TUTORIAL

Self-potential: The ugly duckling of environmental geophysics

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Self-potential (SP) is the method that everyone knows about but nobody seems to appreciate. Out of more than 850 papers published in the Symposium for the Application of Geophysics to Environmental and Engineering Problems (SAGEEP) between 1988 and 2001, 63 included SP as a key word, but most mentioned it only in passing.

This is surprising when you consider that SP is non-intrusive, fast, and inexpensive, requiring little more than a voltmeter and a few nonpolarizing electrodes, and that environmental geophysical surveys are typically low-budget operations. What is doubly surprising is that less than a handful of the 850 SAGEEP papers discussed SP anomalies of electrochemical origin, even though electrochemical potentials associated with ore bodies are by far the most important source of SP in the mining industry.

The majority of environmental papers that focused on SP as the primary geophysical method discussed the mapping of seepage in dams, embankments, leaky containment ponds, and other sources of streaming potential. Two possible reasons for this apparent lack of enthusiasm for SP among environmental geophysicists are electrical noise and difficulties with interpretation.

Exploration geophysicists are familiar with SP noise sources such as telluric currents, electrode drift, topographic effects associated with streaming potentials, photovoltaic potentials, and changes in soil composition, moisture, and vegetative cover. But environmental sites add power lines, buried utilities (some cathodically protected), grounded fences and equipment, corroding scrap metal, and other man-made sources to the list of undesired voltages. For instance, we have observed an electric rail system create an SP interference 1 km away; an interference from electric ore trains more than 20 km from the survey area; and a data logger's large increase in the SP noise levels between about 8 A.M. and 4:30 P.M., coinciding with the day shift at a nearby plant.

Effective 60-Hz notch filters in modern handheld digital voltmeters eliminate most cultural noise. In most cases the SP signal levels are one or two orders of magnitude above background noise.

Mechanisms for self-potentials. SP anomalies arise from a variety of mechanisms:

Diffusion and membrane potentials. SP anomalies are associated with gradients in concentrations of ionic species in the ground that set up diffusion potentials. If the anions and cations involved have different mobilities, then the resulting difference in diffusion rates will create an electric potential, because the faster moving ions of one charge will begin to outpace the ions of the opposite charge. The resultant electric field is just what is required to speed up the slower moving ions and maintain electroneutrality. In equilibrium, the diffusion potential, E_d, is given by:

$$E_d = \frac{RT(I_a - I_c)}{nF} \ln(C_1/C_2)$$

where I_a and I_c are the mobilities of the anions and cations respectively, n is the electric charge/ion, R is the univer-

sal gas constant, T is the absolute temperature, F is Faraday's Constant, and C_1 and C_2 are the solution concentrations creating the diffusion gradient. In general, this mechanism can create anomalies in the tens of millivolts, and is just a source of noise in most SP surveys.

Membrane potentials and diffusion potentials. Consider the "shale potential" familiar to well loggers. If shale is in contact with sandstone, a voltage will develop across the contact, because shale is permeable to Na ions but not Cl ions. Therefore, diffusion of Na from the sandstone into the shale will set up a potential gradient that tends to drive the Na ions back into the sandstone. The equilibrium between diffusion and electrically driven ion migration is given by the Nernst equation, which is the diffusion potential without the difference in ion mobilities:

$$E_d = \frac{RT}{nF} \ln(C_1/C_2)$$

Notice that magnitude of both the diffusion and membrane potentials is directly proportional to temperature, so geothermal activity will enhance these SP anomalies.

Bioelectric potentials. The ion selectivity and water pumping action of plant roots can create SP anomalies. Roots are ion-selective membranes, so it isn't surprising that they generate SP anomalies. Bioelectric anomalies can reach hundreds of millivolts. Abrupt changes in SP have been noted in the field when the vegetation changes, which are, of course, commonly associated with changes in soil composition or the underlying rocks.

Streaming potentials. Also known as zeta or electrofiltration potentials, streaming potentials arise when water or other fluids flow through sand, porous rock, moraines, basalts, etc. In areas of high rainfall, steep topography, and porous rock, streaming potentials can be of large amplitude. A 2693-mV SP anomaly on Agadak Volcano, Adak Island, Alaska, is attributed to streaming potentials. Streaming potentials are also commonly found in SP surveys over geothermal sources. The phenomenon was first studied by Helmholtz in the 19th century. For flow in a capillary tube through which an electrolyte is flowing the electric field, E, (V m^{-1}) is given by

$$E = \frac{\varepsilon \rho \varsigma}{4 \pi \mu} p$$

where ε = dielectric constant of the electrolyte (F m^{-1}), ρ = the resistivity of the electrolyte (Ωm), ζ = a parameter determined by the material of the capillary wall and electrolyte, p = pressure gradient (Pa m^{-1}), and μ = dynamic viscosity of the electrolyte (Pa s). E is in the same direction as the pressure gradient, opposite to the direction of electrolyte flow.

Mineral potentials. Most of the reported and some of the largest SP anomalies are associated with mineral deposits, notably buried sulfides. Measurements of 2 V or more have been reported. These potentials apparently arise from geochemical oxidation-reduction (redox) reactions, equivalent to the galvanic cell defined in electrochemistry.

Electrochemical Cell

Redox SP
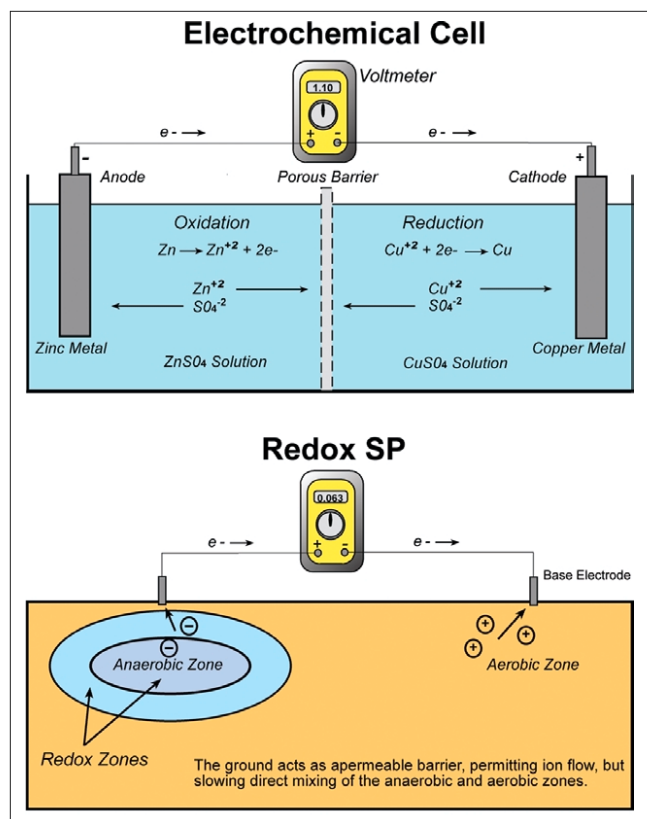
Figure 1. (Top) The redox potential difference between the two halves of a galvanic cell registers as a electrical voltage. (Bottom) The analogous situation in the field, where a redox difference can be produced by, for example, the metabolism of hydrocarbons by bacteria.

Sato and Mooney (1960) proposed the classic model, still cited today in most textbooks and papers. They envisioned a sulfide deposit astride the water table, with oxidation reactions taking place above the water table and reduction reactions taking place below the water table with the ore body acting as an inert conductor. Thus, the upper and lower portions of the sulfide deposit behave like two half-cells of a galvanic cell. The top (anode) becomes negatively charged and the bottom (cathode) becomes positively charged. In response to the electrical charge, ions migrate though the porous rock surrounding the sulfide ore body. The SP anomaly measured at the surface is simply the voltage drop created by current flow through the rock in their model.

This "geobattery" model has remained popular for more than 40 years, despite the following shortcomings (detailed in a 1985 paper by CC) of the Sato and Mooney model.

Amplitude. The Sato and Mooney model cannot account for voltages greater than about 800 mV based on the E_h potentials of sulfides, so the maximum amplitude of an anomaly generated by either pole of the geobattery relative to a reference electrode at infinity is only 400 mV. However, many field measurements of 1000 mV or more have been reported over sulfides.

Gradients. Ion transport along field lines in accordance with the Sato and Mooney model requires reasonably smooth voltage gradients, yet large gradients have been measured at the surface, underground, and by downhole logging.

Lack of a positive pole. A geobattery requires a positive and negative pole. Data show that SP measurements made on

the surface, underground, and in boreholes drilled completely though ore bodies invariably record negative anomalies relative to a base station located away from the ore body.

Water table. The Sato and Mooney model does not explain SP anomalies associated with ore bodies completely below the water table or, as with porphyry sulfide deposits, where no inert central conductor exists.

Stability. Direct measurements show that SP anomalies associated with buried sulfides are stable for at least a decade, and presumably over geologic time. Corry queries why the geobattery does not discharge, and why the voltages do not fluctuate along with the water table. Nor have seasonal voltage variations been observed. Ion transport would certainly slow as temperatures fell. SP anomalies are also found in arctic conditions in which ionic transport would be virtually nonexistent in frozen ground.

We agree with Sato and Mooney that the SP anomalies over buried sulfides are the result of redox chemistry, but we postulate that the SP electrodes merely measure the difference in redox potential between the base and roving electrode, and not the voltage drop associated with a geobattery discharging through resistive rock. In other words, as with any galvanic cell, no current will flow unless the SP electrodes are placed in separate environments where the difference in redox potential would permit spontaneous reactions. The wire between the electrodes, and not the ore body, completes the circuit between oxidizing and reducing zones (Figure 1). This would explain, for example, why there are SP anomalies associated with sphalerite and porphyry ore bodies that are nonconductive.

If a wire is connected between two materials in electrolytic contact and the oxidation-reduction potential between the materials is such that they spontaneously react, a measurable electric potential will result.

The debate over the origin of SP mineral potentials has profound implications for environmental geophysics. The Sato and Mooney model requires both a redox gradient and a buried conductor. However, if a redox gradient alone can produce large SP anomalies, then the future of SP is bright indeed, because many circumstances can lead to large redox gradients at environmental sites, particularly in the growing field of geophysical monitoring of site remediation.

Geophysical monitoring. In the last two decades, the principal application of environmental geophysics was site characterization. Although environmental geophysics has been used for everything from determining depth to bedrock to finding preferential pathways for groundwater flow, the principal application remains looking for buried metal associated with the contaminant. However, it is likely that the emphasis in the environmental field will slowly shift away from using geophysics for site characterization toward using it for site monitoring.

Geophysical monitoring may actually be easier than site characterization for two reasons: (1) By making measurements before and after the start of remediation and looking only at changes in the signal, the influence of heterogeneity can be reduced. (2) Monitoring networks are in place for days, or even years, making it possible to eliminate much of the background noise by filtering and stacking.

There are published examples of using electrical resistivity tomography and electromagnetic induction techniques to monitor site remediation, but at the vast majority of sites, program managers still rely on drilling and groundwater sampling to monitor cleanup. This may have made sense when site remediation was largely a matter of pumping the contaminated groundwater out of the aquifer and treating

it above ground. It is difficult to detect a change in groundwater contamination from levels of a few ppm down to zero using geophysics. But pump and treat technologies are rapidly being replaced by in-situ cleanup, and because this typically involves injecting something into the ground, it opens new opportunities for geophysical monitoring.

An example of this in the United States is the Strategic Environmental Research and Development Program (SERDP) issuing a call for proposals for fiscal year 2003, which reads in part: "Diagnostic procedures are likely to be technology-specific; therefore, proposals should focus on the remedial technologies, such as thermal treatment, bioremediation, permeable reactive barriers, and chemical flooding/addition. Diagnostic procedures for source zone treatment technologies are of most interest, but research that focuses on technologies implemented in groundwater probe will also be considered. Proposals that focus on pump and treat systems will not be considered."

The association between SP and thermal anomalies is well known. However, all in-situ technologies mentioned in this call for proposals may be candidates for SP monitoring given the apparent relationship between SP and redox reactions.

In 1997, researchers from Oak Ridge National Laboratory circulated potassium permanganate between two shallow horizontal wells to oxidize trichlorethelene (TCE) that was leaking off-site in a shallow sand and gravel layer. Potassium permanganate is a salt, and multielectrode resistivity successfully tracked the injection front in conjunction with numerous shallow monitoring wells. However, an SP monitoring network would probably have worked because potassium permanganate is a powerful oxidizer.

The injection of chemicals to treat contamination typically involves concentrations much higher than the contaminant, correspondingly increasing the chance of a measurable SP signal. Because the technique is so fast and inexpensive and the results are immediately apparent, prudence and economy would suggest at least a reconnaissance SP survey at most sites.

A permeable reactive barrier is simply a groundwater treatment filter installed underground. A trench is excavated perpendicular to groundwater flow and all or part of it is filled with a treatment material such as zero-valent iron filings, which will reduce most contaminants and either destroy or immobilize them. Over time, however, the mineral precipitates and iron corrosion products coat the surface, potentially affecting both the reactivity and permeability of the reactive barrier. One can envision a reactive barrier comprised of replaceable canisters, coupled with a geophysical monitoring system to warn of declining barrier performance. Candidates for the geophysical monitoring systems include resistivity, IP, and EM methods. However, to detect changes in redox, both in the barrier and in the groundwater downstream, SP should be included as the least expensive method available for continuous monitoring.

Yet another remedial technology, air sparging, focuses on gasoline and jet fuel, which are also common contaminants at environmental sites. Most fuels have a high vapor pressure, so contaminants in the unsaturated zone can be removed by circulating air between wells and removing the evaporated fuel in treatment equipment at the surface. Below the water table, fuel can sometimes be removed by air sparging, i.e., bubbling air into the groundwater.

Air sparging increases the partial pressure of oxygen in the water. Vichabian and Morgan (1999) used SP to monitor an air sparging and soil vapor extraction effort for more than two years at a test site. They measured an SP anomaly of 800-1000 mV, which they interpreted as being due to an increase in partial pressure of oxygen (they translated SP voltages to PO_2 using the Nernst equation).

Oxygenating the near surface, however, also undoubtedly changed the redox potential of the test area, and it is an open question whether or not some or all of the SP voltage they measured was related to redox changes.

Bioremediation. Natural bioattenuation, the breakdown of untreated contaminants by microbes in the soil and groundwater, may become the method of choice for dealing with gasoline leaks that resulted from corroding underground storage tanks at gasoline stations across the United States. Biodegradation proceeds quickly while there is oxygen to fuel aerobic bacteria. After bacteria use up the oxygen in the soil and groundwater, bioattenuation proceeds anaerobically in the center of the plume, and aerobically at the edges where oxygen is still available.

Anaerobic bacteria use iron, sulfur, nitrates, and other compounds as terminal electronic acceptors to metabolize hydrocarbons, creating a reduced zone in the center of the plume. The contrast between the reduced zone and the surrounding oxygen-rich uncontaminated groundwater represents an SP target.

With Kornewicz, I (JN) conducted a proof-of-principle experiment to test the correlation between SP and anaerobic zones created by microbial respiration. The site, near Oyster, Virginia, is located in the Atlantic coastal sands, and represents about the closest thing to a homogeneous sand tank that nature provides. It had been originally selected by DOE to study groundwater transport of bacteria and colloids. DOE researchers conducted extensive site characterization there, drilling numerous monitoring wells, studying soil horizons in detail at a nearby excavation, collecting ground-penetrating radar and tomographic seismic data, and performing geochemical and microbial studies on groundwater samples. They were surprised to discover a plume of oxygen-depleted groundwater flowing across one corner of the supposedly pristine site.

Researchers eventually learned that there used to be a tomato canning plant nearby, and that the spoils were dumped in waste trenches up groundwater gradient from the study site. Apparently, bacteria feasting on the tomato juice were responsible for the anaerobic groundwater plume. DOE abandoned the site as unsuitable for its purposes. DOE's loss was our gain. We inherited a well-characterized site, removed from cultural noise, with a shallow groundwater table, and with established bioattenuation of a nontoxic material.

Our study involved measuring SP over the site and comparing the results with dissolved oxygen measurements made in the still-standing monitoring wells. E_h is notoriously hard to measure in the field; dissolved oxygen measurements were used to distinguish reducing from oxidizing environments. Dissolved oxygen measurements were made using a pump attached to a custom flow-through cell to prevent oxygenation of the groundwater samples and Chemet sample vials that change color in the presence of dissolved oxygen.

SP data were collected using copper/copper sulfate nonpolarizing electrodes and a high-impedance digital voltmeter. All SP measurements were made relative to a single base electrode positioned outside the low-oxygen area. A consistent correlation was found between SP and dissolved oxygen (Figure 2).

In an SP survey it is very desirable, if not essential, to locate the base electrode in an oxidizing environment because the difference between the base and roving electrodes must

Figure 2. Proof-of-principle test at a field site near Oyster, Virginia. Dissolved oxygen (DO) measured in the groundwater (contour lines) decreased from roughly 8 ppm outside the plume to < 1 ppm inside the plume. The SP voltage measured at the surface also changed dramatically over the plume.

produce a *spontaneous* reaction if a galvanic cell is the mechanism. However, the E_h-pH conditions of the base electrode are never known and the voltage at the base electrode is an arbitrary zero point with regard to which differential voltages are measured. Also, the *negative* lead of the voltmeter is, by convention, connected to the base electrode.

Because the absolute E_h value of the base electrode is unknown, the oxidation, or redox potential, at the roving electrode may be greater (positive anomaly) or less than (negative anomaly) the arbitrary zero of the base electrode. Typically, with the base electrode in an *oxidizing* environment ($+E_h$) distant from a target in a *reducing* environment ($-E_h$), the SP anomaly is negative. But because of the inherent ambiguities, both negative and positive anomalies have been measured by investigators over similar sources. Vichabian and others (2000) measured SP anomalies over hydrocarbon spills and found negative anomalies, which they attributed to reduced zones created by bacteria, although they did not make any geochemical or microbiotic measurements. Similarly, Perry and others (1996) found negative SP anomalies associated with fuel leaks from underground storage tanks. Nash and others (1997), however, found both an unexpected electrical conductivity high and a positive SP anomaly over a hydrocarbon spill.

The future of SP. Many questions remain about the source mechanisms for electrochemical SP at environmental sites. The complexity of quantitative redox chemistry in the field is daunting. Efforts by hydrogeologists and geochemists to directly measure redox potentials in groundwater have been largely ineffective because multiple redox couples participate, and because subsurface redox reactions are rarely in equilibrium.

However, it is relatively easy to make a differential measurement compared to determining an exact value. SP has the potential to become a fast, inexpensive means of determining the areal extent of pollution plumes.

The bacterial action thought to be responsible for producing the reducing zones picked up by SP surveys will migrate downgradient with the plume. Therefore, repeated SP surveys over time will likely show the rate and direction of the pollution plume migration at a tiny fraction of the cost of drilling and water measurements. Research in this area is certainly justified.

Another result is that large-amplitude SP anomalies are likely to arise in many situations where the natural subsurface geochemistry is being altered to clean up contamination in situ, whether by thermal treatment, chemical injection, bioremediation, reactive barriers, air sparging, or other methods. Laboratory measurements can shed light on the mechanisms controlling the associated SP anomalies for better
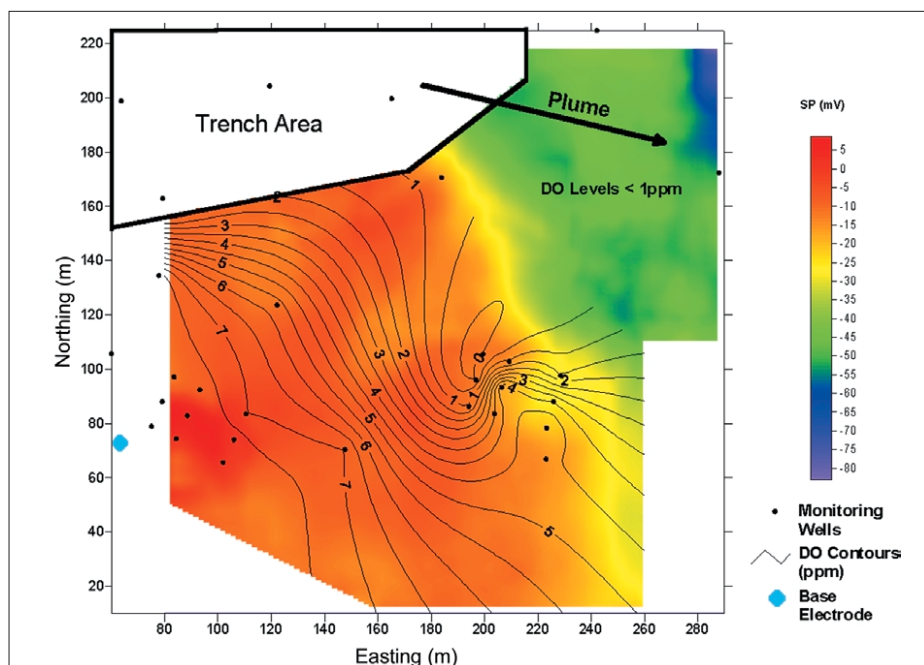
understanding and control of the remediation in the future. In the interim, SP may not replace monitoring wells, but it might reduce the number of wells needed, help site those wells and interpolate geochemical data, and detect temporal changes to trigger each round of groundwater sampling at a fraction of the current cost.

Geophysicists may thus come to view the self-potential method as a swan instead of an ugly duckling.

Suggested reading. For an introduction, read: "Applications of the self-potential method for engineering and environmental investigations," by Corwin (in *Geotechnical and Environmental Geophysics, Review and Tutorial*, SEG, v1, 1990). For a debate of Sato and Mooney's model, read: "Spontaneous polarization associated with porphyry sulfide mineralization" by Corry (GEOPHYSICS, 1985), and the ensuing discussion of Corry's paper by Leney with Corry's reply (GEOPHYSICS, 1986). For more recent papers on the electrochemical origins of SP mineral potentials read "The geobattery model: A contribution to large scale electrochemistry," by Bigalke and Grabner (*Electrochemica Acta*, 1997); "An evaluation of spontaneous mineralization potentials," by Furness (*Exploration Geophysics*, 1992), and "The relation between electric and redox potential: Evidence from laboratory and field measurements," by Timm and Möller (*Journal of Geochemical Exploration*, 2001). Case studies may be found in the Proceedings of the Symposium for the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), including: "Geophysical investigation of anomalous conductivity at a hydrocarbon contaminated site," by Nash et al. (SAGEEP, 1997); "Self potential monitoring of jet fuel air sparging," by Vichabian and Morgan (SAGEEP, 1999), and "Self-potential mapping of contaminants," by Vichabian et al. (SAGEEP, 1999). Additional case studies of interest are: "Monitoring leakage from underground storage tanks (UST) using spontaneous polarization (SP) method," by Perry et al. (SEG *Expanded Abstracts*, 1996), and "DC resistivity monitoring of potassium permanganate injected to oxidize TCE in-situ," by Nyquist et al. (*Journal of Environmental and Engineering Geophysics*, 1999). ⊫

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