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THE FLOW OF FLUIDS THROUGH SANDSTONES

BY

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TRANSLATED BY

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# THE FLOW OF FLUIDS THROUGH SANDSTONES

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## Abstract

The investigation of the flow of various fluids through sandstones with clay contents of 1 to 5 percent shows that the Darcy equation holds for air, carbon tetrachloride, and cyclohexane. For benzene there is possibly some divergence. Water and salt solutions flow more slowly than would be predicted from their viscosity and the air permeability. Moreover, no linear relationship between pressure drop and fluid velocity exists for water and salt solutions. In the case of NaCl solutions, the velocity of flow depends on the NaCl content. Velocities in a given sandstone at a constant pressure drop are higher the greater the salt concentration.

The invalidity of the Darcy relationship for water and solutions of electrolytes is explained by an interaction between these fluids and the pore walls which hinders the movement of fluids in the narrow interstices. It is assumed that this phenomenon can be explained by the fact that water becomes bound to the surfaces of the clay minerals present in the sandstones by dipole forces and osmotic equilibrium (Donnan equilibrium). This bonding of water on pure clay minerals was measured in specific studies.

## 1. General

The laminar flow of viscous fluids through porous substances is customarily described by the well-known Darcy equation (Correns, 1942; Correns and Schumann, 1949; Muskat, 1949; API, 1942) which reads:

[1]

Table 1. Rocks Investigated

No.	Well	Depth meters	Porosity %	Air permeability darcys	Amount of grain size < 20 $\mu$ %	Mean grain size* (diameter) mm
1 V	Georgsdorf 212	960 - 970	28.3	0.530	2	0.10
2 V	Georgsdorf 212	960 - 970	26.7	0.560	2	0.10
3 V	Georgsdorf 212	960 - 970	28.3	0.410	3	0.10
4 V	Georgsdorf 77	1012.2-1023	25.4	1.300	~1	0.17
5 V	Georgsdorf 94a	1134.7-1141.5	26.1	0.189	~5	0.10
6 V	Georgsdorf 94a	1134.7-1141.5	25.6	0.134	~5	0.10
7 V	Georgsdorf 94a	1134.7-1141.5	26.5	0.270	~4	0.10
8 L	Eldingen 4	1575 -1580	25.7	0.500	4	0.10
9 L	Eldingen 13b	1588.8-1592.3	25.0	0.200	2	0.10
10 L	Eldingen 41	1495 -1500	25.3	0.670	5	0.11
11 L	Eldingen 41	1495 -1500	26.0	0.626	5	0.11
12 L	Eldingen 41	1495 -1500	27.6	0.635	5	0.12
13 L	Eldingen 41	1495 -1500	27.3	1.090	4	0.16
14 L	Eldingen 34	1538.5-1543.5	25.3	0.373	4	0.12
15 L	Eldingen 34	1538.5-1543.5	27.0	0.576	3	0.13
16 L	Eldingen 34	1538.5-1543.5	24.3	0.451	6	0.14
17 L	Eldingen 34	1543.5-1548.5	26.5	0.709	5	0.14

\* Mean grain size is defined as the particle diameter corresponding to the 50 weight percent sand (median size).

$$\frac{dQ}{dt} = \dot{Q} = \frac{k}{\eta} \cdot \frac{dP}{dx}$$

where:  $\dot{Q}$  = volume of flow per unit of time per unit of surface through which fluid is passing, or the velocity of flow in cm/sec

$\frac{dP}{dx}$  = pressure drop in the direction of flow in atm/cm

$\eta$  = viscosity of the flowing medium, centipoise

$k$  = permeability of the porous substance in darcys  
(1 darcy =  $10^{-8}$  cm<sup>2</sup>)

Observations on sandstones of North American oil fields by various investigators (Muskat, 1949; API, 1942; Johnston and Beeson, 1945) have shown that the simple Darcy equation does not prove correct in all cases. Large differences result in the permeabilities calculated with this formula, depending on whether air, fresh water, or brine is used. The air permeabilities are always the highest, and those for brine become greater as the salt content increases.

A series of measurements on sandstones of the Lias and Lower Cretaceous (Valendis) formations of German oil fields are herein presented for the purpose of contributing further to the question of the applicability of the Darcy relationship to the flow of fluids through sandstones.

## 2. Rocks investigated and experimental procedure

The sandstones investigated all came from oil wells. Detailed data on the source of the samples, their physical properties, and their mineral composition are presented in table 1.

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### Table 1, Explanatory Note:

Formations: The samples designated with V came from the Bentheimer sandstone of the Valendis formation (Lower Cretaceous), those designated with L came from a sandstone of the Lias  $\alpha$  formation.

Mineral content: In sandstones 1 to 7 the material above  $20\mu$  diameter consists of 70 to 90% quartz; the rest is alkali feldspars. The material less than  $20\mu$  consists of 15 to 25% quartz, about 15% illite, and 30 to 40% kaolinite. In sandstones 8 to 17 the material above  $20\mu$  consists of over 90% quartz; the rest is alkali feldspars. The material less than  $20\mu$  consists of 15% quartz, 10 to 20% illite, and 50 to 70% kaolinite.

Table 2. Permeabilities with Air and Pure Fluids  
at Constant Pressure Drop

(Temperature = 20°C)

No.	Fluid	$\eta$ cp	Fluid velocity	dP/dx atm/cm	$\alpha = \frac{\dot{Q}}{dP/dx}$	Permeability $k = \alpha \cdot \eta$ darcys
			$\dot{Q}$ cm/sec			
10 L	Air	0.018	2.642*	0.071	37.22	0.67
10 L	CCl <sub>4</sub>	0.97	0.051	0.071	0.72	0.70
10 L	Cyclohexane	0.97	0.055	0.071	0.77	0.75
10 L	Benzene	0.65	0.067	0.071	0.95	0.62
10 L	Water	1.00	0.019	0.071	0.27	0.27
11 L	Air	0.018	2.475*	0.072	34.99	0.63
11 L	CCl <sub>4</sub>	0.97	0.045	0.072	0.63	0.61
11 L	Cyclohexane	0.97	0.046	0.072	0.64	0.62
11 L	Benzene	0.65	0.066	0.072	0.91	0.59
11 L	Water	1.00	0.009	0.072	0.13	0.13
12 L	Air	0.018	2.418*	0.068	35.06	0.64
12 L	CCl <sub>4</sub>	0.97	0.047	0.068	0.69	0.66
12 L	Cyclohexane	0.97	0.045	0.068	0.65	0.63
12 L	Benzene	0.65	0.066	0.068	0.97	0.63
12 L	Water	1.00	0.005	0.068	0.07	0.07
13 L	Air	0.018	4.095*	0.067	61.05	1.10
13 L	CCl <sub>4</sub>	0.97	0.077	0.067	1.15	1.11
13 L	Cyclohexane	0.97	0.075	0.067	1.12	1.08
13 L	Benzene	0.65	0.109	0.067	1.63	1.06
13 L	Water	1.00	0.018	0.067	0.26	0.26

\* Disregarding compressibility.

For the permeability measurements, cylindrical specimens 3 centimeters in diameter and 3 centimeters long were cut out of the sand cores. Prior to investigation, all core plugs were freed of oil and water by extraction with chloroform and dried at 100°C. The air permeabilities were measured by generally accepted procedures. For liquid measurements, the dried cores were filled under vacuum with the liquid under consideration. It was especially necessary to utilize fluids that were free of dissolved gases because gas bubbles that can influence the permeability considerably are readily trapped within the core. It was also of greatest importance to have fluids that were free of any extraneous solids. For the air permeabilities, the cores were mounted in a rubber ring that was held firmly in a special apparatus to prevent any bypassage between the core and ring. Temperatures of the fluids entering the core were measured. The viscosity of the fluids was determined with a capillary viscosimeter according to Vogel-Ossag.

### 3. Flowing experiments on sandstones

The Darcy equation contains two assertions. First, it is maintained that for a given fluid flowing through a given porous medium there is a linear relationship between fluid velocity and pressure drop:

$$\dot{Q} = \alpha \cdot \frac{dP}{dx}$$

Second, it is asserted that the proportionality factor ( $\alpha$ ) is defined as the quotient of two specific constants:

$$\alpha = \frac{k}{\eta}$$

The permeability ( $k$ ) should be determined specifically by the geometry of pore spaces of the solid body. The viscosity of the fluid ( $\eta$ ) is measurable with an ordinary viscosimeter.

To investigate these assertions, permeability experiments with air and various fluids were carried out first at a constant pressure drop. The results for the flow of air, cyclohexane, carbon tetrachloride, benzene, and water through the Lias sandstone cores are presented in table 2. The results of experiments on Lias and Valendis cores using various NaCl solutions are given in table 3. The calculated permeabilities are plotted in figure 1 as a function of NaCl content with reference to the values obtained with air.

Another method employed in testing the Darcy law was to vary the pressure gradient. Nonpolar liquids and distilled water were used in this work. As a typical example of the numerous experiments performed, the results obtained with core 10L are listed in table 4. In table 5 are corresponding results with distilled water on five other cores. In addition, the flow of NaCl solutions of different concentrations was investigated at several pressure gradients and the results are shown in table 6.

Table 3. Permeabilities with Various NaCl Solutions  
at Constant Pressure Drop

(dP/dx = 0.002 atm/cm; temperature = 20°C)

No.	NaCl content	$\eta$	Fluid velocity $\dot{Q}$	$\alpha = \frac{\dot{Q}}{dP/dx}$	Permeability $k = \alpha \cdot \eta$
	%	cp	cm/sec		darcys
1 V	10	1.19	0.000880	0.440	0.52
1 V	5	1.07	0.000950	0.475	0.51
1 V	1	1.01	0.000880	0.440	0.45
1 V	0	1.00	0.000880	0.440	0.44
2 V	10	1.19	0.000922	0.461	0.55
2 V	5	1.07	0.001036	0.518	0.55
2 V	1	1.01	0.000998	0.499	0.50
2 V	0	1.00	0.000964	0.482	0.48
3 V	10	1.19	0.000628	0.314	0.37
3 V	5	1.07	0.000636	0.318	0.34
3 V	1	1.01	0.000544	0.272	0.28
3 V	0	1.00	0.000442	0.221	0.22
4 V	10	1.19	0.002218	1.109	1.32
4 V	5	1.07	0.002104	1.052	1.13
4 V	1	1.01	0.001828	0.914	0.92
4 V	0	1.00	0.001661	0.832	0.83
5 V	10	1.19	0.000300	0.150	0.18
5 V	5	1.07	0.000310	0.155	0.17
5 V	1	1.01	0.000310	0.155	0.16
5 V	0	1.00	0.000296	0.148	0.15
6 V	10	1.19	0.000194	0.097	0.12
6 V	5	1.07	0.000206	0.103	0.11
6 V	1	1.01	0.000208	0.104	0.11
6 V	0	1.00	0.000190	0.095	0.10
7 V	10	1.19	0.000368	0.184	0.22
7 V	5	1.07	0.000384	0.192	0.21
7 V	1	1.01	0.000374	0.189	0.19
7 V	0	1.00	0.000362	0.181	0.18
8 L	17	1.37	0.000620	0.310	0.43
8 L	0	1.00	0.000180	0.090	0.09
9 L	17	1.37	0.000234	0.117	0.16
9 L	10	1.19	0.000202	0.101	0.12
9 L	5	1.07	0.000168	0.084	0.09
9 L	0	1.00	0.000044	0.022	0.02

## 4. Interpretation of results

The experiments with pure fluids at constant pressure drop (table 2) using air, carbon tetrachloride, cyclohexane, and benzene in a given core produced permeability values that differ only slightly from one another. The variations are essentially within the range of accuracy of the permeability measurements. To be sure, it appears that somewhat lower values were always obtained with benzene than with cyclohexane, carbon tetrachloride, or air. Orientation studies with alcohols show that these substances also produce somewhat lower permeabilities than the so-called nonpolar media, indicating that among the organic fluids the influence of molecular structure is probably a factor to consider.

The results obtained with water and salt solutions are entirely another matter. In the case of the previously mentioned organic fluids, a definite equilibrium velocity was immediately established, depending on the nature of the core, and remained constant for a long time (it was observed to be constant over a 24-hour period) provided the pressure drop was not too high. At high pressure gradients, a displacement of material often occurred within the cores which caused a decrease in fluid velocity. In the case of water, however, the fluid velocity at the beginning of an experiment decreased quickly and did not become adjusted to a constant value until after approximately two hours. The data in the tables are based on these stabilized end values. Permeabilities calculated from these results show much lower values than those for the organic fluids.

The investigations at various pressure drops (tables 4 and 5) show that the calculated permeabilities for air, carbon tetrachloride, cyclohexane, and benzene are independent of pressure gradient. On the other hand, the permeabilities for water are very strongly dependent on pressure drop. Fluid velocities also increase more rapidly at the higher pressure drops than would be anticipated from the expected linear relationship. The experiments with water were conducted in such a manner that they started with low pressure gradients. After reaching the highest pressure drop, an additional measurement at a low gradient was performed which agreed approximately with previously measured values. In this manner it was ascertained in these investigations that the phenomena observed were reproducible.

The experiments with NaCl solutions at constant pressure drop (table 3) show that the calculated permeabilities depend on the electrolyte concentration. In all cases it was found that permeabilities increased with increasing concentration. The permeabilities obtained at the highest concentration were always equal to or slightly lower than the values for air. This series of tests was carried out so that the individual cores were first measured with the highest concentration, after which the concentration was progressively decreased, ending with distilled water. After each new salt concentration was established, the flowing velocity was not determined until the stabilized end value had been attained. No test was used unless the initial results could be reproduced by returning once more to the initial high concentration, thus ruling out irreversible reactions and plugging effects. The investigations at different pressure gradients (table 6) show that a linear relationship between



Table 4. Permeabilities with Pure Liquids at Various Pressure Gradients

No.	Fluid	$\eta$	$dP/dx$	Fluid velocity	$\alpha = \frac{\dot{Q}}{dP/dx}$	Permeability
		cp	atm/cm	cm/sec		$k = \alpha \cdot \eta$ darcys
10 L	CCl <sub>4</sub>	0.97	0.018	0.0129	0.727	0.71
10 L	CCl <sub>4</sub>	0.97	0.036	0.0260	0.733	0.71
10 L	CCl <sub>4</sub>	0.97	0.071	0.0535	0.753	0.73
10 L	CCl <sub>4</sub>	0.97	0.106	0.0774	0.728	0.71
10 L	CCl <sub>4</sub>	0.97	0.141	0.1050	0.740	0.72
10 L	CCl <sub>4</sub>	0.97	0.177	0.1288	0.727	0.71
10 L	Cyclohexane	0.97	0.018	0.0130	0.738	0.72
10 L	Cyclohexane	0.97	0.036	0.0260	0.733	0.71
10 L	Cyclohexane	0.97	0.071	0.0524	0.738	0.72
10 L	Cyclohexane	0.97	0.106	0.0787	0.740	0.72
10 L	Cyclohexane	0.97	0.141	0.1049	0.740	0.72
10 L	Cyclohexane	0.97	0.177	0.1287	0.727	0.71
10 L	Benzene	0.65	0.018	0.0186	1.051	0.68
10 L	Benzene	0.65	0.036	0.0363	1.023	0.67
10 L	Benzene	0.65	0.071	0.0726	1.022	0.67
10 L	Benzene	0.65	0.106	0.1090	1.024	0.67
10 L	Benzene	0.65	0.141	0.1416	1.000	0.65
10 L	Benzene	0.65	0.177	0.1770	1.000	0.65
10 L	Water	1.00	0.018	0.0012	0.073	0.07
10 L	Water	1.00	0.036	0.0046	0.129	0.13
10 L	Water	1.00	0.071	0.0194	0.273	0.27
10 L	Water	1.00	0.106	0.0295	0.278	0.28
10 L	Water	1.00	0.141	0.0488	0.346	0.35
10 L	Water	1.00	0.177	0.0644	0.363	0.36

fluid velocity and pressure drop does not exist either for NaCl solutions or for pure water. With increasing pressure drop, the fluid velocity increases more quickly than the expected linear relationship.

From these investigations it is concluded that the Darcy equation holds only for the organic liquids investigated, with benzene possibly behaving somewhat differently. The permeability of a given sandstone to these fluids is independent of the nature of the flowing media and of the pressure drop. In other words, it is a specific constant that depends only on the geometry of the pore spaces.

On the other hand, the Darcy equation does not hold for water and salt solutions. Neither is there a linear relationship between pressure drop and fluid velocity, nor can one calculate a "permeability" from the velocity of flow and viscosity that may be regarded as a specific constant. For this reason, it is not feasible to apply permeabilities measured with air or appropriate organic fluids without further considering the flow of water and electrolytes through these rocks. Similarly, it is not sensible to compute permeabilities directly from flowing measurements with various salt solutions assuming the validity of the Darcy law.

To interpret these remarkable anomalies, it will be assumed initially that in the case of salt solutions an interaction occurs between the solid body and the solution. Thus the flowing process cannot be described by the two independent constants - permeability and viscosity. The fluid and solid substances form a new system with other properties that can be deduced to be additive to the behavior of the substances considered independently.

If one desires to divide the proportionality factor ( $\alpha$ ) into a unit of measurement at the geometric boundary of the pore channel that is available to flow, and into a number with reference to the fluid, two fundamental possibilities exist, both of which have already been referred to by other workers in the interpretation of similar phenomena.

First, it can be assumed that the fluid in the porous system has the same viscosity as is measured in the viscosimeter. Then the "permeability," that is, the geometry of the system, must be dependent on the nature of the fluid and the pressure drop. Therefore the effective cross section of flow must be smaller for salt solutions than for nonpolar fluids and, in the case of the former, must increase with a greater velocity of flow. One can imagine that the fluid becomes fixed on the solid surface of the rock boundary and forms an immobile layer which is no longer part of the flowing fluid. The relationship to pressure drop would indicate that the thickness of this immobile layer is dependent on the amount of shearing stress in the pores. It follows therefore that the layer must be several molecules thick. Immobile water layers of this kind on the surface of quartz particles have been accepted by Z. V. Volkova (1948) to explain the fact that water velocities through pulverized quartz of less than  $1\ \mu$  diameter, when compared with those of toluene, were smaller than would be expected from the viscosity difference between the two fluids. For the flow of water through clay, F. Zuncker (1932), J. Kozeny (1932), and P. C. Carman (1939) also accept the existence of immobile water layers on the surfaces of clay particles.

On the other hand, it can be assumed that the same pore cross section is available for the flow of salt solutions as for air or other nonpolar fluids. It

Table 5. Permeabilities with Distilled Water at Various Pressure Gradients

No.	$\eta$	dP/dx	Fluid velocity $\dot{Q}$	$\alpha = \frac{\dot{Q}}{dP/dx}$	Permeability $k = \alpha \cdot \eta$
	cp	atm/cm	cm/sec		darcys
13 L	1.00	0.017	0.0005	0.031	0.03
13 L	1.00	0.034	0.0022	0.064	0.06
13 L	1.00	0.067	0.0177	0.263	0.26
13 L	1.00	0.101	0.0394	0.391	0.39
13 L	1.00	0.134	0.0644	0.480	0.48
13 L	1.00	0.168	0.0886	0.528	0.53
14 L	0.91	0.0325	0.0040	0.123	0.11
14 L	0.91	0.0650	0.0084	0.130	0.12
14 L	0.91	0.0974	0.0142	0.145	0.13
14 L	0.91	0.1300	0.0218	0.168	0.15
14 L	0.91	0.1624	0.0283	0.175	0.16
15 L	0.95	0.0345	0.0032	0.096	0.09
15 L	0.95	0.0690	0.0092	0.139	0.13
15 L	0.95	0.1035	0.0197	0.190	0.18
15 L	0.95	0.1380	0.0278	0.201	0.19
15 L	0.95	0.1725	0.0405	0.235	0.22
16 L	0.95	0.0323	0.0041	0.128	0.12
16 L	0.95	0.0646	0.0086	0.137	0.13
16 L	0.95	0.0968	0.0189	0.196	0.19
16 L	0.95	0.1290	0.0249	0.192	0.18
16 L	0.95	0.1614	0.0354	0.219	0.21
17 L	0.91	0.0333	0.0037	0.111	0.10
17 L	0.91	0.0667	0.0086	0.130	0.12
17 L	0.91	0.1000	0.0156	0.156	0.14
17 L	0.91	0.1333	0.0244	0.183	0.17
17 L	0.91	0.1667	0.0337	0.202	0.18

then must be concluded that the viscosity of the solutions in the tiny pores of the system is higher than in the larger capillary of the viscosimeter. However, as the investigations at various pressure gradients show, there is not only a rise in viscosity, but the microviscosity must decrease with increasing velocity of flow. The fluids in the pore spaces would no longer behave like a Newtonian fluid, whose viscosity is independent of the shearing stress, but would have an intrinsic viscosity, as, for example, solutions of the larger organic molecules. The internal structure of such solutions is explained by the intermolecular forces of the dissolved molecules. The decrease in viscosity with increasing fluid velocity of the salt solutions illustrates the gradual disintegration of this "structure" by the increasing shearing stress. Accordingly, it must be assumed that an analogous structure forms in the vicinity of the pore walls due to the forces which prevail between the fluid and the wall. C. Terzaghi (1925) and A. Macey (1938) have assumed a higher viscosity for water in the minute capillaries of clay.

On the basis of the preceding studies it is not possible to decide between either alternative. However, since quantitative conclusions are not possible, it is unnecessary to obtain a model representation that is precise in every detail. It is certain, in any case, that the deviations from the Darcy equation depend on an interaction between the molecules and ions of the fluid and the pore walls.

Such deviations were not found in the case of nonpolar fluids such as cyclohexane and carbon tetrachloride. These nonpolar molecules do not enter into any perceptible reactions with the internal surfaces of the rock. Whether other organic fluids with different molecular structure will also produce deviations from the Darcy equation remains to be proved. It appears that such deviations do occur in the case of benzene and molecules with OH groups, which might indicate that in these cases the strong anisotropy of the polarizable benzene molecule, or the OH-dipole, leads to the bonding of molecules on the solid surface. In the case of water and salt solutions, however, an especially intensive interaction between fluid and pore walls must occur.

It is presumed that the bonding of water occurs chiefly on the surfaces of the clay mineral particles, although it is also possible that the quartz surfaces themselves fix a certain portion of the fluid. It is remarkable that the small quantity of clay that exists in the sandstones investigated is able to produce such a distinct influence. Rocks richer in clays will show even more noticeable effects.

In the American literature (Muskat, 1949; API, 1942; Johnston and Beeson, 1945), sandstones that show similar permeability anomalies are often called "bentonitic" without imparting any details as to the mineral composition of the clays present. It is therefore assumed that intercrystalline swelling of clay minerals of the montmorillonite group is responsible for the phenomena observed. In the sandstones investigated by us, montmorillonite was not found in measurable quantities. Furthermore, the clay minerals of the mica and kaolin groups that were identified do not exhibit intercrystalline swelling, so that this explanation will not suffice. However, it is quite certain that montmorillonite-free clays are able to unite with considerable quantities of water.

Table 6. Permeabilities with NaCl Solutions at Various Pressure Gradients

No.	NaCl content	$\eta$	dP/dx	Fluid velocity	$\alpha = \frac{\dot{Q}}{dP/dx}$	Permeability
	%	cp	atm/cm	cm/sec		$k = \alpha \cdot \eta$ darcys
14 L	5	1.00	0.0325	0.0039	0.120	0.12
14 L	5	1.00	0.0650	0.0092	0.142	0.14
14 L	5	1.00	0.0974	0.0165	0.169	0.17
14 L	5	1.00	0.1299	0.0205	0.158	0.16
14 L	5	1.00	0.1624	0.0322	0.198	0.20
15 L	5	1.00	0.0345	0.0036	0.105	0.11
15 L	5	1.00	0.0690	0.0142	0.205	0.21
15 L	5	1.00	0.1035	0.0228	0.221	0.22
15 L	5	1.00	0.1380	0.0394	0.285	0.29
15 L	5	1.00	0.1725	0.0506	0.293	0.29
15 L	10	1.21	0.0345	0.0086	0.250	0.30
15 L	10	1.21	0.0690	0.0200	0.289	0.35
15 L	10	1.21	0.1035	0.0337	0.326	0.39
15 L	10	1.21	0.1380	0.0443	0.321	0.39
15 L	10	1.21	0.1725	0.0616	0.357	0.43
16 L	5	1.00	0.0323	0.0022	0.068	0.07
16 L	5	1.00	0.0646	0.0059	0.091	0.09
16 L	5	1.00	0.0968	0.0105	0.108	0.11
16 L	5	1.00	0.1290	0.0167	0.129	0.13
16 L	5	1.00	0.1614	0.0301	0.187	0.19
16 L	10	1.21	0.0323	0.0053	0.163	0.19
16 L	10	1.21	0.0646	0.0148	0.228	0.27
16 L	10	1.21	0.0968	0.0225	0.232	0.28
16 L	10	1.21	0.1290	0.0322	0.249	0.30
16 L	10	1.21	0.1614	0.0393	0.244	0.30
17 L	17	1.37	0.0333	0.0036	0.101	0.15
17 L	17	1.37	0.0667	0.0129	0.193	0.27
17 L	17	1.37	0.1000	0.0240	0.240	0.33
17 L	17	1.37	0.1333	0.0337	0.250	0.35
17 L	17	1.37	0.1667	0.0473	0.283	0.39

To prove this, we have measured the water absorption of powders composed as much as possible of pure clay minerals and quartz. The clays investigated - montmorillonite, kaolinite, and illite - were exchanged with Na or Ca ions by treatment with NaCl or CaCl<sub>2</sub> solutions, respectively, freed of soluble salts by dialysis and dried at 100°C. The water absorption was measured by putting the dry powders in a fritted glass crucible which was placed on a balance scale and partially immersed in a container of water or salt solution so that the glass frit was exactly at the surface of the liquid. The fluid absorption of the powders could then be measured by an exact observation of the weight increase of the crucible. When 20 to 50 mg. quantities were used, the process was completed in from 2 to 3 hours. The fluid absorption of the Na clays and quartz was measured with NaCl solutions, and CaCl<sub>2</sub> solutions were used for the Ca clays.

The results of these experiments are listed in table 7. For montmorillonite, illite, and quartz, the fluid volumes absorbed exceed the pore volumes of the dry powder. Thus for these substances, it appears that in addition to capillary effects, still other forces must be active. In the case of the capillary rise of fluids in a porous system, forces are exerted at the pore walls that strive to diminish the pore cross section, and they probably are also effective in the kaolinite powder where it will be noted that the absorbed fluid volume is less than the dry pore volume. Therefore capillary forces alone cannot explain the results observed. Through intercrystalline swelling, montmorillonite can nearly double its volume at 100°C (Jasmund, 1951). The fluid absorptions observed here are therefore considerably in excess of intercrystalline swelling. Thus for all the powders investigated, including the montmorillonite, the accumulation of water layers on the outer surfaces of the mineral particles is a primary factor.

In the case of montmorillonite and illite, the quantity of fluid absorbed increased with decreasing concentration of electrolyte. Kaolinite and quartz powder exhibit no relationship to electrolyte content.

The action of the dissolved salts can best be understood as an osmotic equilibrium. From electrophoretic investigations, it is known that clay particles are negatively charged. For Na and Ca clays, this charge is compensated for by Na and Ca ions, respectively, which are more or less rigidly bound to the particle surfaces. Each clay particle can be conceived as a salt that consists of a large fixed "anion" with removable cations. In the osmotic equilibrium of such a system with an external electrolyte solution, it is important that the diffusion of these "anions" can be neglected compared to that of the cations. One can therefore use as a model the concept that each clay particle is surrounded by a membrane which is impermeable to the anions enclosed within but permeable to the cations as well as to ions of either sign located outside the membrane. The osmotic equilibrium of semipermeable membranes of this kind is called Donnan equilibrium (Marshall, 1949). The condition for the internal (i) and external (e) concentration of Na and Ca ions with such a membrane is:

$$(a_{\text{Na}^+} \cdot a_{\text{Cl}^-})_i = (a_{\text{Na}^+} \cdot a_{\text{Cl}^-})_e$$

In other words, the product of the activities of the internal Na<sup>+</sup> and Cl<sup>-</sup> must be equal to that of the external ions. The concentration of Na ions enclosed

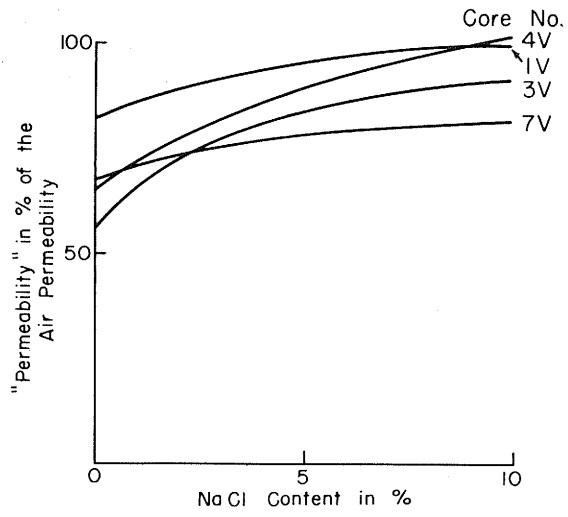


Fig. 1. - "Permeability" measured with solutions of various NaCl content at constant pressure drop ( $dP/dx = 0.002$  atm/cm).

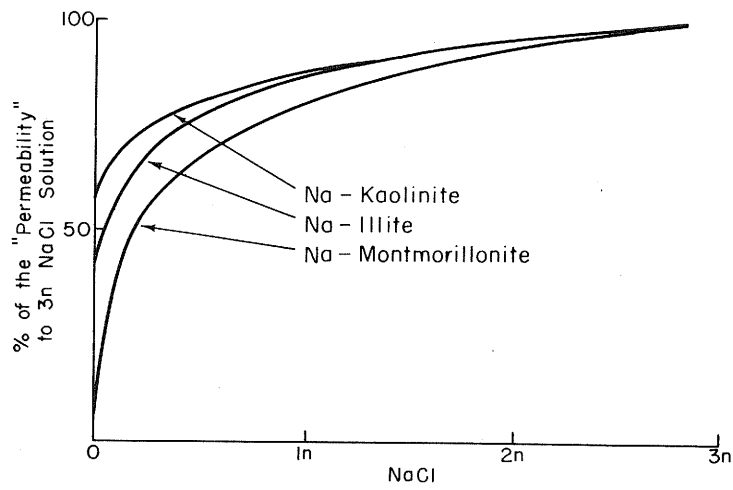


Fig. 2. - "Permeability" of mixtures of quartz sand with 4% Na clay.

Table 7. Fluid Absorptions for Various Mineral Powders

Mineral	Pore volume of dry powder cm <sup>3</sup> /cm <sup>3</sup> solid	Fluid absorbed with NaCl solutions cm <sup>3</sup> /cm <sup>3</sup> of solid				
		0 n	0.1 n	0.5 n	1.5 n	3.0 n
Na montmorillonite (1)	4.75	50.6	32.5	19.1	13.1	10.3
Na illite (2)	6.51	13.1	11.6	10.0	9.6	-
Na kaolinite (3)	8.52	7.4	-	7.8	7.6	-
Quartz (4)	2.32	6.2	-	6.7	6.0	-
		Fluid absorbed with CaCl <sub>2</sub> solutions cm <sup>3</sup> /cm <sup>3</sup> of solid				
		0 n	1 n	3 n	6 n	
Ca montmorillonite (1)	3.65	13.5	12.0	9.2	7.8	
Ca illite (2)	4.75	8.5	8.6	8.4	6.3	
Ca kaolinite (3)	8.65	7.6	7.8	7.3	6.2	

(1) Montmorillonite from Wyoming, U.S.

(2) Illite from the upper Muschelkalk (limestone) of Diemarden near Göttingen (freed of calcium carbonate with dilute acetic acid, quartz content 15%).

(3) Kaolinite from Schnaittenbach (quartz content 6%, muscovite content 12%).

(4) Powdered quartz from Eldingen (Lias  $\alpha_2$  in the Eldingen field).

within the membrane, that is, in the vicinity of the clay particles, is determined by the negative charge of the clay "anions." If the Na concentration in the outer space is lower than in the neighborhood of the clay particles, the Cl concentration near these particles must be less than on the outside of the membrane in order to satisfy the above equilibrium. This means that the water next to the clay particles is fixed. Therefore the action of this osmotic mechanism consists of water being extracted from the external electrolyte solution and becoming strongly attached to the clay. The amount of bound or fixed water thus decreases as the concentration of the electrolyte increases.

This bonding of water on clay surfaces must depend not only on the negative charge of the particles but also on the degree of dissociation of the clay-cation complex. The amount of fixed water becomes higher the stronger the dissociation. The difference observed between the Na and Ca clays was therefore interpreted as an indication that the Ca clays are less dissociated than the Na clays.



In addition to the above effects of osmotic equilibrium, the linkage of water molecules on solid surfaces by dipole forces or hydrogen bonds also can play a role which either is not influenced by the electrolyte concentration or is only imperceptibly so. The bonding of water on the surfaces of the quartz particles may be of this kind.

To illustrate the connection between the osmotic linking of water on clay surfaces and the relationships observed between salt concentration and the velocity of these salt solutions through the sandstones investigated, we have performed experiments on artificial mixtures of quartz sand and the above pure clay minerals. Four percent clay was used in each mixture, and the flowing velocities were measured at a pressure drop of 0.002 atm/cm. Permeabilities were calculated according to the Darcy equation and are expressed as a percent of the value obtained with the 3n salt solutions. The results are presented in figure 2. The curves shown are the averages of a number of individual observations. With reference to the kaolinite, a discrepancy appears inasmuch as the "permeability" is electrolyte-dependent although no relationship between the water absorbed and electrolyte content could be observed (table 7). We would like to assume that the determination of the water absorption is not sensitive enough to detect the effect that probably existed here as well as in the other clays.

#### 5. Conclusions

It is concluded that the described deviations from the Darcy equation must affect all flow processes in the sediments of the earth's crust. Porous sandstones are filled with many different brines. The movement of these solutions (which are important in diagenetic processes, for example) will not be determined by pressure drop alone but will also depend on the salt concentration. Thus a sandstone containing clay may present a barrier to a weak brine and yet allow a salt-rich solution to pass through very quickly. The penetration of fresh surface waters into the deeper sediments could be hindered by such a mechanism. Moreover, if the nonlinear dependence of fluid velocity on pressure drop is to be considered, then it follows that an increase in pressure drop increases velocity more rapidly than would be expected, assuming the validity of the Darcy equation.

The Darcy relationship can be utilized for the flow of oil in petroleum formations. However, the pore spaces of oil-bearing rocks also contain salt water. These so-called connate waters (Haftwasser) adhere to the pore walls and do not take part in the fluid movement. They may be regarded in the same light as the residual oil that cannot be displaced from the pore spaces by the prevailing pressure gradients. The entire pore volume is therefore not available for fluid movement, and the effective permeability is accordingly reduced.

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