DOE/ID/12079--69

DE82 019922

A MODEL FOR THE CROSSCOUPLING
PARAMETERS OF ROCKS

by

W. R. Sill

June 1982

Department of Geology and Geophysics
University of Utah
Salt Lake City, Utah

Work performed under Department of Energy contract DE-AC07-80ID12079

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared to document work sponsored by the United States Government. Neither the United States nor its agent, the United States Department of Energy, nor any Federal employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NOTICE

Reference to a company or product name does not imply approval or recommendation of the product by the University of Utah or the U.S. Department of Energy to the exclusion of others that may be suitable.

CONTENTS

	<u>Page</u>
ABSTRACT.....	1
INTRODUCTION.....	2
MODEL.....	3
Pore Model.....	3
Bulk Electrolytic Conductivity.....	3
Surface and Total Conductivity.....	7
Permeability and Electrokinetic Coupling.....	9
Thermal Conductivity and Thermoelectric Coupling.....	12
TESTS OF MODEL.....	14
MODEL SUMMARY AND DISCUSSION.....	15
TABLES.....	18
APPENDIX A.....	21
REFERENCES.....	28
FIGURES.....	29

ABSTRACT

The self-potential method of geothermal exploration is based on the measurement of naturally occurring electrical potentials generated by flows of fluid (electrokinetic) and heat (thermoelectric) through rocks (Corwin and Hoover, 1979; Sill, 1981; Sill 1982).

The interpretation of self-potential measurements by modeling requires a knowledge of crosscoupling parameters of geological materials (Sill, 1982). In general there is a paucity of such data and one of the largest compilations of crosscoupling parameters consists of data on only 40 samples (Nourbehecht, 1963). Much more common are measurements of porosity, permeability and electrical conductivity.

In an effort to alleviate this problem, a model for estimating crosscoupling parameters has been developed. This model is based on theoretical considerations of crosscoupling in capillaries and on some experimental data. This model is useful as a guide to the modeler/interpreter in estimating the gross crosscoupling parameters. However, its usefulness could be greatly increased if it can be verified that it is capable of accurately predicting crosscoupling effects from more basic data on rocks.

Comparison of the model to existing experimental measurements of crosscoupling parameters is limited by the quality of the data and the lack of knowledge of other parameters crucial to the model. At its most basic level, the model requires a knowledge of the porosity, the mean pore size and the spread of pore sizes and the average surface potential at the silicate-pore water interface. In practice, combinations of measurements of electrical conductivity and permeability can be used to estimate these parameters.

INTRODUCTION

Numerous mixing laws can be used to describe the properties of heterogeneous systems (Madden, 1976). The analytic solutions that have been developed for the primary and secondary flows in capillaries (Appendix A) naturally lead to models that consider the fluid-filled portion of a rock as a network of interconnected capillaries (Mazur and Overbeek, 1951). An example of a somewhat more simple model is given by Ishido and Mizutani (1981). In this model the pore space is modeled by a bundle of non-interconnected capillaries which conduct in parallel. The capillary tubes can be assigned some mean size or a distribution of sizes can be considered with this type of model. Since the pores in a rock cannot be expected to be straight, some bending or twisting of the tubes is allowed and the ratio of the tube length to the external length is incorporated into a tortuosity coefficient. The tortuosity is ultimately combined with the porosity into the formation factor. This type of model sometimes provides a useful description of rock parameters as in the case of electrical conductivity when bulk electrolytic conduction dominates. Such a model is much less useful for fluid flow as it usually overestimates the permeability by many orders of magnitude at the lower range of porosity.

Madden (1976) presents another approach to the modeling of heterogeneous mixtures by using embedded pseudorandom networks. He notes that some of the inefficiencies in rock conduction are due to the fact that wide and narrow conduction paths are to be expected in series with each other as well as in parallel. In his embedded network models, the average network conductance tends toward the geometric mean which is a compromise between series and parallel combinations. The model development that follows utilizes this

strategy (geometric mean) of series-parallel combinations along with a simple capillary model on the small scale.

MODEL

Pore Model

Consider (Figure 1) a small but representative volume of rock sliced into N sections. In each section there are M pores of radii a_1 - a_M in the area A and assume that A is large enough that the pore size distribution is represented in each of the N sections. Ordering the pores in each of the N sections according to size we get the pore element distribution shown in the bottom of Figure 1. If we reconstruct the pore structure by connecting the same pore sizes together, that is running across the rows, we will get an array of M parallel tubes each of a given radius. This will provide the most efficient reconstruction of the pore space. On the other hand we can go through the $N \times M$ elements making N random selections and connecting these in series. This will result in M tubes with N random variations in the radius along their lengths. As long as $N \gg M$ all the pore sizes will be adequately represented in each of these tubes. The variation of tube radius along the length will result in a much less efficient reconstruction of the pore space.

The conductivity of each of these rearrangements can be calculated given the probability distribution $P(a)$ of the pore radius a . The first arrangement of the pores of equal radii will be referred to as the parallel combination and the second arrangement of random pore radii as the series combination.

Bulk Electrolytic Conductivity

The electrical current (I_i) in each tube of the parallel arrangement due

to the bulk electrolyte conductivity (σ_w) is (equation A-8)

$$I_i = -\sigma_w \pi a_i^2 \frac{\Delta V}{Nl}, \quad (1)$$

where ΔV is the voltage change along the tube of length Nl . These currents add in parallel so that the total current (I_T) is

$$I_T = -\sigma_w \pi \left(\sum a_i^2 \right) \frac{\Delta V}{Nl}. \quad (2)$$

The expected value (denoted by $\langle \rangle$) of I_T for the probability distribution $P(a_i)$ of the pore radii is

$$\langle I_T \rangle = -\sum P(a_i) \left[\sigma_w \pi \left(\sum a_i^2 \right) \frac{\Delta V}{Nl} \right] \quad (3)$$

$$= -\sigma_w M \pi \langle a^2 \rangle \frac{\Delta V}{Nl}. \quad (4)$$

For the series arrangement the voltage increments, due to the constant current I in a tube, add so that

$$-\Delta V = \sum \Delta V_i = \frac{Il}{\sigma_w \pi} \sum \frac{1}{a_i^2}. \quad (5)$$

The expected value of the voltage drop along a tube is

$$-\langle \Delta V \rangle = \sum P(a_i) \left[\frac{Il}{\sigma_w \pi} \sum a_i^{-2} \right], \quad (6)$$

$$= \frac{Il}{\sigma_w \pi} N \langle a^{-2} \rangle, \quad (7)$$

and the current is

$$I = -\sigma_w \frac{\pi}{\langle a^{-2} \rangle} \frac{\langle \Delta V \rangle}{Nl}. \quad (8)$$

Since there are M tubes of this type in parallel the total current is

$$I_T = -\sigma_w \frac{M\pi}{\langle a^{-2} \rangle} \frac{\langle \Delta V \rangle}{Nl}. \quad (9)$$

From equations (4) and (9) the effective parallel (σ_1) and series (σ_2) conductivities are

$$\sigma_1 = \sigma_w M \pi \langle a^2 \rangle / A , \quad (10)$$

and

$$\sigma_2 = \sigma_w M \pi / \langle a^{-2} \rangle A . \quad (11)$$

The porosity is

$$\phi = \langle \phi \rangle = \frac{M}{A} \pi \langle a^2 \rangle . \quad (12)$$

Using this expression for the porosity the conductivities are

$$\sigma_1 = \sigma_w \phi , \quad (13)$$

and

$$\sigma_2 = \sigma_w \phi / \langle a^2 \rangle \langle a^{-2} \rangle . \quad (14)$$

Equation 13 shows the familiar form for straight conduction paths and equation 14 shows how the series conductivity depends on the moments of the distribution function. The distribution function for crack widths in some rocks is approximately lognormal (Madden, 1976 and Brace, 1977). Pore shapes in rocks can be roughly categorized as tube-like when the cross section is more or less equidimensional and crack-like when one dimension is much larger than the other. In what follows, a tube-like model will be used with a lognormal distribution for the radius. Crack-like models can also be used but when the conductivities are expressed in terms of the porosity, only minor differences result.

The moments $\langle a^n \rangle$ for the lognormal distribution $P(a)$ are given by the moment generating function (Hamilton, 1964) of the normal distribution $P(x)$ where $x = \ln a$. The moments are

$$\langle a^n \rangle = \int_0^{\infty} a^n P(a) da = \exp(nm_x + n^2 s_x^2 / 2) , \quad (15)$$

where m_x and s_x^2 are the mean and variance of the normal distribution of x .

The mean and variance of a are given by

$$m_a = \langle a \rangle = \exp(m_x + s_x^2 / 2) \quad (16)$$

and

$$s_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = m_a^2 (\exp s_x^2 - 1) . \quad (17)$$

For the lognormal distribution the series conductivity (equation (15)) is then

$$\sigma_2 = \sigma_w \phi \exp(-4s_x^2) = \frac{\sigma_1}{(1 + s_a^2 / m_a^2)^4} . \quad (18)$$

This shows how the series conductivity is reduced relative to the parallel conductivity as the spread of the pore size distribution increases. Since the parallel arrangement of the pore space represents the most efficient recombination, we might expect that typical rocks would be between these limits. Madden (1976) notes that the geometric mean (gm) gives a compromise between series and parallel combinations. Taking the geometric mean of equations (14) and (15) with equal probabilities for the parallel and series combinations we get

$$\sigma_{gm} = \sigma_1^{1/2} \sigma_2^{1/2} = \sqrt{\sigma_1 \sigma_2} , \quad (19)$$

and making use of the lognormal distribution this is

$$\sigma_{gm} = \sigma_w \phi \exp(-2s_x^2) = \frac{\sigma_w \phi}{(1 + s_a^2/m_a^2)^2} \quad (20)$$

For the lognormal distribution it can be shown that equation (20) is the same as the geometric mean of the NxM conductivity elements of Figure 1. In this case the scale at which the geometric mean averaging takes place does not change the final result.

From equation (20) the ratio σ_{gm}/σ_w gives the inverse of the electrical formation factor (F_e). According to Archie's Law this can be expressed as

$$F_e^{-1} = \phi^m = \phi \exp(-2s_x^2) \quad , \quad (21)$$

where the exponent m is usually in the range from 1.5 to 2.0, with the higher values usually associated with tighter rocks. If we let m vary from 1.5 at $\phi = .5$ to 2.0 at $\phi = 0$, we find from equation (21) that s_x ranges from about .4 at $\phi = .5$ to about 1.5 at $\phi = .01$. Brace (1977) shows plots of the crack width probability distributions for two rocks with porosities of a few percent. These plots also show that s_x is close to 1.5 in agreement with the results from equation (21).

Surface and Total Electrical Conductivity

The surface conduction term σ_s (equations (A-8) and (A-10)) is proportional to the capillary radius a. Utilizing the parallel-series combinations and the geometric mean the surface conductivity σ_s is

$$\sigma_s' = \frac{2\sigma^*\phi}{\langle a^2 \rangle} \left[\frac{\langle a \rangle}{\langle a^{-1} \rangle} \right]^{1/2} \quad , \quad (22)$$

where σ^* is the surface conductance (see Appendix A). For the lognormal distribution this is

$$\sigma_s' = \frac{2\sigma^*\phi}{\exp(m_x + 2s_x^2)} = F_e^{-1} \sigma_s \quad , \quad (23)$$

where the equivalent surface conductivity is given by $\sigma_s = 2\sigma^*/\exp(m_x)$.

Taking the sum of the geometric mean conductivities of equations (20) and (23) gives the following expression for the total conductivity:

$$\sigma = F_e^{-1}(\sigma_w + \sigma_s) , \quad (24)$$

which is a modified form of Archie's Law and is the same as the model used by Waxman and Smits (1968). This form is derived by summing the conductivities after averaging and this implies that the surface and bulk conductivity mechanisms are separate or independent. No interactions between the two processes are permitted since the continuity of each of the currents was required, separately. The assumption of no interactions between the two current flow systems is rather restrictive. Interactions are permitted if we sum the effects of surface and bulk conductivity at the element level, then the parallel (σ_1) and series (σ_2) conductivities are

$$\sigma_1 = \phi(\sigma_w + \frac{2\sigma^*\langle a \rangle}{\langle a^2 \rangle}) , \quad (25)$$

and

$$\sigma_2 = \frac{\phi}{\langle a^2 \rangle} \left\langle \frac{1}{(\sigma_w a^2 + 2\sigma^* a)} \right\rangle . \quad (26)$$

The geometric mean of these conductivities can then be used as the average total conductivity. Unfortunately, the expected value operation on the inverse of the sum of the bulk and surface conductivity in equation (26) does not have a simple form in terms of the moments of a . In the limits where σ_w is much greater or less than σ_s , relatively simple expressions result:

$$\sigma \approx F_e^{-1}(\sigma_w + \frac{\sigma_s}{2} \exp(2.5 s_x^2)); \quad \sigma_w > \sigma_s \quad (27)$$

$$\sigma \approx F_e^{-1}(\frac{\sigma_w}{2} \exp(1.5 s_x^2) + \sigma_s); \quad \sigma_s > \sigma_w \quad (28)$$

These equations as well as the geometric mean of equations (25) and (26) give a conductivity which is larger than that given by equation (24). Permitting interactions between the two conduction mechanisms makes for a more efficient conduction process.

Permeability and Electrokinetic Coupling

For pressure problems the coupled equations are

$$v = -\kappa \nabla P, \quad (29)$$

$$J_T = -L_p \nabla P - \sigma \nabla V, \quad (30)$$

where v is the fluid velocity, κ is the permeability, P is the pressure, J_T is the total electrical current, L_p is the pressure crosscoupling conductivity, σ is the total conductivity and V is the electrical potential.

The fluid flow in a capillary (equation (A-6)) can be used to derive the geometric mean permeability (κ) which is

$$\kappa = \frac{\phi}{8\eta \langle a^2 \rangle} \left[\frac{\langle a^4 \rangle}{\langle a^{-4} \rangle} \right]^{1/2} \quad (31)$$

where η is the viscosity.

For the lognormal distribution this is

$$\kappa = \frac{F e^{-1}}{8\eta} \exp(2m_x) = \frac{m^2}{8\eta} \phi^{\frac{(3m-1)}{2}} \quad (32)$$

Brace (1977) and Brace et al. (1968) found that the measured permeability on some rocks showed an approximate ϕ^3 dependence. Equation (32) with $m=2$ would give a $\phi^{2.5}$ dependence which is reasonably close to their results. A slightly different weighting in the geometric mean might be used to get a better agreement but such tinkering at this point is probably not warranted.

The drag current, I_d , (equation (A-7)) can be used to derive expressions for the parallel and series recombinations. The formulation for the parallel arrangement is analogous to that for the current flow in equations (1) to (4). The result for the parallel arrangement is

$$\langle I_d \rangle = \frac{\zeta \epsilon}{\eta} \pi M \langle a^2 \rangle \frac{\Delta P}{Nl}, \quad (33)$$

where ζ is the zeta potential and ϵ is the dielectric permittivity of water. For the series arrangement we start with the drag current in any element expressed in terms of the flow F ,

$$I_d = \frac{-\zeta \epsilon}{\eta} \frac{8F}{a^2}. \quad (34)$$

The flow problem requires that F is a constant down the tube and since a varies in the series arrangement then I_d varies. In order to have a continuity of current, voltage gradients must exist in each element such that the total current (I) is constant,

$$I = \frac{-\zeta \epsilon}{\eta} \frac{8F}{a_i^2} - \pi a_i^2 \sigma \frac{\Delta V}{l}, \quad (35)$$

where σ is, in general, the sum of the surface and bulk conductivities. For the case of interest here, the expected value of the sum of the voltage drops in the elements is zero so that there is no macroscopic voltage developed.

That is

$$\langle \Delta V \rangle = \langle \sum \Delta V \rangle = 0,$$

or

$$I \left\langle \frac{1}{\sigma a^2} \right\rangle + \zeta \epsilon 8F \left\langle \frac{1}{\sigma a^4} \right\rangle = 0. \quad (36)$$

For the sake of simplicity the limiting cases of $\sigma_w > \sigma_s$ and $\sigma_s > \sigma_w$ will be treated separately. When the bulk water conductivity dominates, we have for the current in a series tube

$$I = -\zeta \epsilon 8F \frac{\langle a^{-4} \rangle}{\langle a^{-2} \rangle} . \quad (37)$$

Changing from the flux back to the pressure gradient and summing over the M tubes gives

$$I = \frac{\zeta \epsilon}{\eta} \frac{\pi M}{\langle a^{-2} \rangle} \frac{\langle \Delta P \rangle}{Nl} . \quad (38)$$

Taking the geometric mean of equations (33) and (38) we find that the pressure crosscoupling conductivity is

$$L_p = \frac{-\zeta \epsilon}{\eta} \frac{\phi}{[\langle a^2 \rangle \langle a^{-2} \rangle]^{1/2}} ; \quad \sigma_w > \sigma_s . \quad (39)$$

When the surface conductivity dominates, the averaging results in

$$L_p = \frac{-\zeta \epsilon}{\eta} \phi \left[\frac{\langle a^{-3} \rangle}{\langle a^{-1} \rangle \langle a^{-4} \rangle \langle a^2 \rangle} \right]^{1/2} ; \quad \sigma_s > \sigma_w . \quad (40)$$

Using the lognormal distribution to obtain the moments gives these limiting cases as

$$L_p = \frac{-\zeta \epsilon}{\eta} F e^{-1} ; \quad \sigma_w \alpha > \sigma_s , \quad (41)$$

and

$$L_p = \frac{-\zeta \epsilon}{\eta} \frac{F e^{-1}}{\exp(s_x^2)} ; \quad \sigma_s > \sigma_w . \quad (42)$$

The voltage crosscoupling coefficient or streaming potential, defined as the voltage to pressure ratio at zero total current (equation (30)), is

$$C_p = L_p / \sigma = \frac{\zeta \epsilon}{\eta \sigma_w} ; \quad \sigma_w > \sigma_s , \quad (43)$$

or

$$C_p = \frac{\zeta \epsilon}{n \sigma_s \exp(s_x^2)} ; \quad \sigma_s > \sigma_w . \quad (44)$$

For a given water conductivity, rocks with larger pores will have $\sigma_w > \sigma_s$ and C_p will tend toward its maximum value. In this limit it is independent of the porosity and the pore size distribution. As the pore size decreases, $\sigma_s > \sigma_w$ and C_p will decrease and it is dependent on the pore size distribution in this limit. These effects help to explain the rough correlation between streaming potential and permeability. That is, higher permeability is associated with larger pores (equation (32)), a smaller contribution from surface conduction (equation (23)), and therefore a larger streaming potential.

Thermal Conductivity and Thermoelectric Coupling

The heat flow and coupled current flow equations are given as

$$q = -\sigma_T \nabla T , \quad (45)$$

and

$$J = -L_T \nabla T - \sigma \nabla V , \quad (46)$$

where q is the heat flux, σ_T is the thermal conductivity, T is the temperature and L_T is the thermoelectric crosscoupling conductivity.

Unlike the cases of fluid flow or electric current flow, where only the geometry of the silicate matrix influences the flow, heat flow is strongly influenced by the thermal properties of the silicates. In fact the silicates typically have larger thermal conductivity than the pore water. However the thermal conductivity of a rock (σ_T) can still be expressed as a geometric mean,

$$\sigma_T = (\sigma_{TW})^\phi (\sigma_{TM})^{(1-\phi)}, \quad (47)$$

where σ_{TW} is the thermal conductivity of water, σ_{TM} is the thermal conductivity of the silicate matrix and ϕ is the porosity. The weighting in this geometric mean is the volume fraction of the phase.

The development of the thermoelectric crosscoupling is based on equation (A-29) and follows a course analogous to the development in equations (33) to (38) for electrokinetic crosscoupling. For the limiting cases the crosscoupling conductivities are

$$L_T = 2\sigma^* \alpha \beta \left(\frac{k}{e}\right) \phi \left[\frac{\langle a \rangle \langle a^{-1} \rangle}{\langle a^2 \rangle \langle a^{-2} \rangle} \right]^{1/2}; \quad \sigma_W \gg \sigma_S, \quad (48)$$

and

$$L_T = 2\sigma^* \alpha \beta \left(\frac{k}{e}\right) \phi \left[\frac{\langle a \rangle}{\langle a^2 \rangle \langle a^{-1} \rangle} \right]^{1/2}; \quad \sigma_S \gg \sigma_W, \quad (49)$$

where the terms α , β and k/e are defined in Appendix A and the product $\alpha \beta k/e$ has a value of the order of $1 \text{ mV}/^\circ\text{C}$ for typical geological materials at room temperature. For the lognormal distribution these coefficients are

$$L_T = \sigma_S \alpha \beta \left(\frac{k}{e}\right) \text{Fe}^{-1} \exp(-s_x^2/2); \quad \sigma_W \gg \sigma_S, \quad (50)$$

$$L_T = \sigma_S \alpha \beta \left(\frac{k}{e}\right) \text{Fe}^{-1}; \quad \sigma_S \gg \sigma_W. \quad (51)$$

The corresponding voltage crosscoupling coefficients, defined as the voltage to temperature ratios at zero total current (equation (46)) are

$$C_T = \frac{\sigma_S \alpha \beta \left(\frac{k}{e}\right)}{\sigma_W \exp(s_x^2/2)}; \quad \sigma_W \gg \sigma_S, \quad (52)$$

$$C_T = \alpha \beta \left(\frac{k}{e}\right); \quad \sigma_S \gg \sigma_W. \quad (53)$$

In rocks with small pores where $\sigma_s > \sigma_w$, C_T reaches a maximum and it is independent of the pore size distribution. For rocks with larger pores where $\sigma_w > \sigma_s$, C_T decreases and it is proportional to the ratio of σ_s to σ_w . Thus we might expect to find larger thermoelectric effects in less porous and permeable rocks.

TESTS OF MODEL

Direct comparisons of measured and calculated crosscoupling coefficients cannot be made at the present time, since data consisting of independent measurements of some of the parameters are lacking. Estimates of some parameters can be made from part of the available data and these can be examined in terms of their reasonableness. Table 1 shows some of the better data available from Green (1963) and Nourbehecht (1963). Sample Y-7 is an example where bulk conductivity dominates and S-10 is an example of surface conduction dominating. In these cases the appropriate limiting form of the model equations was used to estimate the various parameters in Table 2. The conductivity measurements are used to estimate the formation factor and the surface conduction. The formation factor and the measured permeability can then be used to estimate the mean of the pore distribution. If the porosity was known the standard deviation of the distribution could also be estimated, otherwise it has to be guessed. This information is used along with the appropriate coupling equation to estimate the zeta and surface potentials. The values in Table 2 all seem reasonable except for the thermal coupling factor $\beta(k/e)$ for sample Y-7. Until better data on crosscoupling measurements becomes available this is about the best that can be done.

Although the original motivation for the model development did not include deriving a model for primary coupling conductivities, it turns out

that some available data (Wyllie and Spangler, 1952) are particularly suitable for testing the permeability equation (32). These data (Table 3) consist of measurements of the permeability, porosity, formation factor and the surface area to volume ratio (S_v) of the pores. If we assume a lognormal distribution, the measured values of S_v can be converted to $\exp(\mu)$ values, given the measured values of the formation factor and porosity. Table 3 gives a comparison of the calculated (κ_c ; equation (32) with $\kappa_c = \eta\kappa$) and measured permeabilities (κ_m). The average error from using equation (32) is about 25 percent. These comparisons are for reasonably large permeabilities characteristic of sediments and, at the other extreme, the data in Brace (1977) on granites permit comparisons in the nanodarcy range. The data on Westerly Granite when used in equation (32) give a permeability which is within an order of magnitude of the observed. The fact that equation (32) describes the permeability reasonable well over 7 orders of magnitude seems like a fair test of the model.

As an example of the use of the model to predict, at least in a gross fashion, the crosscoupling parameters, we can make use of the resistivity and permeability data on Westerly Granite (Brace 1977 and Brace et al., 1965) shown in Table 4. The estimated parameters are given in Table 5. The surface and zeta potentials are modest and the latter gives rise to a fairly sizeable streaming potential. The thermoelectric coefficient will be quite small, given any reasonable value for $\beta(k/e)$. A typical value for this factor would be on the order of $1\text{mV}/^\circ\text{C}$.

MODEL SUMMARY AND DISCUSSION

In the development of the model, pores with circular cross sections were used but other pore shapes can be utilized. Other shapes for the pore cross

sections usually result in models with only minor differences in the derived parameters. The lognormal distribution, which seems to be a reasonable description of the pore apertures, was used to describe the distribution of the pore radii. This distribution is convenient, since relatively simple expressions result for the various moments. Even so, some expressions, such as equation (26), cannot be put in a simple form in terms of the moments. However, relatively simple expressions can be derived for certain limiting cases and with given values for various parameters the numerical evaluation of specific cases should present no great problem.

The fundamental parameters of the model are the mean and the standard deviation of the pore distribution, the surface and zeta potentials, and the pore water conductivity. The model development also assumed that the surface or zeta potential was the same in all the pores of the distribution. Under a given set of conditions the surface potentials of various silicates vary, but not over a wide range (Ishido and Mizutani, 1981), so this assumption is not very critical. In situ conditions can exert a strong influence, since the surface and zeta potentials are strong functions of pH and temperature (Ishido and Mizutani, 1981). The salinity of the pore water has a strong influence on the zeta potential through its effect on the Debye length while the surface potential is relatively insensitive to pore water concentration.

The model has also been based on the surface effects generated in the double layer developed at typical silicate-water interfaces. Clays, with their high concentrations of exchangeable cations and larger surface potentials and charges, present another special case. If the distribution of clays is uniform over the surfaces of the pores, then the model development is exactly the same as for the "normal" surface effects in the previous

section. The distribution of clays in some shaly sands is discussed by Waxman and Smits (1968). In some cases they found that clay surrounds grains (uniform?) and in other cases there is also interstitial clay. For the case where the interstitial clay content is proportional to the local pore volume, the clay contribution to the conductivity would be subject to the same averaging as the bulk conductivity. In this case the total conductivity is in the same form as equation (24) with σ_s replaced by the equivalent clay conductivity σ_c . The equivalent clay conductivity can be expressed in terms of the mobility and concentration of the exchange ions in the pore volume. This form is the same as the model used by Waxman and Smits (1968). In terms of this development, the Waxman-Smits result requires the distribution of interstitial clay proportional to the pore volume or a constant pore volume concentration. If the clay distribution is in the form of a constant pore surface concentration, then equations (27) and (28) would be more appropriate. Since the Waxman-Smits model seems to work for a wide variety of shaly sands, the constant volume distribution of clay may be the more typical case.

TABLE 1

Measured Parameters on Two Rock Samples
(Y-7 Sedimentary; S-10 Dakota Sandstone)

Sample	σ_w (s/m)	σ_r (s/m)	κ (m ²)	Cp(mv/atm)	C _T (mV/°C)
Y-7	2.2-02	3.0-03	1.8-12	26.8	.48
Y-7	1.1-01	1.7-03	1.7-12	13.5	-
S-10	2.2-02	2.7-03	2.3-15	5.6	.24
S-10	1.1-01	7.0-03	2.9-15	11.3(?)	-

TABLE 2

Estimated Parameters for the Samples of Table 1 ($\sigma_w = .022$)

Sample	exp[mx](m)	Fe σ_s (s/m)	σ^* (s)	ζ (mv)	ψ_0 (mv)	β (k/e)
Y-7	1.6-05	7 2.0-05	2.0-11	12	17	>100(?)
S-10	1.0-06	157 3.6-01	2.0-07	110	370	.24

TABLE 3

Comparison Between Calculated (κ_c) and Measured (κ_m) Permeability.

Sample	ϕ	Fe	So(m^{-1})	exp[mx](m)	κ_c (md) ^(a)	κ_m (md)
0	.22	13	5.1+04	5.-06	240	340
151	.16	20	3.9-04	4.-06	100	122
154	.18	14	4.4+04	5.-06	200	267
220	.20	14	3.8+04	6.-06	323	336
250	.21	13	4.2-04	6.-06	332	516
252	.19	17	3.6+04	5.-06	210	296
228	.20	18	4.0+04	5.-06	173	278

(a) 1md = $10^{-15} m^2$

TABLE 4

Data on Westerly Granite

σ_w (s/m)	σ_r (s/m)	Fe	κ (m ²)
2.2-02	1.1-05	16,300	2.0-21

TABLE 5

Estimated Parameters for Westerly Granite

σ (s/m)	$\exp(m_x)$ (m)	sx	σ^* (s)	ψ_0 (mv)	ζ (mv)	Cp(mv/atm)	C_T
1.0-03(a)	2.0-08(b)	1.6(c)	1.0-11(d)	16(e)	13(f)	30(g)	$1.03\beta(\frac{k}{e})$ (h)
	a - eq. (27)		e - eq. (A-10)				
	b - eq. (32)		f - eq. (A-1, $\delta = 2 \times 10^{-9} \text{m}$)				
	c - eq. (21)		g - eq. (43)				
	d - eq. (23)		h - eq. (52)				

APPENDIX A

Crosscoupling in a Capillary

Crosscoupling effects in a capillary provide a simple physical model for understanding the crosscoupling parameters in rocks. At the most fundamental level the crosscoupling effects in capillaries depend on distribution of ions in the diffuse layer. The distribution of ions in turn is determined by the potential. The potential $\psi(x)$ in the diffuse layer near a plane surface is

$$\frac{ze\psi(x)}{2kT} = \ln \left[\frac{1 + A \exp(-\kappa x)}{1 - A \exp(-\kappa x)} \right] \quad A-1$$

where κ is the inverse of the Debye length,

$$\kappa = \left[\frac{2 n_0 z^2 e^2}{\epsilon kT} \right]^{1/2}$$

$$A = \frac{\exp(ze \psi_0 / 2kT) - 1}{\exp(ze \psi_0 / 2kT) + 1}$$

$\psi_0 = \psi(x=0)$, the potential at the surface,

n_0 = concentration in the bulk electrolyte ($\#/m^3$),

z = ion valence = $z_+ = z_-$,

e = electronic charge,

k = Boltzmann's constant,

and T = absolute temperature.

The distribution of ions is given by

$$n_{\pm}(x) = n_0 \exp(\pm ze \psi_0(x) / kT) \quad A-2$$

and the charge density is

$$\rho(x) = ze n_0 [\exp(ze \psi / kT) - \exp(-ze \psi / kT)] . \quad A-3$$

The total charge per unit area in the diffuse layer is equal to the negative of the surface charge q^* , where

$$q^*(\text{coulomb/m}^2) = \int \rho(x) dx = [8n_0 \epsilon kT]^{1/2} \sinh \frac{ze\psi_0}{2kT} . \quad A-4$$

Under the more typical geological conditions ψ_0 and q^* are negative and the diffuse charge (ρ) is positive.

For laminar flow in a circular capillary of radius a , subject to a pressure gradient ∇P , the velocity is

$$v = \frac{\nabla P}{4\eta} (s^2 - r^2) , \quad A-5$$

where $s = a - \delta_x$

η = viscosity,

and δ_x is the distance from the wall of the capillary where the velocity goes to zero. For water flow in a capillary δ_x may be of the order of a few nanometers (Ishido and Mizutani, 1981). The flow, integrated over the area is

$$F(\text{m}^3/\text{s}) = - \frac{\pi a^4}{8\eta} \nabla P , \quad A-6$$

when $a \gg \delta_x$.

The drag current due to the flow is obtained by integrating the product of the velocity (equation (A-5)) and the charge density (equation (A-3)) over the area, and when $a \gg \kappa^{-1}$ the current is

$$I_d(\text{amp}) = + \pi a^2 \frac{\zeta \epsilon}{\eta} \nabla P , \quad A-7$$

where $\zeta = \psi(\delta_x)$ is the so-called zeta potential which is the value of the diffuse layer potential at the point where the velocity falls to zero.

Current flow due to an electric field ($-\nabla V$) along the axis of the capillary is

$$I_e \text{ (amp)} = -\pi a^2 (\sigma_w + \sigma_s) \nabla V . \quad A-8$$

The first term results from the ordinary conductivity of the bulk solution,

$$\sigma_w = 2 n_0 zeU , \quad A-9$$

where U is the mobility of the bulk ions. The second term results from surface conduction effects in the diffuse layer, and it is given by

$$\sigma_s = 2 \sigma^*/a = \frac{2U^*}{a} \left[\frac{4zen_0}{\kappa} \left(\cosh \frac{ze\psi_0}{2kT} - 1 \right) \right] , \quad A-10$$

where σ^* is the surface conductance (Ω^{-1}) and U^* is the mobility of diffuse layer ions. σ^* is determined by an integration of the excess concentration in the double layer and can be related to the surface charge density through equation (A-4), so that equation (A-10) can be rewritten as

$$\sigma_s = U^* \frac{2q^*}{a} \left[\frac{\cosh \frac{ze\psi_0}{2kT} - 1}{\sinh \frac{ze\psi_0}{2kT}} \right] . \quad A-11$$

For large surface potentials,

$$\left| \frac{ze\psi_0}{2kT} \right| \gg 1 ,$$

and

$$\sigma_s = \frac{2|q^*|}{a} U^* , \quad A-12$$

and for small potentials,

$$\left| \frac{ze\psi_0}{2kT} \right| \ll 1 ,$$

and

$$\sigma_s = \frac{2|q^*|}{a} U^* \left| \frac{ze\psi_0}{2kT} \right| . \quad A-13$$

The total current density, from equations (A-7) and (A-8) is

$$J(\text{amp}/\text{m}^2) = \frac{+\zeta\epsilon}{\eta} \nabla p - (\sigma_w + \sigma_s) \nabla V . \quad \text{A-14}$$

When the current goes to zero, the largest potential will be generated and the ratio of the voltage to pressure gradient is the streaming potential coefficient

$$-\left(\frac{\nabla V}{\nabla p}\right)_{J=0} = - \frac{\zeta\epsilon}{\eta(\sigma_w + \sigma_s)} . \quad \text{A-15}$$

For a given zeta potential, the streaming potential coefficient reaches a maximum for larger diameter capillaries where $\sigma_w \gg \sigma_s$.

Thermally induced current flow can be treated as a rate-process in a manner similar to diffusion (Bockris and Reddy, 1970). As a rate-process the flux of charge is

$$J_T = \rho_1 v_1 - \rho_2 v_2 , \quad \text{A-16}$$

where the average charge in the capillary is

$$\rho = - \frac{2}{a} q^* , \quad \text{A-17}$$

and the transport velocities are

$$v_1 = l \frac{kT_1}{h} \exp \frac{-\Delta G}{kT} , \quad \text{A-18}$$

$$v_2 = l \frac{kT_2}{h} \exp \frac{-\Delta G}{kT} , \quad \text{A-19}$$

where l = mean free path,

h = Planck's constant,

and ΔG = activation energy.

The changes in temperature, density and velocity are

$$T_2 = T_1 + l \nabla T \quad \text{A-20}$$

$$\rho_2 = \rho_1 + 1 \frac{\partial \rho}{\partial T} \nabla T \quad A-21$$

and

$$v_2 = v_1 + 1 \frac{\partial v}{\partial T} \nabla T . \quad A-22$$

Introducing the diffusion coefficient defined as

$$D = 1^2 \frac{kT}{h} \exp(-\Delta G/kT) , \quad A-23$$

the current is then

$$J_T = -D \left(\frac{\partial \rho}{\partial T} + \frac{\rho}{D} \frac{\partial D}{\partial T} \right) \nabla T . \quad A-24a$$

A slightly more convenient form results from the use of the relation between the mobility and the diffusion constant $D = kTU^*/e$.

$$J_T = -\rho U^* \left[\frac{1}{\rho} \frac{\partial \rho}{\partial T} + \left(1 + \frac{1}{U^*} \frac{\partial U^*}{\partial T} \right) \right] \nabla \left(\frac{kT}{e} \right) \quad A-24b$$

The term ρU^* is recognized as a conductivity and is related to the surface charge density and surface conductivity by

$$\rho U^* = - \frac{2q^* U^*}{a} = -\sigma_s \alpha , \quad A-25$$

$$\text{where } \alpha = \sinh \frac{ze\psi_0}{2kT} / \left(\cosh \frac{ze\psi_0}{2kT} - 1 \right) .$$

The driving force is just the gradient of the temperature expressed in electron volts (kT/e). The terms in the brackets express the effects due to the change in charge density with temperature and the effects due to the change in diffusion constant or mobility with temperature. From equations (A-17) and (A-4) we have

$$\frac{1}{\rho} \frac{\partial \rho}{\partial T} = \frac{1}{q^*} \frac{\partial q^*}{\partial T} = \gamma , \quad A-26$$

$$\text{where } \gamma = \left[\frac{1}{2T} + \frac{ze\psi_0}{2kT} \left(\frac{1}{\psi_0} \frac{\partial \psi_0}{\partial T} - \frac{1}{T} \right) \operatorname{ctnh} \frac{ze\psi_0}{2kT} \right] \quad \text{A-27}$$

Based on the adsorption/desorption of protons, Ishido and Mizutani (1981) show that $\partial \psi_0 / \partial T$ is about $-0.75 \text{ mv}/^\circ\text{C}$ in the range from 20°C to 100°C . Using this value and $\psi_0 = -200 \text{ mv}$ we find that γT is of the order of unity at 300°K . The temperature-dependent mobility term in equation (A-24) can be found with the aid of equation (A-23) to be

$$1 + \frac{T}{U^*} \frac{\partial U^*}{\partial T} = 1 + \frac{\Delta G}{kT} - \frac{\partial \Delta G}{\partial kT} \quad \text{A-28}$$

Experimental data on the mobility of exchange ions (Waxman and Thomas, 1974) show that $\Delta G/kT$ is around 5 to 10 and $-\partial \Delta G / \partial kT$ is in the range from 10 to 50 for temperatures in the range from 25°C to 50°C . These terms decrease in value as the temperature increases. Equation (A-24) can be rewritten as

$$J_T = \sigma_s \alpha \beta \nabla \left(\frac{kT}{e} \right) \quad \text{A-29}$$

where

$$\beta = \gamma T + 1 + \frac{\Delta G}{kT} - \frac{\partial \Delta G}{\partial kT} \quad \text{A-30}$$

From the above discussion we see that β is in the range from 10 to 60 near room temperature. Combining the thermal and electric flows the total current is

$$J = \sigma_s \alpha \beta \nabla \left(\frac{kT}{e} \right) - (\sigma_w + \sigma_s) \nabla V \quad \text{A-31}$$

When $J = 0$, the ratio of the potential and thermal gradients gives the thermoelectric potential,

$$\left(\frac{\nabla V}{\nabla T} \right)_{J=0} = \frac{k}{e} \frac{\sigma_s \alpha \beta}{(\sigma_w + \sigma_s)} \quad \text{A-32}$$

In the limit of large surface potentials and small radius, $\sigma_S \gg \sigma_W$ and $|\alpha| \rightarrow 1$ so that the thermoelectric coefficient is determined by $\beta k/e$, which has a probable value of a few mv/°c. Thermoelectric effects in larger capillaries, where $\sigma_W > \sigma_S$, will be smaller.

References

- Bockris, J. O'M., and Reddy, A. K. N., 1970, Modern Electrochemistry: Plenum Press, New York.
- Brace, W. F., Orange, A. S., and Madden, T. R., 1965, The effect of pressure on the electrical resistivity of water-saturated crystalline rocks: J. Geophys. Res., v. 70, p. 5669-5678.
- Brace, W. F., Walsh, J. B., and Frangos, W. T., 1968, Permeability of granite under high pressure: J. Geophys. Res., v. 73, p. 2225-2236.
- Brace, W. F., 1977, Permeability from resistivity and pore shape: J. Geophys. Res., v. 82, p. 3343-3349.
- Corwin, R. F., and Hoover, D. B., 1979, The self-potential method in geothermal exploration: Geophysics: v. 44, p. 226-245.
- Green, E., 1963, Streaming potential measurements: Geophysics Laboratory, MIT, report no. 9017-2.
- Hamilton, W. C., 1964, Statistics in physical science: The Ronald Press Co., New York.
- Ishido, T., and Mizutani, H., 1981, Experimental and theoretical basis of electrokinetic phenomena in rock-water systems and its application to geophysics: J. Geophys. Res., v. 86, p. 1763-1775.
- Madden, T. R., 1976, Random networks and mixing laws: Geophysics, v. 41, p. 1104-1125.
- Mazur, P., and Overbeek, J. Th. G., 1951, On electroosmosis and streaming-potentials in diaphragms: Rec. Trav. Chim., v. 70, p. 83-91.
- Nourbehecht, B., 1963, Irreversible thermodynamic effects in inhomogeneous media and their application in certain geoelectric problems: Ph.D. thesis, MIT, Cambridge.
- Sill, W. R., 1981, Self-potential modeling from primary flows: Dept. Geology and Geophysics, Univ. of Utah, DOE report no. DOE/ID/12079-42.
- Sill, W. R., 1982, Self-potential modeling: Geophysics, v. 47, to be published.
- Waxman, M. H., and Smits, L. J. M., 1968, Electrical conductivities in oil-bearing shaly sands: Soc. Pet. Eng. J., v. 8, p. 107-122.
- Waxman, M. H., and Thomas, E. C., 1974, Electrical conductivities in shaly sands: J. Pet. Tech., Feb., p. 213-225.
- Wyllie, M. R. J., and Spangler, M. B., 1952, Application of electrical resistivity measurements to problem of fluid flow in porous media: AAPG Bull., v. 36, p. 359-403.

Figure Captions

Figure 1. A representative sample of a rock of area A and length L , with an average pore number density of M/A . Sectioning the sample into N slices, the pore elements are ordered in the $M \times N$ array shown at the bottom.

REPRESENTATIVE SAMPLE OF ROCK

M x N pore elements sorted by radius a_i

	1	2	•	•	•	•	•	N
a_1			•	•	•	•	•	
a_2			•	•	•	•	•	
	•	•						•
	•	•						•
	•	•						•
a_M			•	•	•	•	•	