ELECTROKINETIC GROUNDWATER EXPLORATION:
A NEW GEOPHYSICAL TECHNIQUE

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ABSTRACT

Electrokinetic potentials, sometimes known as streaming potentials, are generated by fluid-flow, heat fluxes, pressure sources and diffusion potentials across boundaries between a fluid electrolyte and mineral grains or rock particles in fractured rocks and porous media. In the electrical double layer model (Stern model, Figure 1), there is an immobile layer that is divided into two by the Stern plane. The layer nearest the mineral grain is immobile, and the surface of the mineral grain has a net charge so that it adsorbs cations from the fluid in an electrical double layer. Away from the grain boundaries, the mobile part of the fluid may have a surplus of positive or negative ions, depending on the electrostatic charge distribution at the electrical double layer. The excess density of ionic species can be transported with fluid flow producing an advective electric current. The advective flow of charge is balanced by a return electric current; this process is known as coupled flow. The electric potential in the Stern layer varies as a function of distance. The electric potential at the end of slipping plane (the end of the electrical double layer furthest from the mineral grains) is known as the zeta-potential (ζ). To measure such electrokinetic potentials, a good understanding of petrophysical properties of the media, particularly the ζ-potential and electrokinetic coupling-coefficient are required.

This research project aims to establish a new technology to measure fluid-flow and infer hydraulic conductivity from the electrokinetic potential in three approaches. Firstly, measurements of surface electrical potentials will be combined with hydraulic pumping tests to determine sub-surface fluid-flow. Measurements will be made using 36 non-polarized electrodes relative to a reference. This setup will allow monitoring of changes in electrokinetic potentials associated with draw-down. Data will be sampled at a rate of 1Hz with a resolution of 0.1 mV. The second step of this research will be the investigation of the relationship between porous media and water-flow in the laboratory. Experimental work will focus on the properties of clay and sand, which form most of the ground in the area along the River Murray. The key part of this experiment will be defining the ζ-potential and electrokinetic coupling coefficient of these porous media. The final aim of this research is to further develop numerical modelling of the electrokinetic potential data to quantitatively interpret electrokinetic potential data.

INTRODUCTION

The electrokinetic potential occurs by fluid-flow in porous media and in fractured rocks. Interaction between fluid-flow and mineral grains produces an electrokinetic potential (Corwin & Hoover 1979). However, it is not easy to quantitatively interpret electrokinetic potentials because of the complex dependency on parameters such as temperature, pressure, pH and the heterogeneity of porous media in the ground. The theoretical basis of this method was originally described by Overbeek (1952) and Nourbehecht (1963). However, relatively few studies have been carried out to investigate the electrokinetic potential in applied geophysics, and to obtain quantitative interpretation of electrokinetic potentials with numerical modelling (Sill 1983, Wurmstich & Morgan 1994, Titov *et al.* 2002).

When fluid flows through pores and in fractures, it forms two layers which are separated by a slipping plane as immobile and mobile parts of fluid in the Stern model (Figure 1). The layer in the vicinity of the mineral grain boundary, which is immobile, is divided into two again. Next to the mineral grain boundary is the Stern layer, and the other layer is the diffusion layer. Together, these layers form the electrical double layer (EDL). The interaction between mineral grains and fluid generates the electrokinetic potentials. In the Stern layer, the negatively charged surface of the mineral grain adsorbs positive ions from the fluid in the immediate vicinity of the grain's surface. The diffusion layer consists of surplus positive ions which were attracted but not adsorbed. If the negative charge density is very high at the surface of the mineral grain, the voltage may rise above zero in the Stern layer and will then decrease toward zero as a function of distance in accordance with a Boltzmann distribution of the ions (Overbeek 1952) (Figure 1B).

Normally, the surface of silicate mineral grains is negatively charged and attracts cations from the fluid surrounding the mineral grain (Fitterman 1979). By this phenomenon, so-called electrostatic attraction, a distribution of ions is produced, and thus electrical potentials occur. In a system which consists of mineral grains and fluid, there must be an electrical equilibrium (Ishido & Mizutani 1981). This means the total

charge of the system must not change in magnitude. In the electrical double layer, where the voltage approaches zero at the Stern layer, the electrical charge at the hydraulic slipping plane is the zeta-potential (ζ) as shown in Figure1. Thus, the zeta-potential is directly related to the amount of transported electrical charge and is the magnitude of the potential change in the mobile part of the fluid. Values of zeta-potential and of the electrokinetic coupling coefficient are necessary to estimate the magnitude of electrokinetic phenomena (Ishido & Mizutani 1981).
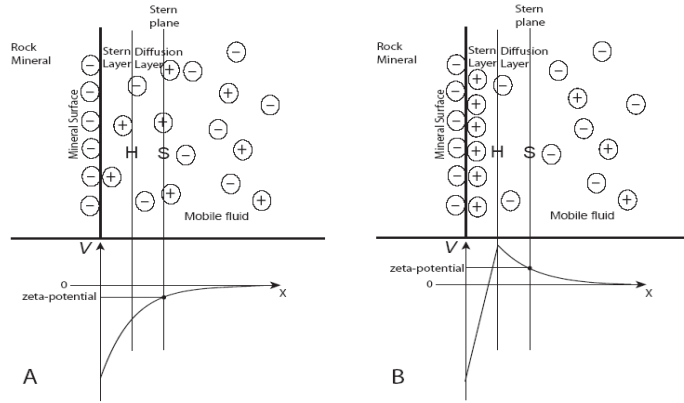

Figure 1: The electrical double layer at a rock–water interface according to the Stern model, and the electric potential (V) as a function of distance (x) from the pore wall. The hydrodynamic slipping plane (S) separates the mobile and immobile phases of the fluid. The potential at this plane is called the zeta-potential (ζ). Depending on amount of specific adsorption in the Stern layer between the pore wall and plane H, ζ can be positive (B) or negative (A). For a negative ζ, more positive than negative ions are transported with the fluid. Adapted from Fagerlund & Heinson (2003).

The convection flow of pore fluid in the diffuse layer produces an advective electric current; such flow yields an electric field which produces a counter electric current (conduction current) through the interface. Assuming that the flow is laminar and the radius of curvature of interface between mineral grains is much bigger than the thickness of the double layer, the advective and conduction currents at equilibrium are equal in magnitude. The total current per unit area i_{total} in the system can, therefore, be expressed as:

$$\boldsymbol{i}_{total} = \boldsymbol{i}_{adv} + \boldsymbol{i}_{cond} \tag{1}$$

The advective electric current per unit area $\boldsymbol{i}_{adv}$, over the interface is given by (Overbeek 1952):

$$\boldsymbol{i}_{adv} = \frac{\zeta \varepsilon_r \varepsilon_0}{\eta} \overline{\nabla_n P} \tag{2}$$

where ζ is the zeta-potential, ε_r is the relative dielectric constant of the liquid, ε_0 is the dielectric constant of vacuum, η is the viscosity of the fluid and $\nabla_n P$ is the mean pressure gradient normal to the cross-section area. In the derivation (2), $\nabla_n P$ is negative because of the fluid flow and ε_r, ε_0 and η are positive constants. This means that if the zeta-potential (ζ) is negative, the value of $\boldsymbol{i}_{adv}$ becomes positive and hence there is a movement of positive ions with the flow.

The conduction current per unit area $\boldsymbol{i}_{cond}$, which is caused by the advection current is given by Ohm's law:

$$\boldsymbol{i}_{cond} = -\sigma \overline{\nabla_n V} \tag{3}$$

where σ is the bulk conductivity of the liquid and $\nabla_n V$ is the potential gradient normal to the cross section. The Helmoltz-Smoluchovsky equation expresses a proportional relationship between $\nabla_n P$ and $\nabla_n V$, and it can be derived by combining Eq. (1), (2) and (3):

$$\overline{\nabla_n V} = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta \sigma} \overline{\nabla_n P} = C_s \overline{\nabla_n P} \tag{4}$$

which can be re-arranged to give:

$$C_s = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta \sigma} \tag{5}$$

where C_s is the electrokinetic potential coefficient. Groundwater flow is driven by the hydraulic head gradient, $\nabla_n H$, rather than $\nabla_n P$. Since $P = \rho g H$, where ρ is the density of the fluid (in kg/m³), g is the normal gravity value (9.81 m/s²) and H the hydraulic head, Eq. (4) can be described as:

$$\overline{\nabla_n V} = \frac{\varepsilon_r \varepsilon_0 \zeta \rho g}{\eta \sigma} \overline{\nabla_n H} = C_s' \overline{\nabla_n H} \tag{6}$$

This can be re-arranged to give

$$C_s' = \frac{\varepsilon_r \varepsilon_0 \zeta \rho g}{\eta \sigma} \tag{7}$$

It can be concluded that the pressure gradient is an important dependency of the electrokinetic potential gradient. Eq. (5) or (7) can be easily adapted to the controlled environment of the laboratory and provides

easy means to computing C_s and ζ. Because groundwater flow can be normally described by Darcy's law, Eq. (6) can also be re-arranged as:

$$\bar{v} = \frac{Q}{A} = -\frac{k}{\eta}\overline{\nabla P} = -\frac{k\rho g}{\eta}\overline{\nabla H} = -K\overline{\nabla H} \qquad (8)$$

The voltage gradient can, therefore, be expressed in terms of fluid flux also:

$$\overline{\nabla V} = \frac{C_s'\eta}{k}\bar{v} \qquad (9)$$

where Q is the fluid flux(volume/time), A is the cross-sectional area, k is the intrinsic permeability, K is the hydraulic conductivity. Q/A=v is the Darcy-velocity in m/s.

Electrokinetic potential phenomena can be explained simply as the interaction of pore fluid flow and mineral grains, but there are many other parameters that contribute to the electrokinetic potentials. As denoted above, the zeta-potential (ζ) and electrokinetic coupling coefficient C_s (given by the ratio $\nabla V/\nabla P$) are the most important parameters. However, the value of these two parameters are affected by other physical properties such as permeability (hydraulic conductivity), pH, electrolyte concentration, pressure, temperature, mineral grain size, the type of mineral, transport properties and the phase of fluid.

Permeability and pH have been reported as important parameters affecting the zeta-potential by Lorne *et al.* (1999) and others (Ishido & Mizutani 1981, Jouniaux & Pozzi 1997, Perrier & Froidefond 2003). These studies showed a correlation between pH and zeta-potential that is dependent on rock type. In general, an increase in pH produces a more negative zeta-potential.

In an experimental study of problems relating to permeability by Perrier & Froidefond (2003), electrokinetic potentials were significantly increased as the permeability increased, as shown in figure 2. In addition, as pressure and temperature decreased, the electrokinetic potentials decreased. Such phenomena relate to mineral grain size; if the mineral grain size is too big the fluid-flow is not laminar, and thus the electrokinetic potentials are not constant and predictable. Electrolyte concentration and mineral types are considered important parameters because the electrokinetic potentials are dependent on the protonation and the deprotonation of the silanol groups in the case of quartz (Glover *et al.* 1994).

Figure 2: EPC (electrokinetic potential coefficient) versus permeability calculated for an electrolyte resistivity of 50 Ωm (fresh water). Adapted from Perrier & Froidefond (2003).
$\square$ – oceanite, $\circ$-hawaiite, $\Diamond$ - trachyte

It has proven to be difficult to interpret electrokinetic potential data quantitatively because electrokinetic potential data involve many interdependent parameters. To interpret electrokinetic potential data quantitatively it is fully required to develop a modelling algorithm (Fitterman 1983, Sill 1983, Wurmstich & Morgan 1994, Darnet & Marquis 2004). Fitterman (1983) presented modelling of streaming potential in a vertical dike with thermoelectric parameters and in a one dimensional layered model to simulate dilatancy associated with earthquakes. At the same time, Sill (1983) presented a modelling approach that connected hydrological problems to geophysical parameters using coupled flows. As with the studies mentioned above, Sill's study is also based on Nourbehecht's (1963) study which defined the generation of streaming potentials with a coupled flow that incorporated the primary driving potential.

Sill (1983) presented an alternative solution of coupled flow problems, discriminating the primary source and induced sources, and using a two-dimensional algorithm to calculate electrokinetic potentials. Sill also proposed a three-step process to model electrokinetic potentials: (1) solving the primary potential problem (solving hydraulic problem); (2) solving the electrokinetic current sources, obtaining the electrical sources of electrokinetic potential from the calculated heads and electrokinetic coupling coefficients; and, (3) determining the resultant electric potential from the calculated electrical sources and subsurface conductivity.
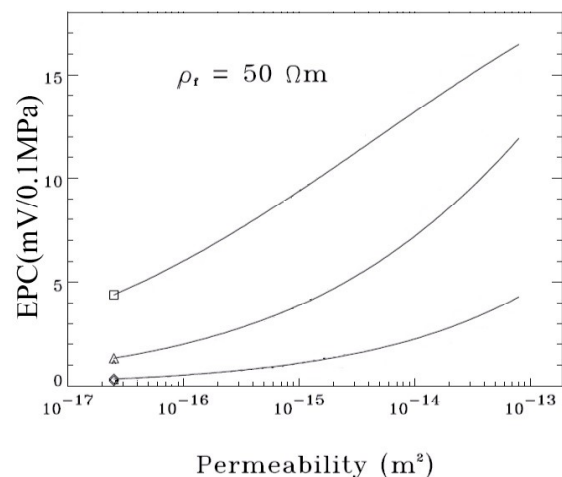
APPROACHES

We plan to measure electrokinetic potentials due to subsurface water-flow in porous media. This project will be combined with pumping tests to generate draw-down. The field work will probably take place around Loxton, where the Department of Water, Land, Biodiversity & Conservation is undertaking hydro-geological work.
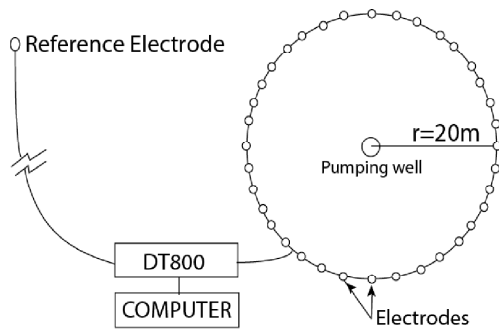

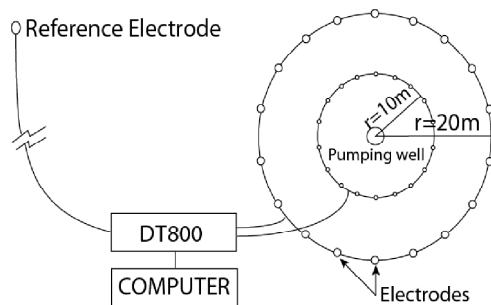**Figure 3:** A sketch of a single line array with 36 electrodes.

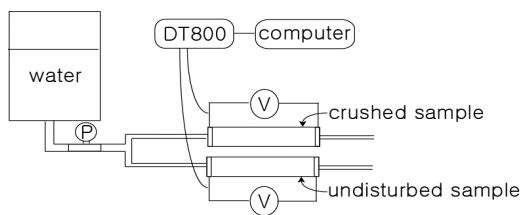**Figure 4:** A sketch of a double-line array with 18 electrodes on each line.

Figure 5: A schematic of the laboratory apparatus

We have developed a multi-electrode logging system, which has 36 non-polarized electrodes relative to a reference, on circled lines with a radius of 10 or 20 meters each around a pumping hole (Figures 3 and 4). This set up will allow monitoring of spatial continuity of electrokinetic potentials. To eliminate electrode drift, data will be sampled at a rate of 1Hz with a resolution of 0.1 mV and the measurements will be carried out for a time period between a few hours to days, using a DataTaker, DT800 that has 42 channels and built-in memory. In addition, we will carry out field work in different seasons to consider the effects of the variation in temperature and other factors such as electrolyte concentrations in the groundwater.

To determine hydraulic conductivity we need to measure the ζ-potential and electrokinetic coupling coefficient from laboratory scale samples. Thus, we will develop an apparatus to measure electrokinetic potentials of porous media under given conditions and in a controlled environment. We will also measure material parameters such as mineral grain size, pore ratio of the porous media, the ratio of clay and silanol group minerals, salinity, pH, temperature and pressure. For the laboratory work, we will measure the voltage difference between the two ends of rock or porous media samples through which an electrolyte is passing with changing parameters, such as fluid type (e.g., deionized water, water from bore holes) and pressure. The measurements will be taken with a DataTaker, DT800. To calculate the electrokinetic potential coefficient C_s and ζ-potential, Eq. (4) can be used directly with the apparatus shown at Figure 5, but if we use elevation instead of pumps (pressure) to generate water-flow, Eq. (7) can be used. To avoid differences in the results that might be due to using natural and laboratory conditions, we will use undisturbed samples and crushed samples of each type of porous media under the same conditions (Figure 5). In addition, as this project is related to salinity problems we will use the water from bore holes as an electrolyte, and then compare the differences from the result using pure water (deionized and degassed).

The numerical modelling will be based on Sill's (1983) approach in three steps. In this regard the new multi-electrode array with pumping tests will have a number of advantages. The first one is that it will directly provide the information on the primary potential, including the water head which is required for the first step of Sill's approach. The second is that it will also provide the hydraulic conductivity of the subsurface, which will allow monitoring of preferential flows and paths. The object of this project is to develop a numerical modelling algorithm for electrokinetic potential data. Our final goal is to develop a 3D modelling and inversion of electrokinetic signals due to water-flow through porous media under the ground surface and also an inversion of geophysical parameters into hydraulic factors.

DISCUSSION

Traditional measurements of electrokinetic potential involve the electric potential gradient between only two

points. This approach does not allow a wide spatial coverage of electric potentials at the same time and is complicated by time variations of electrokinetic potentials. To overcome this problem, this project will develop a multi-electrode array that consists of 36 electrodes around a pumping well (Figure 3). The array can also be changed to two circles in which there are 18 electrodes on each (Figure 4). Using a pumping well means that we control the water-flow, which is a very important factor to investigate hydraulic conductivity in an uncertain environment. Borehole groundwater sampling also provides information on groundwater conductivity, pH and temperature that can be used in the laboratory. Using a multi-electrode array will allow monitoring of the spatial continuity of electrokinetic potentials. The new array with a double-lined multi-channel (Figure 4) will also provide draw-down measurements without the restriction of requiring existing piezometers, and thus excellent information about aquifer parameters such as permeability and anisotropy (Fagerlund & Heinson 2003). Numerical modelling and inversion of electrokinetic signals have not been routinely undertaken. Modelling of electrokinetic potentials due to pumping tests from drill holes can be used to define the drawdown around the bore hole, and the drawdown determined may allow monitoring and mapping of the hydraulic conductivity of the ground. These can then be utilized for general geological and environmental problems.

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