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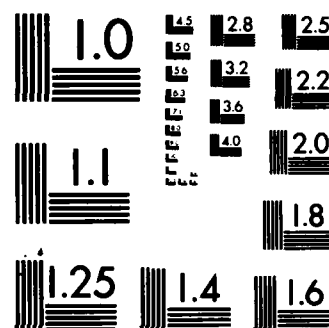
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TRANSPORT OF WATER, DISSOLVED
SUBSTANCES, HEAT AND ELECTRIC
CURRENT THROUGH SHALES AND
CLAY-RICH SEDIMENTS

FINAL REPORT

DONALD L. GRAF
WILLIAM M. BENZEL
ILHAM DEMIR
PAUL HAYDON

MARCH 20, 1984

U. S. ARMY RESEARCH OFFICE

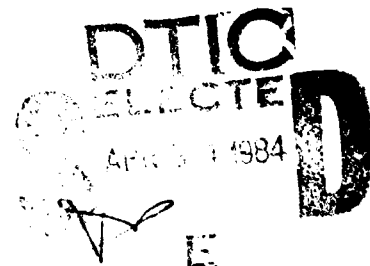
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DEPARTMENT OF GEOLOGY
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <table border="0"> <tr> <td>Water</td> <td>Transport Properties</td> <td>Electric Current</td> </tr> <tr> <td>Sediment</td> <td>Heat Transfer</td> <td>Membranes</td> </tr> <tr> <td>Clay</td> <td></td> <td>Temperature</td> </tr> </table>			Water	Transport Properties	Electric Current	Sediment	Heat Transfer	Membranes	Clay		Temperature
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INTRODUCTION

Contract DAAG 29-80-C-0068 is a continuation of Grant DAAG²⁹77-G-0011.

Research effort during the grant was concentrated upon building two heavy-duty membrane presses, securing adequate bulk samples of natural clays, and reviewing literature. The principal portion of the contract effort reported here is contained in two completed Ph.D. theses, by William M. Benzel and Paul R. Haydon, and one that is nearing completion, by Ilham Demir. These theses consider the effect upon clay-membrane transport at 20° C of the thickness and fabric of the clay cake, the effect of temperature in the range 20°-180° C upon membrane transport and membrane fractionation of the stable oxygen isotopes contained in water molecules, and the electrokinetic behavior of these clay membranes at 20° C. It becomes possible after completion of these many months of experimental runs to evaluate the difficulties encountered with experimental apparatus.

The detailed mechanisms involved in transport through the micropores of the compacted clay cake are of considerable scientific interest. Donald L. Graf spent some contract project time developing a model for electrolyte diffusion in bulk aqueous solutions, as a preliminary to understanding the more complex diffusion processes within the pores. Mindful of the skepticism among many geologists about the significance of reverse chemical osmosis in nature, he evaluated the existence in nature of fluid pressure differentials adequate to drive this process. Together with David E. Anderson, he reviewed the pressure, temperature, and salinity dependences of mineral dehydration reactions that could release liquid water in thick sedimentary sections.

These research results are presented in detail in theses and in scientific papers that have either been published or are in preparation. This report therefore limits itself to offering qualitative summaries of the principal findings.

EFFECT UPON TRANSPORT OF VARYING THICKNESS AND FABRIC OF CLAY LAYER

These experiments were run at 20° C under a confining pressure of 5000 psi, using a solution 0.79 molal in NaCl and 0.079 molal in CaCl_2 . The relatively low salinity, relative to the total range observed in nature, was chosen for ease of comparison of results with the published engineering literature on near-surface slope stability problems.

The clay cakes used were constructed by dispersing the clay crystallites in water, separating out a narrow range of crystallite sizes (0.5 to 2.0 μm diameter), and then sedimenting these particles. The labor involved made it impractical to construct really thick cakes. Within the fourfold range from 0.5 to 2.0 cm, thickness appears to have little or no effect upon filtration efficiency.

It was possible by changing the salinity of the solution to form a cake with either relatively random or relatively well-oriented fabric. These fabrics could be substantially preserved if compaction was carried out slowly and carefully. The salt-filtration efficiencies of the cakes with oriented fabric are roughly twice as great as those of the others, reaching 50 to 68%. There was preferential passage of Ca^{2+} through the cake, relative to Na^+ , in three of the four runs.

TEMPERATURE DEPENDENCE OF TRANSPORT

These experiments were run at 20°, 95°, 140° and 180° C under confining pressures of 5000 and 10,000 psi, using clay cakes with random fabric and a solution 5.0 molal in NaCl and 0.45 molal in CaCl_2 . The temperature range and the high salinity were intended to simulate depths of 5000 to 20,000 feet in thick sedimentary sections.

The filtration efficiencies for these experiments range from 16 to 28% for NaCl and 3 to 32% for CaCl_2 . Those for CaCl_2 increase nearly linearly with temperature, whereas those for NaCl go through a minimum at the two intermediate temperatures. The crossover temperature, above which CaCl_2 is filtered more efficiently than NaCl, is about 160° C at 5000 psi compaction pressure. At 10,000 psi, it is somewhere below 140° C.

Qualitative arguments involving the pressure and temperature dependences of various physical parameters suggest that fluid viscosity must be involved in explaining the general increase in filtration efficiency with temperature. The effect of compaction pressure upon mean pore size affords a satisfactory explanation for the increased filtration efficiencies observed at the higher compaction pressure.

Quantitative calculations using the Teorell-Meyer-Siever and Fritz-Marine models for predicting effluent chemical composition are partially completed. The TSM values at 20° C are in excellent agreement with experimental values.

FRACTIONATION OF STABLE OXYGEN ISOTOPES

The isotopic enrichment of the oxygen in water passing through a well-oriented smectite cake at 20° C is 0.96 o/oo, in good agreement with the value of -0.8 o/oo found earlier by T. B. Coplen and B. B. Hanshaw. Possible small shifts in this value occasioned by change of fabric or cake thickness are masked by uncertainties in our experimental procedures.

The enrichments found at 140° and 180° C, 0.15 and 0.05 o/oo, are effectively zero considering the uncertainties in measurement and data reduction. We are attempting to decide whether the rate of decrease of enrichment between 20° and 140° C favors a particular one of the possible isotopic fractionation mechanisms.

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ELECTRICAL ASPECTS OF TRANSPORT

These experiments are being run at 20° C under a confining pressure of 5000 psi, using clay cakes with either random or oriented fabric and either a 1.087 m NaCl solution or a solution 0.92 m in NaCl and 0.075 m in CaCl_2 . The membrane press is modified for these electrokinetic studies by adding four planar Ag-AgCl mesh electrodes, two on either side of the clay cake. In one type of experiment, for example, a voltage potential is imposed across a pair of electrodes (one on either side of the cake) and the flow of current is monitored using the other pair.

Streaming potential values decreased by 18 to 27% during the 8 to 10 weeks it took for mechanical and chemical steady state to be reached. This determination affords some insight into the effect that continuing compaction in nature might have on values obtained in borehole logging. Varying hydraulic potential produced an approximately linear variation in streaming potential, but the plot of these two variables had a different slope for each run.

Hydraulic conductivities found in runs in which the streaming potential is allowed to develop are about one-fifth those for runs in which streaming potential is short-circuited, so that streaming potential and the electroviscous effect modify significantly the hydraulic transport through shales.

Adding CaCl_2 in modest amounts to the NaCl solution has an appreciable effect. The Ca dominates electrokinetically over the Na. It appears that the potential difference at the downstream cake-brine interface is mainly responsible for salt filtration in the NaCl system, but that the upstream interface is equally important in the NaCl- CaCl_2 system.

Saxen's Law of nonequilibrium thermodynamics, which relates the magnitudes of current and fluid flows for impose fluid and electrical potentials, is

obeyed very closely by the experimental system smectite-1.087 m NaCl solution at room temperature. This conclusion was made possible by a new data analysis procedure that corrects for such effects as fluid compressibility and chemical osmotic transport.

RELIABILITY AND PERFORMANCE OF EXPERIMENTAL APPARATUS

The membrane presses have required a good deal of machine-shop and electronic-shop support for repair and minor modification. The amount of down time has not been excessive for such complex apparatus, but it has generally not been possible to sustain experiments of several months without interruption. Valving in the system has made it possible to preserve the clay cake and its immediately surrounding fluid environment during most interruptions, but perturbations of fluid composition in the input and stirring reservoirs have extended the time to reach steady state.

Specific difficulties have included leaks because of scoring of moving pistons, requiring polishing of these components, cracking of the high-purity alumina liner in the sample assembly when temperature was raised high enough to release the compressive stress placed upon the liner earlier by shrink fitting, and deterioration of Viton and ethylene polypropylene O-rings because of heat, abrasion, and possibly chemical attack. The advantages of Teflon O-rings in resisting temperature and chemical attack could not be utilized because this material is so stiff that it did not deform in response to changing pressure, and leaks resulted.

A certain amount of leakage can be tolerated, by increasing the fluid input rate to compensate. Mass balance calculations are made more difficult, but they are not very satisfactory anyway because of uncertainty about how much water is expelled from the clay cake during the final stages of compaction.

A MODEL FOR AQUEOUS ELECTROLYTE DIFFUSION

Current chemical models for mutual diffusion in aqueous electrolyte solutions derive from the classic work of Lars Onsager in the 1930's. Although his treatments of the electrophoretic and relaxation effects are impressive mathematical feats, the failure of Onsager-type models to predict diffusion coefficients at concentrations beyond about 0.05 molar suggests that the physical assumptions involved are inadequate or erroneous. The model proposed by D. L. Graf, D. E. Anderson and J. B. Woodhouse starts by unifying currently available descriptions of diffusion based upon nonequilibrium thermodynamics and transition-state theory. The residual error between the predictions of this combined theory and the values obtained by experimental measurement can be largely eliminated by introducing a negative exponential in concentration. Adjustment of the single variable parameter in the exponential gives diffusion-coefficient prediction for $\text{NaCl-H}_2\text{O}$, $\text{KCl-H}_2\text{O}$ and $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ within the experimental error of measurement, 0.1-0.2%. The maximum error of prediction for individual compositions within $\text{CaCl}_2\text{-H}_2\text{O}$, $\text{SrCl}_2\text{-H}_2\text{O}$, $\text{BaCl}_2\text{-H}_2\text{O}$, $\text{MgCl}_2\text{-H}_2\text{O}$ and $\text{MgSO}_4\text{-H}_2\text{O}$ is about 4%, a huge improvement over what was possible previously.

The experimentally-measured diffusion coefficients can be reproduced with errors comparable to those of the empirical fits by further postulating that individual ion-water molecule exchanges are coupled to yield hydrated neutral exchange complexes (the activated complexes), and producing the required negative exponents by calculating probabilities for specific complexes. Verification by other experimental methods of at least one of the hydrated neutral exchange complexes would be desirable, but it appears that not a great deal is known about the hydration state of such neutral species.

IMPORTANCE OF REVERSE CHEMICAL OSMOSIS IN NATURE

A number of workers in the decades following World War II have invoked reverse chemical osmosis to help explain subsurface brine compositions. Water moves upward across shales from the more saline brines below, overcoming the downward-directed chemical osmotic pressure differential. Doubts about this mechanism involve the existence in nature of adequately large upward-directed fluid pressure gradients, and the possibility that the observed brine compositions might more easily be explained by ion exchange and/or chemical reaction.

Donald L. Graf concluded that an unequivocal demonstration of the operation of reverse osmosis in nature probably requires that several parameters, e.g., Na^+ concentration, Ca^{2+} concentration, fluid pressure, and self-potential be shown to have the proper values to have resulted from the effects of a shale membrane superposed on the regional values of these quantities.

Calculations showed that overpressuring from the rapid deposition of fine-grained sediments was more than adequate to drive reverse chemical osmosis, but that from topographic relief was not. Occurrence of overpressuring in sedimentary sections older than Cretaceous indicate that post-depositional mechanisms such as tectonic compression and aquathermal pressuring must also operate.

In published discussion after the appearance of Graf's paper, it was pointed out that he had not considered the inefficiency of chemical osmosis, and that even topographic relief was adequate in many localities to drive reverse chemical osmosis.

MINERAL DEHYDRATIONS IN SEDIMENTARY ENVIRONMENTS

Calculations about the effect of shale membrane processes upon fluid pressure and brine composition distributions in subsurface sedimentary environments have to consider the water added to the system with time because of mineral dehydrations.

D. L. Graf and D. E. Anderson reviewed what was known about the dehydrations of gypsum, smectite, halloysite, vermiculite, and the zeolite minerals. Simple dehydrations such as those of gypsum and halloysite occur at sharply-defined temperatures and thus contribute a time-limited fluid pulse at a given point. The dehydrations of analcime and smectite proceed by reactions involving other sedimentary minerals. The smectite reaction proceeds by way of a succession of mixed-layered illite/smectites and may require several million years for completion at a given stratigraphic interval. The great variety of zeolite compositions and crystal structures makes it difficult to generalize about their behavior.

PUBLISHED PAPERS AND ORAL PRESENTATIONS

Because most of D. L. Graf's files are still in storage after moving from Illinois to Arizona, it has been necessary to give paraphrased titles for some of the talks listed below. These titles are shown in parentheses.

Oral Presentations

Graf, D. L., and Anderson, D. E., (Contributions from diffusion and membrane transport to subsurface water compositions): Invited paper, Joint Meeting of the International Geological Congress and the International Association of Scientific Hydrology, Paris, July, 1980.

Benzel, W. M., and Graf, D. L., (Experimental measurement of transport through clay layers at room temperature): Clay Minerals Society Meeting, Urbana, Illinois, October, 1981.

Graf, D. L., (Mechanisms in nature for generating high pore-fluid pressures to drive reverse osmosis in sedimentary environments): Symposium on "Shales and Subsurface Hydrology" (Y. K. Kharaka and D. L. Graf, co-convenors), Geological Society of America Annual Meeting, Cincinnati, Ohio, November, 1981.

Graf, D. L., (A model for predicting aqueous electrolyte diffusion coefficients): Schlumberger Research Laboratory, Ridgefield, Connecticut, February, 1982.

Graf, D. L., Benzel, W. M., and Haydon, P. R., Membrane properties of clay-rich rocks in diagenetic environments: Invited paper, Symposium on "Colloidal Properties of Clays" (P. Low, convenor), American Chemical Society Meeting, Las Vegas, Nevada, March 29-April 2, 1982.

Graf, D. L., and Haydon, P. R., (Osmotic phenomena in natural sedimentary environments): Geological Society of America, Pemrose Conference on "Hydrodynamics and Geochemistry of Ore Generation in Sedimentary Environments"

(D. E. White, W. C. Kelly, and J. Sharp, convenors), Lake of The Ozarks, Missouri, May 20-25, 1982.

Haydon, P. R., and Graf, D. L., (Ion filtration by smectite membranes, 20°-180° C): Fall Meeting, American Geophysical Union, San Francisco, December, 1982.

Demir, Ilham, and Graf, D. L., Electrokinetic phenomena in an experimental smectite-brine system: Clay Minerals Society Meeting, Buffalo, New York, October 2-5, 1983.

Demir, Ilham, and Graf, D. L., Verification of Saxen's Law for a smectite membrane compacted under simulated subsurface pressures: Abstract submitted for 1984 Spring Meeting of the American Geophysical Union, Cincinnati, Ohio.

Published Papers

Graf, D. L., and Anderson, D. E., Geochemical inputs for hydrologic models of deep-lying sedimentary units: loss of mineral hydration water: J. Hydrol., 54, 297-314, 1981.

Graf, D. L., Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines: Geochim. Cosmochim. Acta, 46, 1431-1448, 1982.

Graf, D. L., Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines (reply to a Comment by F. M. Phillips): Geochim. Cosmochim. Acta, 47, 1333, 1983.

Graf, D. L., Anderson, D. E., and Woodhouse, J. B., Ionic diffusion in naturally-occurring aqueous solutions: transition-state models that use either empirical expressions or statistically-derived relationships to predict mutual diffusion coefficients in the concentrated-solution regions of 8 binary systems: Geochim. Cosmochim. Acta, 47, 1985-1998, 1983.

Benzel, W. M., and Graf, D. L., Studies of smectite membrane behavior: importance of layer thickness and fabric in experiments at 20° C: Revised

manuscript to be returned shortly to Geochimica et Cosmochimica Acta for publication.

Manuscripts in Preparation

Haydon, P. R., and Graf, D. L., Studies of smectite membrane behavior: temperature dependence, 20°-180° C: Largely completed, to be submitted to Geochimica et Cosmochimica Acta.

Demir, Ilham, and Graf, D. L., Studies of smectite membrane behavior: electrokinetic processes at 20° C: Probably to be submitted to Geochimica et Cosmochimica Acta.

Graf, D. L., Bauerle, J. F., Benzel, W. M., Demir, I., Dodson, D. D., Fruth, L. S., and Haydon, P. R., Apparatus for measuring flows of water, dissolved ions and electric current across compacted clay cakes to 250° C. and 3 kb. compaction pressure: To be submitted to Review of Scientific Instruments.

Ph.D. Theses

Benzel, W., The effect of smectite layer thickness and fabric upon salt filtration at room temperature: Department of Geology, University of Illinois (Urbana-Champaign), May, 1982.

Haydon, P. R., Ion filtration and stable oxygen isotopic fractionation resulting from the passage of sodium calcium chloride brine through compacted smectite layers at elevated temperatures and pressures: Department of Geology, University of Illinois (Urbana-Champaign), February, 1983.

Demir, Ilham, (Electrokinetic phenomena in experimental clay-brine systems at 20° C.): Thesis defense expected in May, 1984, with Ph.D. degree to be awarded at October, 1984 graduation.

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