\[ S = \text{specific surface area of clay, \text{sq cm/gm clay}} \]
\[ S_o = \text{fractional oil saturation} \]
\[ S_{or} = \text{residual oil saturation} \]
\[ S_w = \text{fractional water saturation} \]
\[ x = \text{geometric cell constant for shaly sand, Eq. 2} \]
\[ y = \text{geometric cell constant for shaly sand, Eq. 2} \]
\[ \delta = \text{constant defined by Eq. 10, mho cm}^{-1} \]
\[ \lambda_{Na} = \text{maximum equivalent ionic conductance of sodium exchange cations associated with clay (25°C), \text{sq cm equiv}^{-1} \text{ohm}^{-1}} \]
\[ (\lambda_{Na})' = \text{equivalent ionic conductance of sodium exchange cations associated with clay (25°C) at C_HO = 0, \text{sq cm equiv}^{-1} \text{ohm}^{-1}} \]
\[ \mu_{Na} = \text{maximum sodium exchange ion mobility (25°C), \text{sq cmvolt}^{-1} \text{sec}^{-1}} \]
\[ \phi = \text{porosity} \]

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REFERENCES