THE FLOW OF SALT SOLUTIONS THROUGH COMPACTED CLAY[1]

by

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ABSTRACT

Experimental evidence of the salt filtering ability of compacted bentonite and clay material is presented. Apparatus has been developed in which samples of semi-dry powdered bentonite and shale are compacted under pressures of 10,000 psi and subjected to flow with sodium chloride solutions under fluid pressures up to 10,000 psi. Porosities of 34–41 percent have been obtained with the bentonite and 24 percent with the shale. Permeabilities of 10^{-5} to 10^{-6} millidarcies have been measured. A ratio of input to output solution concentration as high as 8 has been found with the bentonite samples and dilute (0.164 N) NaCl solutions. The ratio falls off with increased input concentration and with increased porosity. The shale sample has given a ratio of 1.7 with an input concentration of 0.129 N NaCl.

Streaming potential differentials of approximately 1 mV per 100 psi have been measured during the flow experiments. The potential differential is highest with the shale material and shows a decrease with increasing salt concentration.

INTRODUCTION

It has been demonstrated in earlier papers (McKelvey, Spiegler and Wyllie, 1957; 1959) that certain synthetic ion-exchange membranes under hydraulic pressure permit the passage of water but restrict the movement of dissolved salts. Under such conditions an increase in concentration of the dissolved salt takes place on the high-pressure side and a solution of lower concentration appears on the low-pressure side. The possibility that a similar effect could be obtained with clay minerals, particularly in their natural association within shales, has been suggested (McKelvey, Spiegler and Wyllie, 1957). Such a process could be responsible not only for the concentration of brines within the subsurface but also for separation of various salts.

The salt filtering phenomenon is related to the ion-exchange properties of the membrane. It is, therefore, reasonable to expect that clay minerals with cation exchange properties could produce salt filtering under conditions of compaction. The complex particle system comprising a shale, however,

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presents many problems which are not found in a synthetic ion-exchange membrane. The clay system must be confined mechanically under pressures great enough to reduce the porosity to a point where the exchange capacity of the clay matrix represents a significant concentration in the fluid-filled pore space of the system.

The primary aim of this phase of the investigation has been to demonstrate experimentally the salt-filtering phenomenon with clay materials. Bentonitic montmorillonite, with its large surface area and relatively high exchange capacity, represents the most favorable clay mineral for this purpose, and accordingly Wyoming bentonite was selected for the first experiment. Subsequently the experiments were extended to include the investigation of a disaggregated shale.

Attempts have been made, with rather limited experimental data, to relate salt filtering to hydraulic permeability, hydraulic pressure, porosity and matrix material. The electrical property called "streaming potential" has been measured in each case.

THEORETICAL BACKGROUND

Membrane transport processes, including both the mechanical, or hydraulic, and electrical phases of the problem have been treated in the literature by numerous authors with varying degrees of success. The latest and most notable of these have been the papers of Staverman (1952), Schmid (1952) and Spiegler (1958). Since a quantitative discussion of the theory is beyond the intention of this paper, only a brief qualitative description of these transport processes as they apply to this investigation will be given here.

Cation exchange materials, either of the clay mineral or the synthetic resin type, contain negatively charged groups which are firmly attached to the solid phase of the system. These charges are balanced by cations which, within the water-filled pores of the system, are free to move in the vicinity of the attached groups. The negative electrical charge of the matrix groups prevents the close approach of solution anions, and therefore, if located in pores of sufficiently small diameter, will effectively exclude the solution anions and cations from the pores. If now the clay material is compacted in the form of a plug or membrane with a fixed volume and equilibrated with a solution of sodium chloride, the internal pore solution will be less concentrated in chloride ions than the external solution. The pores of the plug will contain water, sodium "exchange" ions and a smaller number of sodium and chloride ions from the external solution. Exclusion of the solution ions will be dependent on the magnitude of the cation exchange capacity of the clay per unit interstitial volume.

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Application of hydraulic pressure to the solution at one side of the clay membrane with the other side open to atmospheric pressure will initiate flow of water, and ions. Since the concentration of sodium ions (including the "exchange" ions) is much greater than that of the chloride ions in the membrane, a "streaming potential" appears immediately to counterbalance the unequal flow of oppositely charged particles. The streaming potential prevents the emergence of excess sodium ions at the low-pressure side of
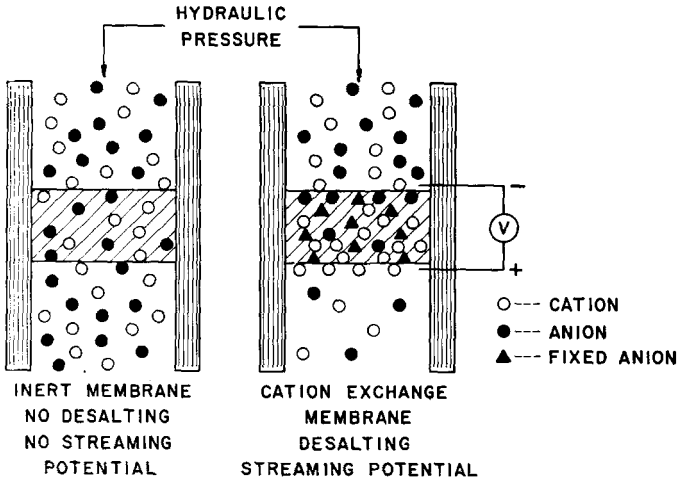

FIGURE 1.—Permeability of membranes to salt solutions.

the membrane and movement of sodium chloride through the membrane is controlled by the movement of the chloride ion.

The movement of the electrically neutral water through the membrane is not directly influenced by the electrical potential but is impeded by the slow-moving sodium ions. The salt content of the solution emerging from the low-pressure side of the membrane will be determined by the concentration of the chloride ion in the pore solution, suitably modified by the interaction between the ions and water. Although the theory of desalting has not progressed to the point where the interaction effect can be assessed quantitatively, it is probable that the streaming potential is the best measure of the ion–water interaction.

The flow of a salt solution through an inert membrane is compared with flow through a cation exchange membrane in Fig. 1.

APPARATUS

Preliminary experiments with available apparatus indicated that compaction pressures of 10,000 psi would be required to attain porosities at which salt filtering would be significant. Time considerations indicated also

that flow pressures of several thousand pounds per square inch would be required in most experiments to obtain reasonable throughput rates. The sample would have to be confined such that the input and output faces were insulated electrically from each other to avoid short-circuiting the streaming potential. These requirements resulted in the apparatus shown diagrammatically in Fig. 2.

The confining steel cylinder is fitted with a nylon liner to give the required electrical insulation. The sample is compressed within this cylinder between
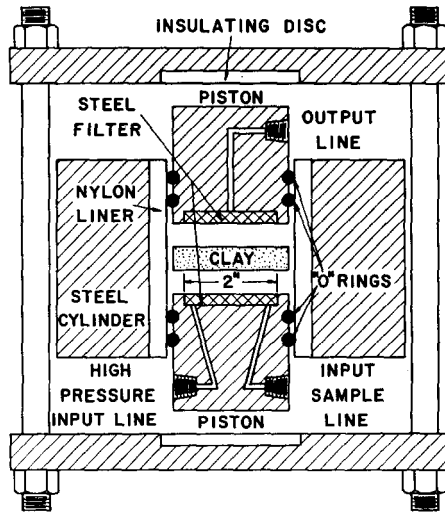

FIGURE 2.—Diagram of flow cell.

pistons fitted with metallic filters for passage of solution into and out of the sample. The input piston is fitted for entry of solution under high pressure from a reservoir tank and with an exit for sampling the fluid at the input face or for continuous flow past the input face. The output piston contains a single exit for the filtered solution.

Compaction of the sample, carried out with the aid of a hydraulic press, is maintained as indicated in Fig. 2, by end plates held together by bolts. Additional electrical insulation is provided by bakelite inserts in the end plates.

The complete apparatus is indicated in Fig. 3. An air-operated pump forces oil into the top of the salt solution reservoir (750 ml) at pressures up to 10,000 psi. Salt solution from the bottom of the reservoir is carried to the input piston through high pressure steel tubing and the output is collected in a graduated pipette.

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The sample cross section in this apparatus is approximately 20 cm² which permits the flow of several ml of fluid per day through samples approximately 0.5 cm thick.

A Leeds and Northrup pH meter connected to a Brown recorder was used for the streaming potential measurements. No provisions were made for reversible electrodes, the steel pistons being used for this purpose. This was possible because the high input impedance of the pH meter minimized electrode reactions. The pressure-dependent portion of the potential was determined in mV per 100 psi.
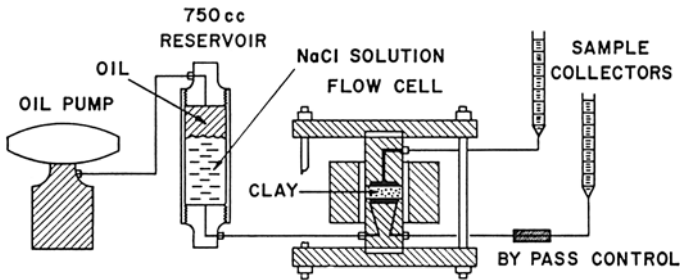

FIGURE 3.—Cross-sectional view of flow apparatus.

EXPERIMENTAL METHODS AND RESULTS

The materials studied are Wyoming bentonite and a disaggregated shale composed of calcite, quartz, montmorillonite, illite and kaolinite. Calcite was removed from the shale by treatment with a dilute HCl solution. The bentonite was dried at 100 °C and ball-milled as a dry powder for several hours. The bentonite powder then was rehydrated in a humid atmosphere until it contained more than 10 percent water. The shale was ball-milled with water, washed with dilute HCl to remove calcite and finally washed with a NaCl solution to ensure sodium saturation. The shale was partially dried to a water content of approximately 25 percent without removal of excess sodium chloride.

The flow cell was prepared by compressing 15–30 g of clay between the pistons for 24 hr under a load of 40,000 lb or about 10,000 psi. The end plates were bolted together while pressure was maintained. Strain in the bolts, as measured by strain gage, was sufficient to maintain the compaction load. A sodium chloride solution was then forced into the lower piston under pressures of from 5000 to 10,000 psi. Fluid flowing through the clay disc was collected in a graduated pipette in 3–10 ml portions. Analysis of solutions was carried out by titrating the chloride ion with silver nitrate in the presence of potassium chromate as the indicator. Periodically the solution samples were dried and weighed, and then titrated to verify that the sample consisted

only of a solution of sodium chloride. Salt content of the solution in the input piston filter was determined initially by intermittent sampling, and in a later modification by a continuous by-pass flow system. This modification was accomplished satisfactorily by the use of a line filter packed with asbestos fiber to give a flow rate close to that of the clay disc.

The first bentonite sample prepared using 30 g of the hydrated powder was compacted into a disc, which on completion of the experiment contained 16 percent water and was 0.51 cm thick. The results of flow with a 1.03 N reservoir solution are shown in Fig. 4. In this experiment salt was allowed
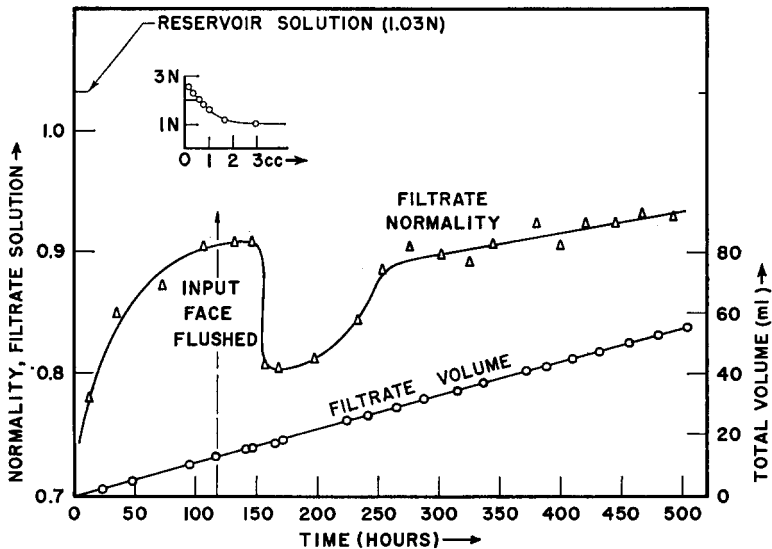

FIGURE 4.—Flow properties and salt filtering effects of bentonite disc, 0.51 cm × 20 cm², with 1.5 N NaCl solution at 10,000 psi.

to accumulate at the input face. The results of sampling the concentrate in a series of small volumes after a flow of approximately 12 ml output are indicated on the diagram. At the time of sampling the filtered solution had reached 0.9 N and a maximum solution concentration of 2.5 N was measured at the input face. The filtered solution continued at 0.9 N for 4 ml after sampling and then dropped to 0.8 N, rising again rapidly to 0.9 N and continuing a slow rise to 0.92 N. The experiment was terminated after a total flow of 60 ml of filtrate and again the maximum normality at the input face was 2.5.

The salt content of the reservoir solution was increased to 1.51 N and flow continued under 10,000 psi to a total throughput of 25 ml. Salt concentration of the filtered solution rose from 0.92 N to 1.3 N (Fig. 5). At the completion of the experiment a maximum of 3.5 N salt concentration was determined

at the input face. These experiments indicate clearly that sodium chloride is accumulated at the high-pressure face of the clay disc. It is evident of course that this experimental procedure does not give a reliable relationship between filtrate and concentrate since the distribution of rejected salt at the input face is unknown.

An effort to create a more uniform solution at the input face was made in the next experiment in which the input solution was permitted to flow continuously across the face of the sample by means of a flow regulating
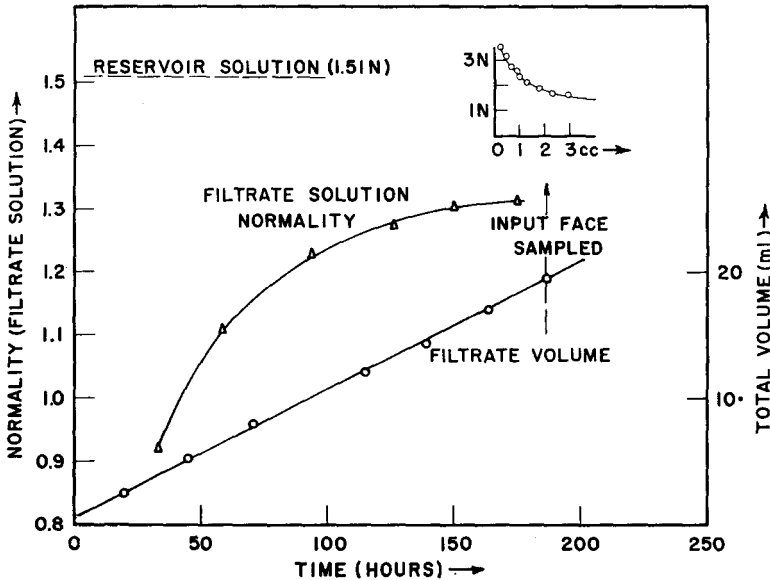

FIGURE 5.—Flow properties and salt filtering effects of bentonite disc, 0.51 cm × 20 cm², with 1.5 N NaCl solution at 10,000 psi.

valve. The results of this experiment are given in Fig. 6. Operation of the flow regulating valve was unsatisfactory, but a fairly constant filtrate normality of 0.94 was obtained with the concentrate also remaining fairly constant at 1.65 N.

A bentonite disc in the flow cell was prepared with 15 g of clay compacted in the same way to give a thickness of one-half that of the first sample. Flow through this sample was carried out with a reservoir solution of 0.103 N sodium chloride at pressures of 10,000 and 5000 psi (Fig. 7). A constant flush of the input face was arranged by means of the asbestos-packed line filter. Under 10,000 psi hydraulic pressure the filtrate solution became constant at 0.046 N while the input face flush reached a concentration of 0.155 N. Reduction of the flow pressure to 5000 psi resulted in a greater desalting effect, with filtrate dropping to 0.019 N while the concen-

trate increased to 0.164 N. Finally a return to 10,000 psi tended to restore the original conditions.

The increased efficiency of desalting which results from a drop in the driving pressure may be due in part to changes in degree of compaction of the sample. In these experiments, the bolts that hold the flow center together act as springs. The spring action is amplified further by elastic bending of the end plates and elastic compression of the bakelite inserts. Upon reduction of the hydraulic pressure within the cell, the bolts contract,
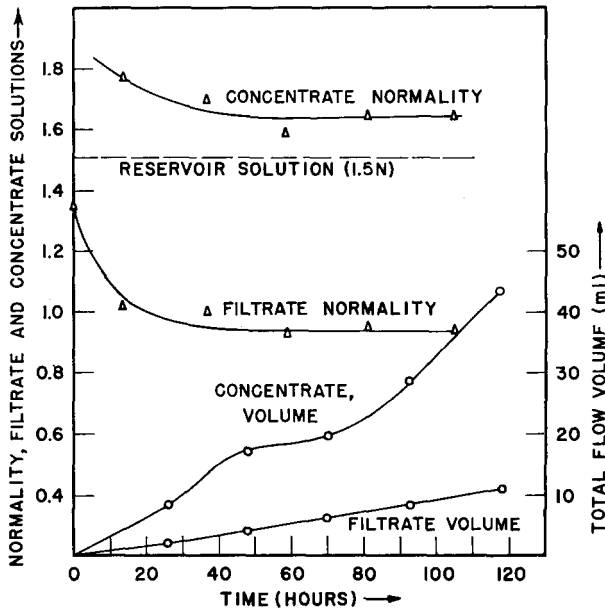

FIGURE 6.—Continuous flushing of bentonite disc input face under flow with 1.5 N NaCl solution at 10,000 psi.

thus reducing the volume of the sample. Crude calculations based on measurement of the strain in the bolts during the experiment indicate that the total porosity of the bentonite sample may drop from 41 percent to 39 percent upon reduction of the hydraulic pressure from 10,000 psi to 5000 psi. This would be expected to produce a significant increase in desalting efficiency.

A disc prepared from the disaggregated shale material with a compacted thickness of 0.41 cm and a saturated water content of 10.7 percent was flowed with the same 0.103 N sodium chloride solution at pressures of 10,000 and 5000 psi. The information shown in Fig. 8 indicates clearly that shale material prepared in this way does restrict the passage of salt in solution under flow conditions. Filtrate/concentrate normalities of 0.092/0.121 at

10,000 psi and 0.076/0.129 at 5000 psi were obtained under apparent steady conditions. Again the increased desalting efficiency at the lower pressure is not understood completely.
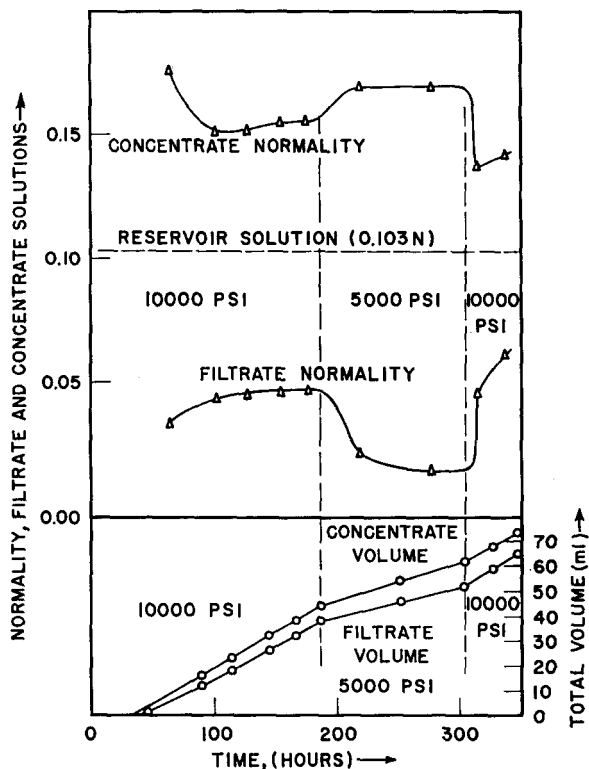

FIGURE 7.—Flow and salt filtering properties of bentonite disc, 0.25 cm × 20 cm², with 0.1 N NaCl solution at 10,000 and 5000 psi.

STREAMING POTENTIAL

During each experiment that has been described, the streaming potential differential (mV per 100 psi) was determined in the vicinity of the operating pressure. Determinations of the slope of the potential-pressure curve eliminates problems of spurious potentials due to solution-electrode interaction. Values are shown in Table 1 along with other information from the flow experiments. The values range from 0.72 to 1.11 mV/100 psi for the bentonite membranes under various conditions, and from 1.0 to 1.35 mV/100 psi for the shale under the two pressure conditions. Assuming that the thickness of the bentonite sample is not an important variable, the more dilute solution gives a higher streaming potential differential. Reduction of the driving pressure with attendant increased desalting efficiency results in a

drop of streaming potential differential. The shale gives generally higher streaming potential differentials compared with the bentonite and shows the same drop with reduced flow pressure and increased desalting effect.
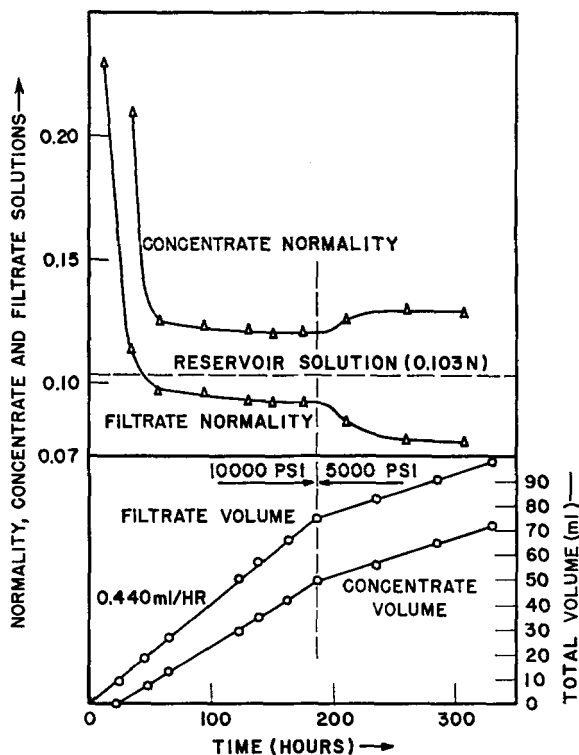

FIGURE 8.—Flow and salt filtering properties of shale disc (recompacted), 0.40 cm × 20 cm², with 0.1 N NaCl solution at 10,000 and 5000 psi.

It is hoped that further study of this phenomenon along with other electrical and mechanical properties of the clay membranes will be fruitful in understanding the process.

SUMMARY

The physical properties and flow data for each of the three clay membranes are given in Table 1. The salt filtering ability is expressed simply as the ratio of input to output normality. The water content of the clay membranes, determined at the completion of each experiment, is assumed to be the same as that existing under flow conditions except for the thinner bentonite (0.26 cm) where some information on expansion under hydraulic pressure was obtained. Porosities, calculated from the water content and

TABLE 1. — PERMEABILITY AND SALT FILTERING DATA

Material	Thick-ness (cm)	Water Content (percent)	Porosity (percent)	Flow Pressure (psi)	Flow Rate (ml/hr)	Permeability (md)	Filtrate Normality	Concen-trate Normality	Concen-trate/ Filtrate Ratio	Streaming Potential (mV per 100/psi)
Bentonite	0.51	16.0	34	10,000	0.110	4.0×10^{-6}	0.93	2.5^2	2.7	0.75
Bentonite	0.51	16.0	34	10,000	0.102	3.7×10^{-6}	1.31	3.5^2	2.7	0.77
Bentonite	0.51	16.0	34	10,000	0.099	3.6×10^{-6}	0.94	1.65	1.7	0.74
Bentonite	0.27^1	—	41^1	10,000	0.261	5.0×10^{-6}	0.047	0.155	3.3	1.11
Bentonite	0.26	19.0	39	5,000	0.118	4.2×10^{-6}	0.019	0.164	8.0	0.72
Shale	0.41	10.7	24	10,000	0.440	12.9×10^{-6}	0.092	0.121	1.3	1.35
Shale	0.41	10.7	24	5,000	0.154	9.0×10^{-6}	0.076	0.129	1.7	1.10

[1] Estimated.
[2] Maximum concentration.

a grain density of 2.7 are 34 and 39–41 percent for the thicker and thinner bentonites and 25 percent for the shale. Permeabilities are in the range of 3.6×10^{-6} to 5.0×10^{-6} md for the bentonites and 9.0×10^{-6} to 12.9×10^{-6} md for the shale under different hydraulic pressure conditions.

Experiments with the thick bentonite membrane in which sodium chloride was allowed to accumulate at the input face of the clay probably do not give a meaningful ratio of filtrate to concentrate normalities since the maximum concentration observed may have been very local. The remaining results, obtained with continuous sampling of the input face, are considered to give a better expression of the desalting ability of the particular membrane. It is obvious, as expected, that the bentonite is a much better salt filter than the shale and that it filters a dilute solution better than a more concentrated one.

The increased desalting ability of both the bentonite and shale at lower input pressure may, as already suggested, be due largely to lower porosity. This suggestion is substantiated by the observed lower permeability at lower hydraulic pressures.

These experiments give observational proof of the salt filtering ability of natural cation exchangers and give some quantitative information on the magnitude of this property under the particular conditions of the experiments. Since the shale material which has been used is reasonably similar to the majority of shales of post-Paleozoic age, it is probable that circulation of solutions through such systems in the subsurface can result in some filtration of salts.

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