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CONCENTRATION GRADIENTS IN AQUIFERS

Submitted to

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Oklahoma State University
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by

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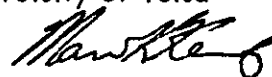University of Tulsa

FINAL REPORT

PROJECT: A-025-OKLA

TITLE: CONCENTRATION GRADIENTS IN AQUIFERS

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PERIOD: July 1, 1970 - June 30, 1971

ABSTRACT

An investigation of the effects of a thermal gradient on the transfer of electrolyte across clay membranes was begun. The purpose of the study was to determine the role of this phenomenon, thermal pumping, on the observed concentration increase of subsurface brines with depth. Little, if any, transport has been observed for Wyoming Bentonite membranes with dilute sodium chloride solutions. Preliminary electromotive force measurements with Ag/AgCl electrodes indicate an increasing potential with increasing temperature gradient (hot side positive). This result indicates that transport should occur. The absence of transport may be indicative of a very slow process.

CONCENTRATION GRADIENTS IN AQUIFERS - M. K. Kemp

Introduction

This project was begun to investigate the effects of a thermal gradient on the transfer of electrolyte across a clay membrane. This transfer phenomenon, which is called thermal pumping, has been advanced as a partial explanation of the observed concentration increase of subsurface brines with depth[1]. Several effects have been considered in an attempt to explain the noted increase in concentration. However, all have been unable to predict changes as large as those that are known to exist.

A preliminary theoretical treatment of the thermal pumping phenomenon[1] indicated that it too was not sufficient to explain observed data. Since many approximations were required in the theoretical treatment, an experimental study was begun to determine the actual size of the thermal pumping effect.

Experimental

Each thermal pumping cell that was constructed consisted of the following features:

1. Two solution compartments separated by a clay membrane;
2. Temperature control for each compartment;
3. Temperature measurement capability on each side of the membrane;
4. A magnetic stirring bar in each half of the cell; and
5. A conductivity cell in each compartment.

The temperature control system consisted of a thermoregulator which was inserted into the solution, a quartz immersion heater in the solution, and an electronic control circuit. Magnetic stirring bars were utilized for solution mixing with magnetic stirring motors outside the cells. Calibrated conductivity cells were inserted into each solution compartment for measurement of electrolyte concentration.

Figure 1 shows the configurations of the three plexiglas cells constructed for this project. In cell 1 the membrane (d) is formed between two porous glass plates. Since the glass plates were thick (1/4"), and possibly could interfere with ion diffusion and make the temperature at the membrane surface unpredictable, cell 2 was constructed. In cell 2 no membrane support was required for the membrane (d). However, this configuration required very thick membranes which might impede ion movement across the membrane considerably. Cell 3 was designed to eliminate the objectional features of cells 1 and 2. In cell 3, thin (1/32") porous stainless steel (30-40 micron
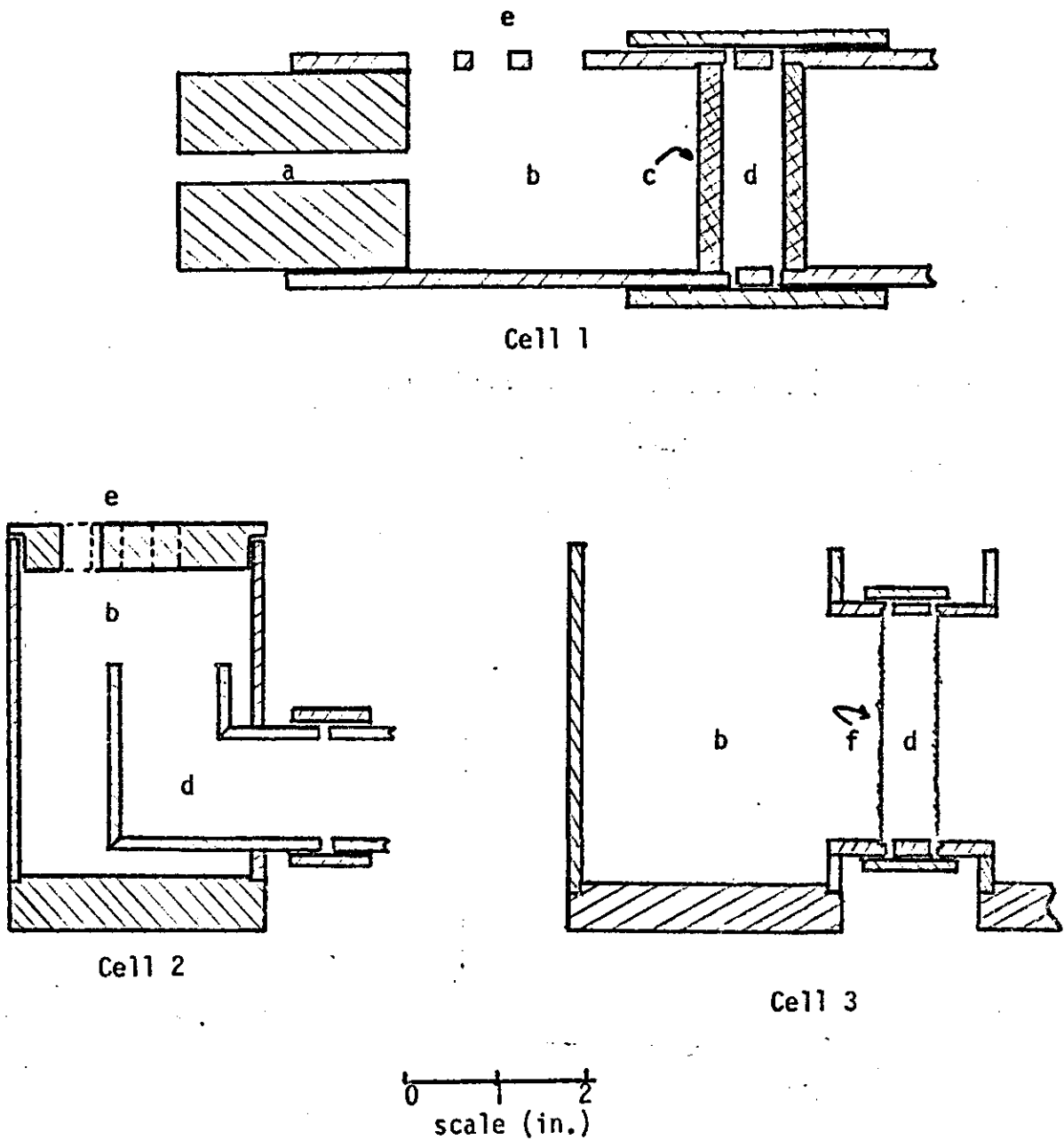
FIGURE 1. Sketches of the three thermal pumping cell types used. a – thermoregulator opening; b – solution compartment; c – porous glass membrane support; d – membrane compartment; e – probe openings; f – porous stainless steel membrane support. Top of cell 2 fits cell 3 also.

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pores) plates are used as the membrane supports. The thickness of the membrane could be varied from about 1/16 in. up by use of appropriate spacers. The membrane had a surface area of about 5.9 sq. in.

Sodium chloride solutions were used in all experiments and were made by dissolving the appropriate weight of dried sodium chloride in deionized water. The clay membranes were all made from sodium bentonite (Wyoming) by slurrying with the appropriate concentration of sodium chloride solution until a gel was formed. To remove air from the gel, it was placed in a vacuum dessicator; a vacuum was pulled on the dessicator and then dry nitrogen gas was released into the dessicator to break the vacuum. The process was repeated two or three times. The gel was stored in the dessicator over water under nitrogen gas until time for use. The per cent water in the clay was not determined since the thermal pumping effect was not observed.

The conductivity electrodes were the miniature type from Yellow Springs Instrument Company. Each electrode was calibrated in various sodium chloride solutions (1, 3, 5 g/l) versus temperature. All agreed with each other to within 1%. Conductance was measured on a Leeds and Northrup #4959 Multipurpose Electrolytic Resistance/Conductance Bridge at 1000 ∿ .

The experimental procedure for measurements was as follows:

1. A membrane was formed between the supports.
2. Solution was added to each side to the same level.
3. Stirring bars were inserted.
4. A thermoregulator, thermometer, immersion heater and conductance cell were inserted through holes in the top in each half of the cell. These were cemented in with G.E. Silicone Seal.
5. The system was equilibrated with both sides at the same temperature until no changes were noted in the conductance of the solution.
6. The temperature of one side was raised to a new value and conductance readings were taken as a function of time.

Some preliminary potential measurements have been made using Ag/AgCl electrodes and a Leeds and Northrup #8691 Millivolt Potentiometer. Electrodes were made by plating onto platinum wires using the method of Janz[2]. The same cells as above were used for these experiments. The only modification required was connection of the electrode compartment to the solution compartment by means of a glass tube (6 mm.) filled with the appropriate sodium chloride solution. An electrode was connected to each solution compartment in this manner. The electrode compartments were kept in the same water bath to assure that no temperature difference existed between them. The potential across the membrane was measured as a function of temperature.

Results

Experiments with cell 1 were unfruitful. Possible problems associated with the

porous glass plates as membrane supports such as impedance of transport and poor temperature control at the membrane surface led to the design of cell 2. The long membrane of cell 2 was not conducive to rapid transport. Cell 2 was utilized for potential measurements which will be described later. Cell 3 was constructed for further pumping studies. A 1/8 in. membrane was formed between the two porous stainless steel plates (1/32 in. thick) and solutions of 1 g NaCl/l were added to the two solution compartments. After equilibration at 36° C, side 1 was set to 40° C and side 2 to 26° C. Resistance data are shown in Table 1 and Figure 2.

TABLE 1. Resistance vs Time for Cell 3. NaCl Solution 1 g/l; Sodium Bentonite
Membrane; $T_1 = 40°$ C; $T_2 = 26°$ C.

R_1 (ohms)	R_2 (ohms)	Time (hours)	Δt (hours)
385	494	7119.7	0.0
384	495	7137.3	17.6
381	495	7187.3	67.6
380	495	7211.0	91.3
381	495	7282.3	162.6
380	494	7306.8	187.1
383	497	7335.7	216.0
383	497	7360.3	240.6
383	492	7478.5	358.8
382	491	7545.7	426.0
382	491	7650.3	530.6
382	489	7840.1	720.4
375	484	8193.1	1073.4
373	488	8342.0	1222.3
372	479	8817.5	1697.8
373	479	8964.9	1845.2
371	477	9140.0	2020.0
371	476	9390.0	2170.0

Both R_1 and R_2 decrease by about the same amount, 2.5% and 3.2% respectively. This means both compartments are becoming more concentrated. This can occur only if solution is evaporating or if salt from the clay is being leached into solution. The latter possibility seems unlikely since the system was equilibrated before the experiment was conducted. Thus, it appears as though evaporation is responsible for part of the noted change in concentration. One would expect evaporation to be faster in the hot side. The constant decrease in R_2 with time which is greater than the decrease in R_1 would seem to indicate that there is some transport of electrolyte from the hot to the cold side. This conclusion is tenuous at present and must be verified. Especially in view of the fact that theory predicts the opposite effect.
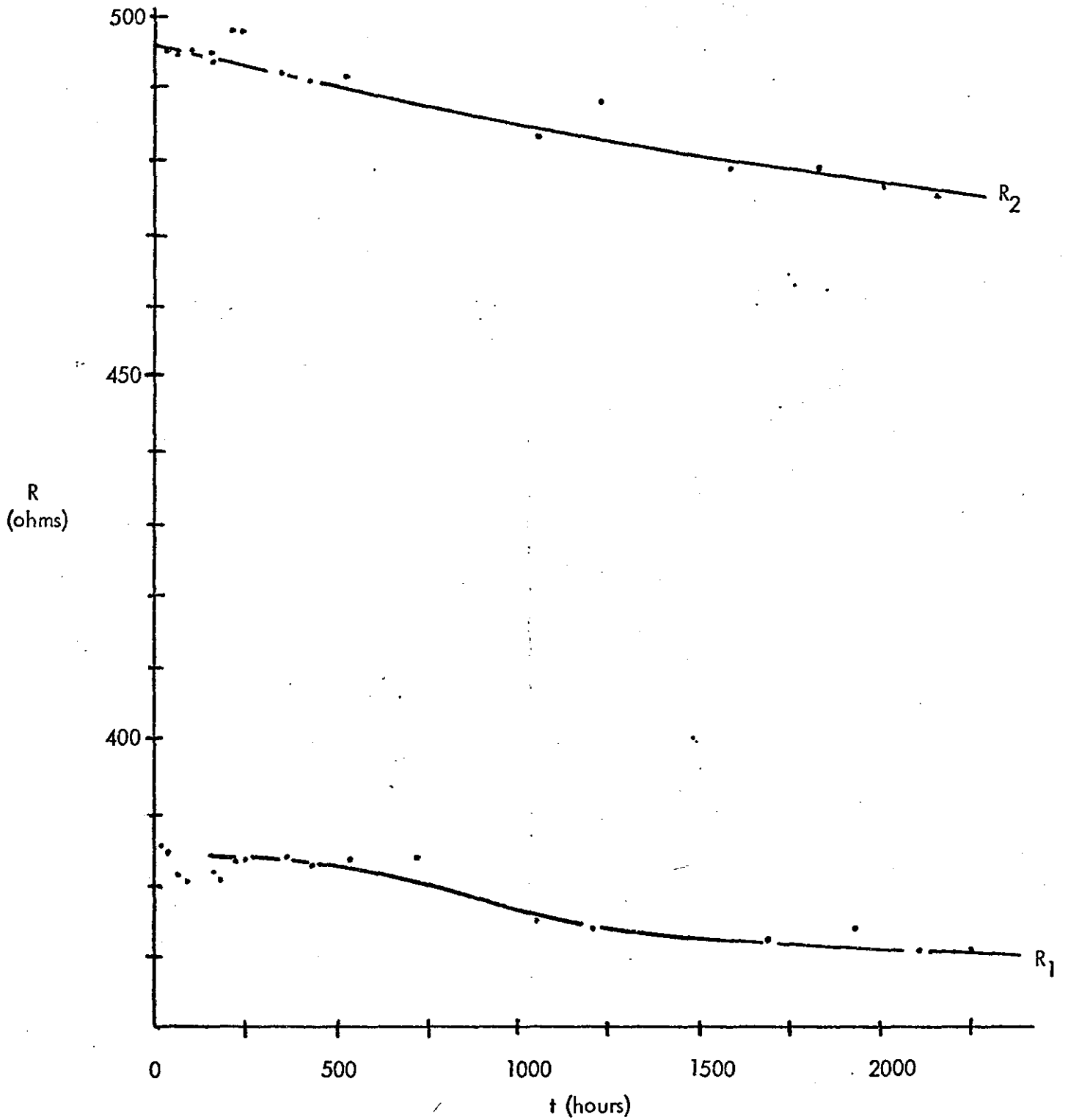
FIGURE 2.   Solution Resistance vs Time for 1/8" Membrane of Wyoming Bentonite, 1 g NaCl/l Solution. $T_1 = 40°$ C; $T_2 = 26°$ C.

In the absence of evaporation one would expect one side to increase in concentration (a decrease in resistance) as the opposite side decreases in concentration if thermal pumping were taking place. Thus far conclusive evidence has not been found to indicate that thermal pumping is actually occurring. The absence of thermal pumping over a period of more than 2000 hours may only indicate that the process is very slow, even for thin membranes. The possibility of thermal pumping occurring over a longer time period is not ruled out.

Since the thermal pumping phenomenon is slow, if it exists at all, a new set of experiments have been started in an attempt to optimize conditions by a more rapid method. This method involves measurement of the electrical potential (EMF) across the membrane. These potential measurements can be made rapidly (hours or days) relative to the previous concentration measurements (months). Since the configuration which produces the largest EMF should exhibit the greatest thermal pumping, it should be possible to find an optimum system more rapidly by measuring potentials across the membrane.

This work has just begun and will be carried out during the following year under a new grant from the Oklahoma Water Resources Research Institute.

Conclusions

Little, if any, thermal pumping has been observed thus far even with very thin membranes. One difficulty which may make detection of small concentration changes difficult is the large ($\sim$ 250 ml) volume of the solution reservoir. For this volume and a 1 g/l solution, a 5% change in concentration would represent transfer of .0125 g of sodium chloride. This may take an inordinate amount of time even with thin, large diameter membranes. Two changes that can ameliorate this situation are: decrease reservoir volume, and/or use of less concentrated solutions. If potential measurements yield an optimum membrane thickness and type and an optimum solution concentration, the design change will be made and the thermal pumping experiments will be continued.

A theoretical investigation involving irreversible thermodynamics has been begun. This coupled with the potential measurements should allow prediction of the magnitude of the thermal pumping phenomenon which can then be checked experimentally.

References

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2.   David J.G. Ives and George J. Janz, Reference Electrodes, Academic Press, New York, 1961, pp. 204-207.