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Study of Electrokinetic Effects to Quantify Groundwater Flow

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Study of Electrokinetic Effects to Quantify Groundwater Flow

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**Work conducted while at New England Research White River Junction, Vermont 05001

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Abstract

An experimental study of electrokinetic effects (streaming potential) in earth materials was undertaken. The objective was to evaluate the measurement of electrokinetic effects as a method of monitoring and predicting the movement of groundwater, contaminant plumes, and other fluids in the subsurface. The laboratory experiments verified that the electrokinetic effects in earth materials are prominent, repeatable, and can be described well to first order by a pair of coupled differential equations.

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1 Introduction

The electrical conductivity of a porous medium is directly linked to the porosity and permeability structure [e.g. *Brace, 1977; Corwin and Hoover, 1979; Sill, 1983; Berryman, 1990*]. This fact is one of the primary reasons that many conventional electrical methods in geophysics such as electrical resistance sounding are employed, since often the goal is to obtain information on fluid flow properties by remote means. In this paper we focus on an alternative geophysical method, which is based on the measurement of self potential (SP) due to electrokinetic sources (effects arising from fluid motion). In contrast to conventional electrical methods, where an external electrical current or field is applied and the entire electrically conductive zone in the subsurface is illuminated, electrokinetic sources originate from fluid moving in the permeable regions of the subsurface. The appeal of electrokinetic methods over conventional ones is that they offer means to identify preferred flow paths and their spatial distribution. Using electrokinetic methods it may also be possible to track the fluid flow front and, under certain conditions, to remotely characterize the fluid properties.

Several investigators have considered the measurement and interpretation of electrical and electromagnetic signals generated by electrokinetic sources [*Poldini, 1938; Poldini, 1939; O gilvy et al., 1969; Bogoslovsky and O gilvy, 1970a; Bogoslovsky and O gilvy, 1970b; Bogoslovsky and O gilvy, 1972; Bogoslovsky and O gilvy, 1973; Mizutani and Ishido, 1976; Dorfman et al., 1977; Fitterman, 1978; Corwin and Hoover, 1979; Ishido and Mizutani, 1981; Martin et al., 1982; Sill, 1983; Erchul, 1988; Erchul and Sli fer, 1989; Corwin and Butler, 1989; Morgan et al., 1989; Haupt and Martin, 1990*]. This work includes theoretical, laboratory, and field studies. Field observations indicate that measurable natural electric potentials and electromagnetic fields can result from water flowing from reservoir leaks, dam leaks, drainage structures, subsurface karsts, sinkholes, pumping wells, geothermal fields, and earthquake sources. As an example, tectonic stress variations are thought to induce groundwater flow in the focal region during earthquakes, as depicted by the dilatancy-diffusion hypothesis [*Nur, 1972; Scholz et al., 1973*]. *Mizutani et al. [1976]* proposed that the magnetic field variations measured during the Matsushiro earthquake swarm were caused by fluid diffusion into the epicentral region. It was proposed that an electric potential was produced by the fluid flow by means of electrokinetic phenomena and the resulting electric current generated a magnetic field. In a complementary example, *Martin et al. [1982]* observed electromagnetic variations associated with fluid flow in laboratory experiments. A measurable magnetic field was observed, the sign of which depended on the fluid flow direction. These results agreed with predictions of differential equations describing electrokinetic phenomena.

Despite ample evidence for the existence of these phenomena acting at large scales in the earth, quantitative interpretation of electrokinetic signals in the field have not been as successful as one might hope. For example, while *Dorfman [1977]* was successful in tracking the heat fronts in a thermal oil recovery flood at the Slocum Oil Field in Texas (≈ 150 meters depth) by profiling the transient electric field from surface measurements, he reported difficulty in the data interpretation due to a lack of theoretical development. *Schiavone and Quarto [1984]* used electric field anomalies to study groundwater movement in underground springs near Taranto, Italy. They found that natural electric potentials produced by electrokinetic phenomena were more effective in characterizing the site than with conventional electrical techniques using externally applied fields. The study area was a complex system involving both geological and fluid heterogeneities. Again, however, detailed quantitative interpretations were limited by simplified models and an inability to account for both heterogeneous fluids and geology.

Self-potential modeling by *Sill [1983]* has enabled better understanding of some of these elec-

trokinetic effects. While Sill's model provides an excellent foundation for future work, it has been limited to simple two-dimensional geological features, steady-state flow conditions, and single component fluids in a totally saturated zone. Variations in pore fluid chemistry that arise during flow, chemically driven diffusion, and electromigration along with changes in pH and zeta potential have not been incorporated. Furthermore, many interpretation difficulties arise in that the electric field pattern observed for fluid flow and contaminant transport can be significantly influenced by natural heterogeneities and time variation during transient flow.

To understand these difficulties more fully, in this report we describe the current theory of electrokinetic effects and provide some extensions to the model which account for time-dependence and fluid chemistry variability. We then demonstrate the applicability of the steady-state theory through controlled laboratory experiments, and thereby suggest that measurement of electrokinetic potentials can be a practical geophysical technique to quantify groundwater flow.

2 Electrokinetic Theory

Electrokinetic phenomena arise from the movement of electrically charged particles contained in pore fluid relative to charged surfaces in a porous medium. These effects result in a coupling of electrical, chemical, and fluid transport. There are several mechanisms which can initiate motion of charged particles in pore fluid, including gradients in pore fluid pressure, temperature, chemical concentration, and electric potential. There are four electrokinetic effects recognized [Shaw, 1970]: (1) streaming potential or the streaming current - the electric field or current created when a fluid is forced to flow along a stationary charged surface, (2) sedimentation potential - the electric field created when charged particles move relative to a stationary fluid, (3) electrophoresis - movement of a charged surface and attached material relative to a stationary fluid by an applied electric field, and (4) electro-osmosis - movement of a fluid relative to a stationary charged surface by an applied electric field.

In the following, we will first review the microscopic model responsible for these effects and the constitutive relations describing the macroscopic behavior. Then we will discuss the important effects of fluid chemistry and flow through a heterogeneous porous medium.

2.1 Electric Double Layer

Electrically charged particles in pore fluid interact with electrical charge on pore walls. Ions in solution are attracted to the mineral grain surfaces to complete unsatisfied bonds producing a highly viscous low-mobility layer immediately adjacent to the pore. A second more weakly held layer of ions forms next to the first layer. This configuration is referred to as the electric double layer [Bockris and Reddy, 1970; Rieger, 1987]. This process results in a slight deficit of charge in the remaining pore fluid.

The Stern Model is an accepted configuration of the electric double layer and is depicted in Figure 1, although it is widely appreciated that it is still a simplification of a complex phenomenon. The region adjacent to the rock/mineral pore wall is the Stern Layer and is composed of two sub-layers. The Inner Helmholtz Plane (IHP) defines the area where the fluid charge is partially attached to the pore wall surface. The Outer Helmholtz Plane (OHP) consists of hydrated ions in contact with the hydrated pore wall. The region between the Stern Layer and the bulk of the pore fluid contains a diffuse distribution of charge influenced by the electrical forces of the rock/fluid system and is called the Gouy Diffuse Layer.

Figure 1: Stern Model of the electric double layer at a pore/fluid boundary where the solid has an excess of negative charge at the interface.

If an electric field is applied tangential to the charged surface, a force is exerted on both parts of the electric double layer. The charged surface and the charges bound tightly to it tend to move in one direction, while the more mobile ions in the outer layer will move in the opposite direction, carrying the fluid along with them through viscous forces. On the other hand, an electric field is created if the charged surface and the diffuse part of the double layer are forced to move with respect to one another as occurs in viscous laminar flow.

The surface within the Gouy Diffuse Layer where charge first becomes transported relative to the mineral surface by the fluid motion is known as the slipping plane. The position of this slipping plane is a function of the electrical forces of the system. The electric potential at the slipping plane is known as the electrokinetic or zeta potential, ζ [Glasstone, 1944]. Ishido and Mizutani [1981] and Morgan *et al.* [1989] have experimentally determined zeta potentials for samples of crushed silicate minerals containing various aqueous solutions. Their studies examined the variations in fluid properties such as pH, available ionic species, and temperature, all of which affect the zeta potential. They find that for common rock-forming minerals in groundwater the zeta potential ranges approximately from -10 to -100 millivolts.

2.2 Coupled Flows

When fluid flow and electric fields are coupled in the above manner, the processes can be described by the general equation for coupled flows [Marshall and Madden, 1959; Nourbehecht, 1963; Sill, 1983]:

$$\Gamma_i = \sum_j L_{ij} X_j \quad (1)$$

The Γ_i depict the fluxes of charge, matter, heat, etc. which are related to various potential gradients, X_j such as gradients of electric potential, pressure, temperature, etc. and coupling coefficients L_{ij} describing electrical, hydraulic, thermal conductivities, etc. Onsager showed that with a proper choice of fluxes and forces L_{ij} is symmetric [DeGroot and Mazur, 1963], i.e. $L_{ij} = L_{ji}$. This symmetry condition is known as the *Onsager Reciprocal Relation*. We consider only the streaming potential and the streaming current, where the primary fluxes are fluid flow and electric current. For this case, the following two coupled equations result [e.g. Ishido and Mizutani, 1981]:

$$Q = -\frac{k}{\mu} \nabla p - G \frac{\epsilon \zeta}{\mu} \nabla v \quad (2)$$

$$J = -G \frac{\epsilon \zeta}{\mu} \nabla p - \frac{1}{F\rho} \nabla v, \quad (3)$$

where Q is the fluid flux (volume flow rate per unit area or 'Darcy velocity'), J is the current density, p is the fluid pressure, v is the electric potential, k is the fluid permeability, F is the formation factor, G is a geometric factor, μ is the viscosity of the fluid, ρ is the electrical resistivity of the fluid, ϵ is the electrical permittivity of the fluid, and ζ is the zeta potential (which contains properties of both the fluid and solid medium). The terms k , F , and G depend solely on the geometry of the porous medium.

The first term on the right hand side of (2) is Darcy's Law and the second term on the right hand side of (3) is Ohm's Law. The two terms describe the flow of fluid and electric current due to gradients in fluid pressure and voltage. The other terms couple the two equations and are responsible for the streaming potential and the streaming current. The cross-coupling term $G\epsilon\zeta/\mu$, relating the streaming potential or streaming current to the zeta potential is easily derived for the case of a single circular capillary where laminar flow prevails [Shaw, 1970]. A more general derivation for flow through a porous plug gives the same relationship [Overbeek, 1952].

2.3 Effect of Fluid Chemistry

In reality, fluid motion in a porous medium results in not only the development of gradients in fluid pressure and electric potential, but also gradients in chemical concentration. The perturbation of any of these gradients can have a significant effect on the other gradients, altering electrokinetic processes, electric current, fluid flow, and contaminant mobilization. When fluid flow, electric current, and chemical concentration are coupled, the processes can be still be described by the general equations for coupled flows (1). The coupled equations for these three processes in their time-dependent form are given explicitly in Appendix A. The third equation introduced in the appendix describes the flux of a chemical species in the pore fluid due to coupled pressure, electric, and chemical gradients. In its steady state form this equation is:

$$M_i = D_i \nabla c_i + c_i (U_{ei} - Q), \quad (4)$$

where c_i is the concentration of chemical species i , M_i is the molar flux of the chemical species, D_i is the diffusion coefficient, U_{ei} is the migration velocity of the chemical species resulting from the electric potential gradient (electromigration or electrophoresis), and Q is the net bulk fluid (Darcy) velocity caused by the combined fluid pressure and electric potential gradients as described in Equation (2) (fluid flow + electro-osmosis).

In addition to those effects predicted by equation (4), varying the chemistry of pore fluid can have further significant effects on the resulting electric current and fluid flow by altering other mechanisms important to electrokinetic phenomena. First, it has been shown that the magnitude and sign of the zeta potential depend on the pH of the pore fluid [e.g. *Ishido and Mizutani*, 1981]. Variations in zeta potential will produce gradients in the coupling coefficients described in Equation (1) and thus produce sources of electric current. Second, the bulk fluid electrical conductivity is directly proportional to the concentrations of the ionic species in the pore fluid. The effects of pH on zeta potential and effects of chemical concentrations on electrical conductivity are discussed in further detail in Appendix B.

In the following, we will restrict ourselves once again to steady-state bulk fluid flow and electric current transport to consider the important problem of coupled flows through a heterogeneous porous medium.

2.4 Effect Of Heterogeneities

The coupled equations (2) and (3), when considered in more detail, indicate that the streaming potential and current should be quite sensitive to heterogeneities in the porous medium [Sill, 1983]. In what follows, this sensitivity will be shown.

Following the discussions of *Fitterman* [1978] and *Sill* [1983], we will assume that the first term on the right hand side of equation (2) dominates the fluid flow, so that the second term can be neglected. Thus, fluid flow is controlled by Darcy's Law:

$$Q = -L_{11} \nabla p, \quad (5)$$

where $L_{11} = k/\mu$.

Secondly, for simplicity, we write equation (3) as $J_{\text{total}} = J_{\text{conv}} + J_{\text{cond}}$; identifying the left hand side of equation (3) as the total electric current density J_{total} , the first term on the right hand side as the convective current density J_{conv} , and the remaining term as the conductive current density J_{cond} . The convective current results from charge carried by fluid movement. Through Ohm's Law, the redistributed charge drives the conductive current. If there are no external current sources and the system is in steady state (i.e. $\partial/\partial t = 0$), then the divergence of the total current density is $\nabla \cdot J_{\text{total}} = 0$ (total charge is conserved). Although there can be no net sources for electric current, from (3) we find that an electrokinetic source S exists:

$$\nabla \cdot J_{\text{cond}} = -\nabla \cdot J_{\text{conv}} = S. \quad (6)$$

Since the total current density is zero and is comprised of two parts, a local source in the conductive current is balanced by a sink of identical magnitude in the convective current and vice versa. S is identified as a source of electric current, since wherever it is nonzero the electric charge carried from a small elemental volume in the medium by the convective current does not equal that coming in

through the convective current from neighboring volumes. This excess or deficit in the convective current is made up by the conductive current. Thus, charge is traded among the two components within the volume. It is important to remember that the conductive and convective currents are not necessarily equal in magnitude, only their sources/sinks are.

To further identify the origin of the electrokinetic sources, we expand the second term in (6) using (3) and substitute the simplified notation $L_{21} = G\epsilon\zeta/\mu$ to obtain:

$$S = -\nabla \cdot J_{\text{conv}} = \nabla \cdot (L_{21} \nabla p) = \nabla L_{21} \cdot \nabla p + L_{21} \nabla^2 p. \quad (7)$$

Finally, we differentiate (5) and substitute the result for $\nabla^2 h$ in (7) to obtain:

$$S = \underbrace{\nabla L_{21} \cdot \nabla p}_a - \underbrace{\frac{L_{21}}{L_{11}} (\nabla L_{11} \cdot \nabla p)}_b - \underbrace{\frac{L_{21}}{L_{11}} (\nabla \cdot Q)}_c. \quad (8)$$

Thus, we can identify the following three induced sources for electric current (equation 8): (a) locations of gradients in the cross-coupling term $L_{21} = G\epsilon\zeta/\mu$, (b) locations of gradients in the fluid permeability term $L_{11} = k/\mu$, and (c) sources of fluid flow (i.e. $\nabla \cdot Q \neq 0$). The importance of these induced sources is as follows. Fluid flow carries charge along with it through the convective current. At heterogeneities charge can accumulate, producing a gradient in the electric potential. This gradient will tend to drive a counter current through ionic conduction. At locations of the exchange of charge a unique electric potential distribution results which may be used to identify the underlying heterogeneities.

It appears that there are two ways that heterogeneities can produce a source of electric current: (a) and (b) above. However, the geometric terms k , F , and G are related to one another at a microscopic level by the geometry of the pore space. Specifically, as in the equivalent channel model [Paterson, 1983; Walsh and Brace, 1984], $F = \tau^2/\phi$, $G = -1/F$, and $k = CR^2/F$, where τ^2 is the tortuosity, ϕ is the porosity, R is the hydraulic radius (typical pore dimension), and C is the pore shape constant ($C = 1/2$ for tubes with circular cross-section, $3/5$ for tubes with equilateral triangle cross-section, and $1/3$ for crack-like pores). If properties of the fluid (e.g. ϵ , ζ , and μ) are uniform and constant, then there is really only one independent source of electric current due to heterogeneity in the porous medium: that due to gradients in the microscopic pore geometry as described collectively by τ^2 , ϕ , and R .

The net effect of a particular heterogeneous pore geometry on the transport properties of a system cannot be easily predicted in all cases. For example in some of our previous work on the uncoupled transport of fluid, solute particles, and electric current through single fractures [Brown, 1987; Brown, 1989; Thompson and Brown, 1991], the differences in the dependence of each physical process to the microscopic pore geometry leads to quite different spatial patterns of, say, fluid velocity and electric current density for the same porous medium. These differences may lead to potential problems in inferring the properties of one process from another. For example, we have found that electrical resistivity cannot be used in a simple way to infer the fluid permeability if there are complex spatial correlations in the geometry of the porous medium.

For these reasons, we feel that the influence of heterogeneities in the porous medium on electrokinetic effects is an extremely important topic to understand if we intend to quantify groundwater flow. In what follows, we present some experimental results which demonstrate the effect of heterogeneities in the electric field resulting from fluid flow.

Figure 2: Schematic of one-dimensional column apparatus. Along the specimen there are 11 measurement electrodes and one ground (reference) electrode and 12 fluid pressure measurement ports.

3 Experiment

3.1 Procedure

One dimensional experiments were done in packings of sand in a long cylindrical column (Figure 2). The sample column was constructed from an acrylic plastic tube with an inside diameter of 2.54 cm and nominally 50 cm long. The column contained compaction plugs at each end to maintain the mechanical integrity of the sample during the experiments. A number of electrodes and fluid pressure transducers were placed along the axis of the column 2.54 cm apart. The electrodes were offset from the fluid pressure ports by approximately 0.635 cm along the sample holder. Common arkosic sand (containing quartz, feldspars, and clays), rinsed to remove extremely fine components, in approximate chemical equilibrium with Albuquerque, New Mexico tap water was used in these experiments.

With the exception of the electrodes, care was taken to make all parts of the sample holder and fluid delivery system from non-reactive/non-conductive materials. Fluid was supplied by a peristaltic pump, with Tygon^R tubing and plastic fittings. Fluid was drawn from a NalgeneTM reservoir containing the same arkosic sand and tap water residing in the sample holder. Fluid leaving the sample holder was placed in another NalgeneTM reservoir, electrically isolated from the first. The effluent fluid was used to replenish the main reservoir between experiments.

Electrode composition and construction was an important consideration for these measurements. Ideally, reversible electrodes should be used to avoid transient signals arising from the slow formation or dissolution of the oxide coating on bare wire surfaces. In fact, monitoring of the background noise level for zero flow (Figure 3) shows a slow but erratic drift in electric potential through time. However, in these experiments transient flow was not the primary consideration. Therefore, for simplicity, the electrodes consisted of platinum wire residing in circumferential grooves machined on the inside of the acrylic sample holder tube. Platinum was chosen for its nearly inert properties in the water used here. Tests indicate that the spurious potentials developed from reaction of the fluid with the electrodes is a second-order effect compared to the potentials induced from fluid flow. Further, following the suggestions of Korpi and deBruyn [1972] the experiments consisted of short duration flow pulses (Figures 4 and 5) and only the changes in the electric potential corresponding to the pressure changes were considered significant. In this way, the slow electrode drift did not interfere with the interpretation of the results.

The pressure transducers were solid-state devices with a full scale range of approximately 0–10⁵ Pa (0–15 psi). The pressure sensing components were electrically isolated from the fluid via air in the Tygon^R tubing leading to the sample holder. The tubing connecting the pressure transducers to the sample column was nominally 20 cm in length and approximately half filled with air. The air served to electrically isolate the pressure sensing elements from the fluid. The action of the peri-

Figure 3: Background noise levels for zero fluid flow. **Top:** Noise at each electrode relative to electrode number 0 (see Figure 2). **Bottom:** Noise in pressure transducers. Note the long-term spurious drift on several electrode signals due to chemical interaction of the fluid and the metal electrodes.

static pump produced small sinusoidal pressure pulses superimposed on the background pressure in the sample fluid (Figures 4 and 5). The long air-filled tubing acts as a low pass filter, thus these pulses do not appear in the pressure measurements.

The data was acquired with a multiple channel, high input impedance ($> 10^8 \Omega$), 16 bit analog to digital converter interfaced to a computer.

3.2 Flow Experiments

One end of the sample was subjected to repeated pulses of fluid flow at various velocities allowing a steady state pressure to be reached and then the flow was shut off (Figure 4). The fluid pressure and electric potentials were measured as the flow was turned on and off by fitting straight line segments by least squares to the stable portions of the pressure and voltage records immediately before and after the pressure pulses (Figure 5). The obvious transient parts of these curves were not considered in the analysis. Changes in electric potential were measured at all electrodes with respect to a ground (reference) electrode at one end of the specimen. Two general features of these experiments are worth mention. First, if the flow was reversed, then the voltage pulses measured relative to electrode zero changed sign relative to the data of Figures 4 and 5 as expected. Second, within each sand type, the magnitude of the electric potential pulses generated by flow is proportional to

Figure 4: Fluid pressure at pressure port number 11 at the upstream end of the specimen (see Figure 2) for various on/off fluid flow pulses. The fluid flow rate is indicated in ml/min above each pulse. *Bottom:* Electric potential developed for each flow pulse at electrode number 11 relative to electrode number 0 (ground). Note that the “noisy” pulses in electric potential are real and are due to actual fluid velocity fluctuations caused by the action of the peristaltic pump. This higher frequency noise does not appear on the pressure records due to low-pass filtering by the air gaps in the pressure lines.

the length scale over which it is measured (distance between electrodes).

This pulse method was used to determine the change in electric potential and the change in fluid pressure at each sensor location for a variety of flow rates (Figure 6). For these experiments there were two types of sand present in the sample holder simultaneously (Figure 2) and therefore two distinct pressure and potential gradients appear in the data. For the highest flow rate (400 ml/min) the fluid pressure and electric potential gradients were the largest and most distinct, and were therefore used for analysis of the coupled flows model.

3.3 Evaluation of Models

To test the coupled flows model (2) and (3) we first attempt to estimate or measure each parameter independently. Table 1 gives the various geometric and physical parameters for the specimen and the flow system used in these experiments. The parameters presented in this table were obtained as follows. The geometry of the specimen is known by direct measurement. The basic properties of water, viscosity μ and permittivity ϵ , are obtained directly from handbooks. The electrical conduct-

Tap Water	resistivity ρ , at 22.3°C	28.01 ohm-m
	viscosity μ	0.001 Pa-sec
	pH	8.17
	permittivity ϵ	$7.08 \times 10^{-10} \text{ C}^2/\text{J-m}$
Salt Water Solution	resistivity ρ , at 20.9°C	2.95 ohm-m
	pH	8.21
Specimen Geometry	length	0.45 m
	area	$5.0 \times 10^{-4} \text{ m}^2$
	sensor spacing	0.0254 m
	offset between pressure sensors and electrodes	0.00635 m
Coarse Sand	porosity ϕ	0.35
	formation factor F , from $F \approx \phi^{-1.3}$	3.91
	permeability k	$7.2 \times 10^{-10} \text{ m}^2$
	pressure gradient ∇P , $Q = 400\text{ml/min}$	18496 Pa/m
	voltage gradient ∇v , $Q = 400\text{ml/min}$	-21.3 mV/m
	hydraulic radius R , from $k(\text{darcy}) = 1/2R^2/F$	75 μm
	hydraulic radius R , from $k(\text{darcy}) = 3/5R^2/F$	68.5 μm
	zeta potential ζ	-58 mV
	grain size distribution, diameter:% by weight	850-1700 μm : 75% 500-850 μm : 22.5% <500 μm : 2.5%
	grain size d , from $k(\text{darcy}) = 6.17 \times 10^{-4} d^2$	1080 μm
Fine Sand	porosity ϕ	0.35
	formation factor F , from $F \approx \phi^{-1.3}$	3.91
	permeability k	$9.2 \times 10^{-11} \text{ m}^2$
	pressure gradient ∇P , $Q = 400\text{ml/min}$	144160 Pa/m
	voltage gradient ∇v , $Q = 400\text{ml/min}$	-107 mV/m
	hydraulic radius R , from $k(\text{darcy}) = 1/2R^2/F$	28.6 μm
	hydraulic radius R , from $k(\text{darcy}) = 3/5R^2/F$	24.5 μm
	zeta potential ζ	-37 mV
	grain size distribution, diameter:% by weight	500-850 μm : 2.5% 425-500 μm : 12.5% 355-425 μm : 15% 250-355 μm : 47.5% 180-250 μm : 12.5% <180 μm : 10%
	grain size d , from $k(\text{darcy}) = 6.17 \times 10^{-4} d^2$	386 μm

Table 1: Summary data for electrokinetic experiments.

Figure 5: To overcome problems with unpredictable slow drift of electrode potential only rapid changes (pulses) in fluid pressure and electric potential were used for analysis. Changes in electric potential and fluid pressure were estimated for each new flow rate by fitting line segments through noise in the data and extrapolating forward and backward in time to find the average signal offset due to electrokinetic processes. The lower curve on the pressure plot is a time marker used to determine the start/stop time of pulses.

ivity and pH of the water was measured with standard test equipment.

As mentioned previously, we assume that the second term of (2) is small relative to the first. Therefore, we have Darcy's Law:

$$Q \approx -\frac{k}{\mu} \nabla p. \quad (9)$$

The permeability k can be calculated for a given flow rate Q given the pressure gradient ∇p implicit in Figure 6.

We can also measure the voltage gradient $\nabla \phi$ from Figure 6. However we did not perform an electrical conductivity measurement for the entire sample, thus the formation factor F of (3) cannot be measured directly. We did estimate the porosity ϕ by measuring the volume of water required to saturate a dry packing of sand. From this information we apply Archie's Law to estimate the formation factor F as [Paterson, 1983]:

$$F \approx \phi^{-1.3}. \quad (10)$$

Figure 6: Summary plot of pressure and voltage changes for various flow rates as determined by the pulse method. Each point was calculated from the pulse method illustrated in Figure 5. Groups of points tied together by a solid line were obtained from pulses at the same flow rate. The flow rate in ml/min is shown to the right of each curve. The pressure and voltage gradients presented in Table 1 were derived from the 400 ml/min data. The coarse sand gradients were determined from data at positions 0–6 and the fine sand gradients were obtained from data at positions 7–11. The boundary between coarse and fine sand is approximately at pressure port 6.

Therefore, we have estimates for most of the parameters in (2) and (3), including k , F , μ , ρ , ϵ , ∇p , and $\nabla \phi$. The zeta potential of our specimen is still unknown. If we were given an estimate of the zeta potential, we could predict Q and J for our specimen given any arbitrary pressure and voltage gradients.

We can derive the zeta potential for our specimen as follows. Knowing that $G = 1/F$, equation (3) can be written as:

$$J = -\frac{1}{F\rho} \nabla \phi + \frac{1}{F} \frac{\epsilon \zeta}{\mu} \nabla P. \quad (11)$$

Since the inlet reservoir was electrically isolated from the outlet reservoir, then we can set $J = 0$ in (11) [Fitterman, 1978; Sill, 1983] and solve for the zeta potential ζ in terms of the other known parameters as:

$$\zeta = \frac{\mu}{\epsilon \rho} \frac{\nabla \phi}{\nabla P}. \quad (12)$$

We find through this analysis that the zeta potential is approximately -58 mV for the coarse sand and -37 mV for the fine sand. These values are consistent with the range $-100 < \zeta < -10$ mV presented widely in the literature for rock-forming minerals within this pH range [e.g. *Ishido and Mizutani*, 1981; *Morgan et al.*, 1989]. We conclude that the coupled flows model (2) and (3) describes our experimental results to a good approximation.

As an aside, we were also able to measure the grain size distribution for both sands by sieving and weighing. The size distributions can be compared to the grain diameter estimated from yet another published empirical relationship to permeability. The grain size d in μm is related to permeability as [*Bear*, 1972]:

$$k(\text{darcy}) = 6.17 \times 10^{-4} d^2 \quad (13)$$

The grain diameter estimated in this way is $1080 \mu\text{m}$ for the coarse sand and $386 \mu\text{m}$ for the fine sand. These values compare closely to the modes of the grain size distributions measured by sieve analysis: $850\text{--}1700 \mu\text{m}$ for the coarse sand and $250\text{--}355 \mu\text{m}$ for the fine sand.

The grain diameter can be also compared to the hydraulic radius R , estimated from the equivalent channel model [*Paterson*, 1983; *Walsh and Brace*, 1984], which for pores in the shape of circular tubes is:

$$k(\text{darcy}) = 1/2 R^2 / F, \quad (14)$$

and for pores in the shape of equilateral triangle tubes is:

$$k(\text{darcy}) = 3/5 R^2 / F. \quad (15)$$

The term hydraulic radius actually refers to $1/2$ of the pore radius. For various packing arrangements of uniform size spherical particles, the pore diameter is typically a small fraction of the particle diameter. From our data we find that the average pore diameter is approximately $1/3$ of the mode in the grain diameter distribution.

3.4 Solute Transport Experiments

Some additional experiments were performed where steady state flow was established and then 1-2 ml of saline solution (with an electrical conductivity of 10 times that of the baseline fluid) was injected into the flow system. A strong electrical signal was observed as this slug of contaminant passed through the system (Figure 3). The large central dip in this anomaly was observed to move through the specimen at the average pore velocity V_{pore} :

$$V_{\text{pore}} = \frac{Q}{A\phi}, \quad (16)$$

where Q is the volumetric flow rate, A is the cross-sectional area of the sample holder, and ϕ is the porosity. A similar effect with a different anomaly shape was seen by introducing a slug of deionized water (lower electrical conductivity) into the upstream end of the flow system.

4 Discussion

Analysis of the data from these experiments shows that the coupled differential equations (1) and (2) adequately describe electrokinetic effects in earth materials to first order. These results show:

Figure 7: Electric potential at each electrode (labels 1-11) at a constant flow rate of 100 ml/min. Flow is from coarse to fine sand (Figure 2) with electrode 1 being at the fluid inlet end. The interval over which the potential is measured increases from the bottom trace (fluid inlet) to the top trace. A transition from high permeability coarse sand to low permeability fine sand occurs at about electrode 7. Just after 100 seconds of elapsed time a 2 ml slug of high conductivity brine moved through the system. The signal from this event is much larger in the fine sand. The large local minimum in these curves moves at the average pore fluid velocity.

(a) A measurable electric potential is developed due to fluid flow. This potential is proportional to the fluid velocity in both magnitude and sign. The magnitude of this potential is also proportional to the length scale over which it is measured. (b) Heterogeneities in the fluid permeability manifest themselves in the gradient of the electric potential. The ratio of electric potential gradients can be used to determine the ratio of permeabilities across a boundary. (c) The injection of a contaminant with different electrical conductivity (e.g brine) strongly perturbs the electric potential suggesting the ability of this technique to track the migration of contaminant plumes.

Knowing the conditions under which anomalies due to electrokinetic sources are measurable allows the possible use of self potential (SP) measurements for groundwater flow and environmental problems. *Hämmann et al.* [1996] present a method for imaging the location and depth of SP sources useful in this context.

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A Coupled Flows Including Contaminant Transport

Fluid movement in porous media results in the development of gradients in fluid pressure, electric potential, and chemical concentration. The perturbation of any of these gradients can have a significant effect on the other gradients, altering electrokinetic processes, electric current, fluid flow, and contaminant mobilization. When fluid flow, electric current, and chemical concentration are coupled, the process can be described by the general equation for coupled flows (1) [Marshall and Madden, 1959; Nourbehecht, 1963; Sill, 1983].

The potentials and fluxes describing current, fluid, and chemical concentration in Equation (1) can be determined by solving the coupled set of differential equations using linear decomposition. To model transient flows and contaminant transport, the divergences of the electric current flux J , molar flux of an ion species M_i , and fluid flux Q , need to be solved simultaneously. The potentials necessary to determine are: voltage v , concentration (of species i) c_i , and fluid pressure p . The expressions for the coupled set of differential equations describing conservation of mass, charge and chemical concentration are compiled and synthesized from a number of sources [Nourbehecht, 1963; Martin et al., 1982; Sill, 1983; Shapiro et al., 1989] and are as follows:

$$S \frac{\partial p}{\partial t} = -\nabla \cdot Q = -\nabla \cdot U, \quad (A1)$$

$$C_s \frac{\partial v}{\partial t} = -\nabla \cdot J = -\nabla \cdot [-\sigma \nabla v - F \sum z_i D_i \nabla c_i + F U \sum z_i c_i], \quad (A2)$$

$$R_{di} \frac{\partial c_i}{\partial t} = -\nabla \cdot M_i = -\nabla \cdot [-F v_i z_i c_i \nabla v - D_i \nabla c_i + U c_i] + R x_i. \quad (A3)$$

The bulk convection is $U = -k_h \nabla p - k_e \nabla v$ and

- F - Faraday's constant
- C_s, S - soil capacitance and specific storage
- σ - electrical conductivity parameters
- v_i, z_i, D_i, R_{di} - ion mobility, valence, diffusion coefficient, and retardation factor
- $R x_i$ - molar production rate due to chemical reactions
- k_h, k_e - hydraulic and electro-osmotic conductivities.

Equation (A3) is a form of the Nernst-Planck Equation [Bockris and Reddy, 1970] and is used to compute the concentration of an ion species in space and time. The equation accounts for ionic mobilization due to electromigration, chemical diffusion, and fluid convection. In order to solve Equation (A3), it is necessary to first solve Equations (A1) and (A2) and determine the voltage, fluid pressure, pH, and zeta potential distributions.

B Sensitivity to pH and Ion Concentration

Significant variations in pH are expected in groundwater. Moreover, these variations can arise as ionic or contaminant plumes diffuse and migrate through the subsurface. Specifically, pH can have a significant effect on the magnitude and sign of the zeta potential. For example, *Lorenz* [1969] derived an empirical expression relating zeta potential and pH in kaolinite from streaming potential measurements and is stated as follows:

$$\zeta(\text{mV}) = -38.6 + 281.0e^{-0.48 \times \text{pH}} \quad (\text{B1})$$

Variations in zeta potential produce gradients in the coupling coefficients that are associated with electrokinetic sources. These sources can then occur where different chemical concentrations come in contact. Another important aspect is the effect of ionic concentration on the bulk electrical conductivity. Shapiro, et al. [*Shapiro et al.*, 1989] showed that electrical conductivity can be computed from the sum of the ion species concentrations in pore fluid as:

$$\sigma = F^2 \sum z_i^2 v_i c_i \quad (\text{B2})$$

As ion concentrations vary, gradients in electrical conductivity will arise producing electrokinetic sources.

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