Electrodic Voltages Accompanying Stimulated Bioremediation of a Uranium-Contaminated Aquifer

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Received 31 August 2009; revised 30 December 2009; accepted 29 January 2010; published 16 June 2010.

The inability to track the products of subsurface microbial activity during stimulated bioremediation has limited its implementation. We used spatiotemporal changes in electrocyclic potentials (EP) to track the onset and persistence of stimulated sulfate-reducing bacteria in a uranium-contaminated aquifer undergoing acetate amendment. Following acetate injection, anomalous voltages approaching −900 mV were measured between copper electrodes within the aquifer sediments and a single reference electrode at the ground surface. Onset of EP anomalies correlated in time with both the accumulation of dissolved sulfide and the removal of uranium from groundwater. The anomalies persisted for 45 days after halting acetate injection. Current-voltage and current-power relationships between measurement and reference electrodes exhibited a galvanic response, with a maximum power density of 10 mW/m² during sulfate reduction. We infer that the EP anomalies resulted from electrochemical differences between geochemically reduced regions and areas having higher oxidation potential. Following the period of sulfate reduction, EP values ranged from −500 to −600 mV and were associated with elevated concentrations of ferrous iron. Within 10 days of the voltage decrease, uranium concentrations rebounded from 0.2 to 0.8 μM, a level still below the background value of 1.5 μM. These findings demonstrate that EP measurements provide an inexpensive and minimally invasive means for monitoring the products of stimulated microbial activity within aquifer sediments and are capable of verifying maintenance of redox conditions favorable for the stability of bioreduced contaminants, such as uranium.


1. Introduction

Radionuclide contamination of groundwater is an ongoing problem at many former uranium ore-processing sites under the control of the U.S. Department of Energy. Continued leaching of residual uranium at such sites has resulted in low-level but persistent contamination of both groundwater and sediments within local aquifers. Research efforts are currently underway to promote the in situ removal of soluble U(VI) species via stimulated bioremediation at the Rifle Integrated Field Research Challenge (IFRC) site near Rifle, Colorado (Figure 1), the site of a former mill tailings facility. Repeated biostimulation experiments at the site [Anderson et al., 2003; Vrionis et al., 2005] have shown that acetate injection into the aquifer promotes the growth of dissimilatory metal-reducing bacteria of the family Geobacteraceae and a decline in the U(VI) content of groundwater downgradient from the injection site. The reproducible, stimulated growth of Geobacteraceae along with the correlated loss of U(VI) suggests that these organisms are responsible for the in situ reduction of U(VI), a fact corroborated by both laboratory [Finneran et al., 2002; Holmes et al., 2002; Ortiz-Bernad et al., 2004] and field studies [Senko et al., 2002; North et al., 2004; Peacock et al., 2004; Ginder-Vogel et al., 2005; Wu et al., 2006].

Prolonged addition of acetate to the aquifer results in a shift in the dominant terminal electron-accepting pathway from iron to sulfate reduction. This is evidenced by groundwater and sediment samples enriched in members of the order Desulfobacterales [Vrionis et al., 2005] and a decrease in ferrous iron and sulfate within the aquifer. An unintended consequence of this shift in metabolism is an initial decrease in the rate of removal of soluble U(VI) from groundwater [Anderson et al., 2003]. At longer time points, however, and upon cessation of acetate injection, sustained
removal of U(VI) under conditions of sulfate reduction does occur, ultimately reaching levels comparable to those achieved during the initial period of iron reduction.

While the process of U(VI) removal both during and after the period of sulfate reduction is still under investigation, it is believed to result from a variety of causes, including reductive immobilization of U(VI) by nonacetae oxidizing sulfate reducers and sorption onto a combination of cell surfaces [N’Guessan et al., 2008] and altered mineral phases [Catalano and Brown, 2005]. While these results suggest the importance of maintaining conditions of iron reduction for optimizing the reductive immobilization of U (VI), the sustained removal of U(VI) during and after stimulated sulfide reduction indicates that its onset is not completely undesirable, especially under geochemical conditions (i.e., high sulfate) where it is likely to be an unavoidable outcome of organic carbon amendment. Furthermore, the production of redox-poising constituents accompanying stimulated sulfide reduction (e.g., FeS, reduced phyllosilitates, and $\text{H}_2\text{~S}$) may offer a means for prolonging the stability of insoluble, bioreduced phases, such as $\text{UO}_2$. 

There is growing interest in the use of geophysical methods to better inform the decision-making process during environmental remediation activities. The inherent variability in rapidly delineating subsurface transformations accompanying remediation activities, such as those that occur during stimulated bioremediation, often limit the speed with which the remediation approach may be modified to improve its success. Among such methods, the self-potential (SP) technique has shown promise as an inexpensive yet sensitive means for delineating variations in subsurface geochemical conditions resulting from biological processes [Nyquist and Corry, 2002; Naudet et al., 2003; Naudet and Revil, 2005; Arora et al., 2007]. The SP method is a passive technique that measures the open-circuit voltage potential between electrodes located at the ground surface or within boreholes, with the potential-generating mechanism varying according to environmental and measurement conditions [Sato and Mooney, 1960; Corry, 1985; Bigalke and Grabner, 1997; Nyquist and Corry, 2002; Cameron et al., 2004; Minsley et al., 2007].

Under conditions where the measurement and reference electrodes are (1) located in geochemically distinct redox environments and (2) exposed to their local geochemical environment, a subset of the SP method, referred to as the electrode potential (EP) method, has been shown to be sensitive to electrochemical reactions involving the electrodes themselves [Corry, 1985; Nyquist and Corry, 2002; Williams et al., 2007; Slater et al., 2008]. When bridged through a measuring voltmeter, electrodes located in the electrochemically distinct regions constitute a galvanic cell, generating a voltage potential that persists as long as the concentration gradient is maintained. Under conditions that lead to the spontaneous flow of current when the two electrodes are connected, electrons flow from the anode during an oxidation reaction to the cathode in a coupled reduction reaction. Charge balance is maintained via electrolytic conduction through the pore space, which also acts to complete the overall circuit. Under conditions where the geochemical environment directly interacts with the electrode surface (e.g., during a corrosive process), the electrode composition will determine the nature of the measured half-cell reaction. The magnitude of the anomalous open-circuit potentials may be quantitatively interpreted in the same manner as voltages that result when using an ion-selective electrode, albeit over a scale of meters rather than millimeters.

The galvanic mechanism underlying the EP response (Figure 2) may be illustrated using the electrode pair in which the measurement and reference electrodes are composed of $\text{Cu}^0$ and $\text{Cu}^0/\text{CuSO}_4$, respectively, with the latter being a nonpolarizing electrode design frequently used for SP measurements. When a reduced electroactive species (e.g., bisulfide or $\text{HS}^-$) is present near the measurement electrode and the reference electrode is maintained in a more oxidized environment, a sulfide-dependent voltage potential of 700–900 mV will result from the coupling of the two half-cell reactions: the oxidation of $\text{Cu}^0$ (as $\text{CuS}$ or $\text{Cu}_2$) at the measurement electrode (i.e., the anode) and the reduction of $\text{CuSO}_4$ (as $\text{Cu}^0$) at the reference electrode (i.e., the cathode). Because of the high input impedance of the voltmeter (>10 M$\Omega$), there is negligible transfer of electrons during the measurement process and consumption of electroactive species is insignificant. For anodic reactions that are both thermodynamically and kinetically favorable, such as those occurring between dissolved sulfide and base metals, such a galvanic response will dominate the measured EP signal.

In the absence of $\text{HS}^-$, anomalous EP voltages may still be the result of a galvanic effect where the measurement electrode acts as a nonreactive surface sensitive to the dominant electrochemical half-cell reaction in its vicinity. In such a configuration, the measurement electrode serves the same function as the platinum electrode in an oxidation reduction potential (ORP) probe. The mechanism is relevant in the presence of aqueous ferrous iron, the byproduct of microbial iron reduction. A ferrous iron dependent voltage
potential of 550–700 mV will result from the coupling of the two half-cell reactions: oxidation of Fe$^{2+}$ at the measurement electrode surface and the reduction of CuSO$_4$ (as Cu$^0$) at the reference electrode.

Interpreting the electrode response within the context of a galvanic model makes it possible to use temporal EP anomalies to monitor geochemical changes induced by the stimulation of microbial activity. Here we show that the appearance and persistence of dissolved sulfate correlates with the generation of significant EP voltage anomalies indicative of subsurface microbial sulfate reduction. Furthermore, spatiotemporal variations in the onset and sustenance of the EP anomalies appear to track the location of active metabolism within the aquifer, offering an indirect means for verifying geochemically reduced conditions conducive to the removal of aqueous uranium. By interpreting such potentials within the context of predictable and quantifiable galvanic reactions, the EP monitoring approach offers a sensitive, inexpensive and minimally invasive means for detecting the presence of metabolic end products, such as dissolved sulfide and ferrous iron.

2. Materials and Methods: Site Description and Experimental Approach

A comprehensive description of the local geology, hydrology and geochemistry of the Rifle IFRC site, as well as the general methodological approach to acetate injection, has been presented elsewhere [Anderson et al., 2003; Vrionis et al., 2005; Yabusaki et al., 2007]. Briefly, the site is located on a floodplain, ∼9.0 ha in area, in northwestern Colorado (Figure 1). The local aquifer is composed of an unconsolidated mixture of alluvial sands, silts, clays and gravels deposited by the adjacent Colorado River. The aquifer thickness is ca. 6.5 m, with the saturated interval occurring at a depth of approximately 3.5 to 4.0 m below ground surface (bgs). The hydrology of the site is characterized by relatively high groundwater velocities (∼0.30 m d$^{-1}$) and a water table that varies according to river stage, rising by as much as 1.5 m during periods of peak runoff. Large variations in hydraulic conductivity exist over the saturated interval, with values ranging from 0.50 to 50 m d$^{-1}$. Core recovery during well installation has repeatedly identified a 0.5–0.7 m thick, high-permeability sandy layer at depth of ∼3.7 m bgs and spanning the water table. This unit may contribute to enhanced rates of groundwater flux during recharge events, acting as a conduit for the introduction of partially oxygenated groundwater. The site is underlain by the relatively impermeable weathered clays-tone of the Wasatch formation, which acts as a lower boundary to fluid flow.

Groundwater samples were obtained from a series of monitoring wells located within a test area encompassing approximately 50 m$^2$. A single background monitoring well was located 3.5 m upgradient from an injection gallery positioned perpendicular to groundwater flow and composed of five boreholes spaced at 0.6 m intervals (Figure 1). Four downgradient monitoring wells were located at 1.5 m intervals, beginning at a distance of ∼1.0 m from the injection gallery. Two specially designed well casings incorporating metallic copper (Cu$^0$) electrodes were located 2.0 m downgradient (SP-1) and 1.0 m upgradient (SP-2) from the injection gallery (Figures 2 and S1, available as auxiliary material). The casing materials (PVC; 5 mm slot size) and method of completion of the two electrode wells were identical for all injection and monitoring wells. Each of the electrode-modified casings incorporated eleven bands of Cu$^0$ (5.7 cm diameter, 2 cm width) located at 25 cm intervals along the casing length (Figure S1). After installation, the upper and bottommost electrodes in each well were located at 4.0 m and 6.5 m bgs, respectively. The electrodes were attached to the outside of the well casing using copper rivets and connected to the surface via insulated wires; all connections were made water tight using an epoxy sealant. After installation, the electrodes were allowed to equilibrate for 30 days before beginning acetate injection.

Ten electrodes from each of the two wells spanning the 4.0–6.25 m bgs depth interval were connected to a high-

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1Auxiliary materials are available in the HTML. doi:10.1029/2009G001142.
impedance, multichannel voltmeter programmed to measure the open-circuit potential between each electrode and a surface-based reference electrode at 6 h intervals. Continuous recording of the EP signals began 2 days prior to the onset of acetate injection. The measurement convention was such that the negative lead of the voltmeter was connected to the reference electrode and the positive lead connected to the downhole electrode. The reference consisted of a Cu\(^{0}/\text{CuSO}_4\) nonpolarizing electrode located in a shallow, tarp-covered hole in the vicinity of the southeastern most injection well; the contact resistance between the reference and each of the cabling-affixed Cu\(^{0}\) electrodes ranged from 500 to 900 \(\Omega\). Allowing time for equilibration, installation of the reference electrode occurred immediately after installation of the borehole electrodes. The tarp prevented excess moisture from submerging the reference electrode during rainfall events and sporadic measurements of contact resistance fell within the aforementioned range.

Current-voltage and current-power relationships were periodically determined between the bottommost electrode (6.5 m bgs) in each well and a second surface-based Cu\(^{0}/\text{CuSO}_4\) reference electrode by measuring the voltage drop across a range of resistances from 4 M\(\Omega\) to 10 \(\Omega\). A second surface-based electrode was used in order to minimize disturbance of the reference electrode resulting from current flow during the current-voltage and current-power measurements. These measurements were made before, during (days 58 and 85), and after biostimulation (day 115). Following reequilibration of the open-circuit electrode response, current flow between the same two electrode pairs was determined by measuring the voltage drop across a known resistance (500 \(\Omega\)) for a fixed length of time (ca. 20 h) both before and during biostimulation (day 59).

Groundwater was pumped from an upgradient portion of the aquifer into a surface storage tank and amended with sodium acetate and potassium bromide in quantities sufficient to achieve in situ concentrations of 10 mM and 1 mM, respectively, upon injection. Acetate-amended groundwater was introduced to the aquifer over the entire saturated thickness (18 mL/min per borehole; 3.5 to 6.5 m bgs) using a combination of peristaltic and crosswell mixing pumps to continuously cycle the injectate between the five injection wells to achieve better uniformity in the distribution of acetate during the injection phase.

Acetate was injected over a 68 day period between July and September 2006, during which time groundwater was systematically sampled at 2 to 14 day intervals from each of the monitoring wells to characterize changes in geochemical composition. While groundwater samples were obtained for each of the nonelectrode monitoring wells prior to the injection of acetate, samples were not obtained from the electrode-bearing wells until 42 days after starting the injection of acetate. After this time, groundwater samples were obtained from all of the wells at regular intervals for the duration of the experiment. Both the geochemical sampling and the multielectrode voltage logging continued for a total of 185 days, or 117 days following the cessation of acetate injection.

Groundwater was sampled from each well over the 4.1–4.4 m bgs depth interval using a peristaltic pump connected to a flow-through multiparameter probe designed to measure dissolved oxygen, fluid conductivity, pH, and redox potential. All wells were purged until the parameters stabilized (ca. 12 L; 0.5 L min\(^{-1}\)), after which time the probe was disconnected and groundwater samples were taken directly from the pump outflow. All samples were filtered with 0.2 \(\mu\)m pore size syringe filters before preservation. Samples designated for U(VI) and \(\text{SO}_4^{2−}\) analysis were placed into sterile, no-headspace 15 mL tubes, while those designated for acetate analysis (19 mL) were placed into no-headspace glass containers and preserved with 1 mL of 0.1 M H\(_2\)SO\(_4\). These samples were returned via overnight courier to the laboratory and stored at 4°C prior to analysis. Ferrous iron and sulfide analyses were performed immediately upon sampling, with the samples diluted, as needed, using deionized water.

Uranium was measured by kinetic phosphorescence analysis as previously described [Finneran et al., 2002]. Acetate was measured with high-pressure liquid chromatography using a fast-acid analysis column with an 8 mM H\(_2\)SO\(_4\) eluent and absorbance detection (210 nm). Sulfate was determined via ion chromatography using an AS4A-SC analytical column with a carbonate/bicarbonate eluent (1.8 mM/1.7 mM). Ferrous iron and sulfide concentrations were determined colorimetrically by previously described techniques [Cline, 1969; Lovley and Phillips, 1987].

3. Results

3.1. Impact of Acetate Injection on Electrodic Potential Response

During the 30 day equilibration period prior to acetate injection, the open-circuit potentials reached quasi steady state values ranging from \(-310\) to \(-440\) mV. The range of baseline voltages is likely due to variability in the immediate geochemical conditions surrounding each electrode and the extent to which each electrode was electrically coupled to the sediments. Following the injection of acetate, a pronounced increase in voltage magnitude was observed for both wells at all electrode locations (Figures 3 and 4). As a result of the measurement convention, the anomalous EP effect is reported as an increase in voltage magnitude, with values becoming more negative with time (e.g., \(-400\) mV to \(-900\) mV).

In the case of the downgradient electrode well (SP-1), increases in voltage magnitude from preinjection values were observed for all electrode locations within the first 20–25 days (Figure 3). Across the depth interval, there was considerable variability in the time it took to reach the most negative EP values. In general, the shallowest electrode locations, and in particular, the locations closest to the water table, exhibited the longest lag times before reaching their most negative value. Upon reaching values between \(-850\) and \(-900\) mV, the EP values fluctuated within the range from \(-740\) to \(-900\) mV throughout the period of acetate injection.

Although injection of acetate into the aquifer was halted after 68 days, EP values more negative than \(-800\) mV persisted for an additional 50 days (Figure 3). The length of time that such voltages persisted generally increased with depth. After a total elapsed time of 115 days, or 47 days after acetate injection was halted, EP values across the entire measurement interval approached relatively uniform levels of \(-550 \pm 40\) mV.
Electrodes located upgradient from the injection gallery never yielded EP anomalies in excess of $-810 \text{ mV}$. Shortly after beginning the acetate injection, voltages along the length of SP-2 reached relatively stable values of $-650 \pm 25 \text{ mV}$ (Figure 4). Voltages remained within this range for the duration of the injection period, except for a few electrode locations where EP values approached $-800 \text{ mV}$ over the final 5–7 days of the injection period. Immediately following cessation of acetate addition, EP values rebounded to levels of $-500$ to $-550 \text{ mV}$ remaining relatively constant for the duration of the experiment.

Figure 3. Electrode voltages acquired along well SP-1. The depth to each measurement electrode and the time elapsed since the start of acetate injection are shown on the vertical and horizontal axes, respectively, with the color bar representing the magnitude of the electrode potential signal. The potentials were diagnostic of stimulated sulfate reduction, with elevated sulfide concentrations present during the indicated interval (letters a–c). Acetate injection was halted on day 68, with levels falling below detection by day 84 (letter b).

Figure 4. Electrode potential data acquired along well SP-2, with axes, color scale, and letters a–c identical to those shown in Figure 3.
Direct comparison of the temporal voltage response for a discrete electrode location in each well (5.0 m bgs) reveals several interesting features (Figure S2). Although the onset of the EP anomalies occurs at a similar time following the injection of acetate, the persistence of the anomalies and their absolute magnitude is distinct for both locations. Following the first 20 days, voltages in SP‐2 reach a relatively stable value of \(-670\) mV, while the values recorded in SP‐1 continue to decrease for another 8 days, reaching a value of \(-840\) mV by day 28. Subsequently, the voltages in both wells fluctuated within a narrow range before transitioning to relatively stable, postamendment levels. The transition was delayed in SP‐1 relative to SP‐2 by 31 days.

Current‐voltage and current‐power relationships were determined for each EP monitoring well before, during, and after acetate injection. While there was negligible current flow between the measurement and reference electrodes prior to starting acetate injection (data not shown), when measured 58 and 85 days into the experiment, current and power densities for both electrode pairs were significantly elevated above baseline (Figure 5). Following the postinjection rebound in EP values, current flow increased by approximately 2 orders of magnitude. Power density decreased rapidly over the first 1.5 h of measurement, reaching a quasi steady state value of \(1.0 \pm 0.15\) mW/cm\(^2\) for the remaining 18 h recording interval.

3.2. Impact of Acetate Injection on Aquifer Geochemistry

Prior to the injection of acetate, the geochemical composition of the groundwater was fairly consistent across the experimental plot, having very low dissolved oxygen (<6 µM), circumneutral pH (ca. 7), relatively high specific conductivity (ca. 2400 µS cm\(^{-1}\)), and SO\(_4^{2-}\) and U(VI)
an increase in pH (Figure 6c). Neither geochemical indicator returned to baseline levels until significant depletion of sulfide occurred approximately 24 days after acetate injection ceased. Subsequently, downgradient concentrations of Fe$^{2+}$ increased steadily over the remainder of the experimental period, whereas upgradient concentrations remained unchanged or decreased somewhat over the same interval. The rebound in EP values observed in both electrode wells after halting acetate injection closely tracked the transition from a sulfide-dominated system to one characterized by elevated concentrations of Fe$^{2+}$ (Figure S4). Overall an excellent temporal correlation was found to exist between the downgradient EP response and the sulfide and ferrous iron concentrations, $E_h$, and pH values observed in M-21.

[28] As expected given its upgradient location, sulfide concentrations in SP-2 were typically below detection over the same sampling period (data not shown). Sulfide concentrations measured in SP-1 after day 42 were similar to concentrations in the other downgradient wells, although higher levels were occasionally detected (Figure S5). The accumulation of sulfide in the downgradient wells was always accompanied by a concomitant decrease in sulfate (data not shown), levels of which did not return to background values until 30 days after acetate injection ceased.

[29] Dissolved uranium concentrations began to decrease downgradient of the injection gallery within 5 days after starting acetate injection (Figure S6). Uranium concentrations decreased to their lowest level after 27 days, after which time they rebounded somewhat for the duration of the injection. The initial decrease coincided with the accumulation of Fe$^{2+}$ and extended into the period of sulfide accumulation. The rebound in uranium closely tracked the rapid increase in pH (Figure 6c) and the near complete removal of sulfate (data not shown). Following the end of acetate injection, uranium concentrations fell to their lowest levels, with a high degree of removal occurring for another 50 days. EP values in excess of $-800$ mV correlated generally with high rates of uranium removal over the entire experimental period and strongly in the period following the cessation of acetate injection. Once EP values fell below $-650$ mV, significant removal of uranium continued for a period of less than 15 days.

3.3. Galvanic Assessment of Self-Potential Signals

[30] Laboratory EP measurements were made using a galvanic cell to explore the mechanism underlying the anomalous voltages observed during sulfate reduction. As sulfide concentrations within the anodic chamber were increased from 0.004 to 4 mM, the absolute value of the EP voltage measured between the cathodic reference electrode ($Cu^0/CuSO_4$; 1 M CuSO$_4$) and anodic measurement electrode ($Cu^0$) increased from 120 to 938 mV, respectively (Figure 7). A strong correlation existed between the EP values and the sulfide-mediated cell potentials for concentrations in excess of 0.01 mM. Below this concentration, the theoretical cell potentials significantly overpredicted the measured EP response, in agreement with previous findings [Williams et al., 2007]. Current-voltage and current-power relationships using the 1 mM concentration confirmed the transfer of electrons from anode to cathode upon completion of the circuit, with the results (data not shown)

Figure 6. Temporal relationship between three key geochemical parameters measured in well M-21 and the electrochemical potential (EP) response of a discrete electrode located 5.0 m below ground surface in well SP-1 (bold line, no squares). (a) Sulfide, (b) $E_h$, and (c) pH. Variation in the EP response during the period of sulfate reduction (15–100 days) is believed to result from differences in the dominant sulfide-mediated anodic half-cell reaction. Geochemical conditions that favor the stability of either CuS or Cu$_2$S will result in EP values that differ by approximately 180 mV (Figures 7 and S7).

concentrations ranging from $7.2 \pm 0.2$ mM, and $1.5 \pm 0.1 \mu$M, respectively. Background concentrations of ferrous iron ($Fe^{2+}$) showed greater variability, ranging from $4.5 \mu$M in the upgradient well to $3.5$–$45 \mu$M in the downgradient wells.

[27] Following the injection of acetate, geochemical conditions downgradient from the injection gallery changed rapidly. Acetate and bromide (data not shown) were detected in the downgradient wells within 3 days. Both species remained at detectable levels for the duration of the 68 day injection period, with acetate not falling to levels below detection until 16 days after injection was suspended. The concentration of sulfide in the downgradient wells rose rapidly after day 15, fluctuating somewhat, but remaining elevated for the duration of the injection period and beyond (Figure 6a). A significant decrease in redox potential (Figure 6b) accompanied the accumulation of sulfide, as did
Our results confirm that electrochemical interactions between both sulfide concentration gradients and yield voltages predictable from electrode configurations EP anomalies reflect geochemical species mediating the galvanic reactions may either be reactive or passive with respect to the electrode surface. In the case of the former, bisulfide (the dominant aqueous sulfide phase at pH ≥ 7) can react directly with the measurement electrode while the latter is the dominant aqueous phase as long as sulfite is present. Bisulfide oxidizes to sulfate at the measurement electrode and serves the same function as the reference electrode, here written as a reduction reaction:

\[ \text{CuS}_{(s)} + \text{H}^+ + 2e^- \rightarrow \text{Cu}^0_{(s)} + \text{HS}^-_{(aq)} \quad E^0 = -0.338 \text{ V} \quad (1) \]

\[ \text{Cu}_2\text{S}_{(s)} + \text{H}^+ + 2e^- \rightarrow 2\text{Cu}^0_{(s)} + \text{HS}^-_{(aq)} \quad E^0 = -0.516 \text{ V} \quad (2) \]

where the copper sulfide phase favored (CuS or Cu\textsubscript{2}S) depends upon the sulfide concentration and the specific pH and Eh conditions surrounding the electrode (Figure S7). Under persistent sulfidic conditions, variations in these three parameters yield potentials that can vary over a range of nearly 180 mV.

Under conditions where Fe\textsuperscript{2+} is the dominant aqueous species in proximity to the electrode, the measurement electrode surface is inert and serves the same function as the platinum electrode in an ORP probe:

\[ \text{FeOOH}_{(s)} + 3\text{H}^+ + 1e^- \rightarrow \text{Fe}^{3+}_{(aq)} + 2\text{H}_2\text{O} \quad E^0 = 0.661 \text{ V} \quad (3) \]

where the form of the iron oxide (here, goethite) determines the value of the reduction potential. Mineralogical analysis of aquifer sediments from the Old Rifle site has identified goethite as a dominant oxide phase, and its inclusion in (3) yields cell potentials in excellent agreement with the EP values observed under Fe\textsuperscript{2+}-rich conditions (Figure S8).

In the absence of competing reactions, the cathodic half-cell reaction is simply that of the standard Cu\textsuperscript{2+}/Cu\textsubscript{2}S\textsubscript{4} reference electrode, here written as a reduction reaction:

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0_{(s)} \quad E^0 = 0.340 \text{ V} \quad (4) \]
[37] With the measurement and reference electrodes thus configured, the reduction potentials for the coupled half-cell reactions may be calculated, corrected for concentration-specific effects using the Nernst equation, and subtracted to yield the overall cell potential for the galvanic pair.

[38] Laboratory experiments in which sulfide concentration gradients were systematically varied showed a positive correlation between the magnitude of the measured EP anomaly and the theoretical cell potentials (Figure 7), particularly for sulfide concentrations in excess of 10 µM. Given the sulfide concentrations observed during the field biostimulation experiment (30–600 µM), equations (1) and (2) yield theoretical cell potentials of 740–970 mV, respectively, in close agreement with the observed EP anomalies. Consequently, the EP anomalies may be used as a semiquantitative means for assessing redox zonation under field conditions, especially as it pertains to the activity of sulfate-reducing microorganisms.

[39] Hydrogeological variability influences the pattern of acetate delivery, thereby controlling the onset of sulfate reduction within the Rifle aquifer. The initial accumulation and subsequent dispersal of sulfide can be documented using the temporal EP response. In general, the deeper electrodes responded more rapidly than the shallower electrodes. Furthermore, EP values for locations closer to the water table rebounded faster than deeper locations after acetate addition ceased. The high-permeability sandy layer straddling the water table may provide a conduit for oxygenation of groundwater, inhibiting the onset of sulfate reduction and limiting its persistence at shallower as compared to deeper locations in the aquifer. These results indicate the utility of EP measurements for assessing the impact of vertical heterogeneity on remediation efficacy, an important criterion when implementing remediation approaches across large spatial scales.

[40] The EP monitoring results suggest eventual delivery of nutrients throughout the saturated profile downgradient of the injection gallery, an important criterion for bioremediation success at this site [Vrionis et al., 2005]. The strong depth dependence of the onset of sulfate production in downgradient locations, as indicated by the vertical stratification in EP values (Figure 3), indicates that growth of sulfate-reducing bacteria exclusively within the wellbore is not the primary source of the EP response. Geochemical stratification within the wellbore should be rapidly eliminated by diffusion and direct mixing resulting from weekly pumping of 5 to 7 L purge volume during fluid sampling.

[41] As shown in Figures 3, 6, and S2, the temporal electrode response during the period of active sulfate reduction varied within the 178 mV range bracketed by the CuS- and Cu2S-forming reactions. Voltage fluctuations within these bounds are expected and diagnostic of sulfate reduction, and they need not be ascribed to an erratic electrode response that yields noisy or questionable data. As shown in Figure S7, expansion of the stability field of CuS occurs as sulfide concentrations increase. Consequently, EP values indicative of CuS rather than Cu2S formation may be diagnostic of higher sulfide concentrations in proximity to the electrode surface. However, changes in pH and Eh also alter the stability of the two copper sulfide phases.

[42] It is important to note that sustained uranium removal corresponded to EP values in excess of ~800 mV, reflective of geochemical conditions favorable to the stability of the CuS/S, rather than the CuS couple. Fluctuations of EP anomalies toward conditions conducive to the stability of CuS correlate with higher aqueous uranium concentrations in the downgradient wells. This may result from either the remobilization of formerly sequestered uranium or reduced rates of uranium removal. Regardless, geochemical conditions that yield EP anomalies more negative than ~800 mV appear to offer a diagnostic means for assessing conditions favorable for the sustained immobilization of uranium.

[43] The predicted potentials when coupling the anodic oxidation of Fe2+ to the cathodic reduction of Cu2+ at the reference electrode for a range of Fe2+ concentrations are shown in Figure S8. The abrupt transition in downgradient EP values following termination of sulfate reduction correlates with the steady increase in Fe3+ above background levels (Figure S4). Measured Fe2+ concentrations correspond to those estimated from EP data (Figure S8). While the mechanism of Fe2+ generation was not confirmed, the postinjection increase in Fe2+ in the downgradient wells is inferred to result from residual microbial iron reduction, the subsequent release of Fe2+ following the oxidation of FeS precipitated during sulfate reduction, or both. The steady decrease in EP magnitude for the downgradient locations even under conditions where Fe2+ concentrations increase from 10 to 40 µM is explained via the galvanic model when the predicted cell potentials are corrected for the temperature decrease from 17°C to 10°C observed during geochemical sampling (Figure S8).

5. Conclusions

[44] Our results show the potential of using galvanic techniques for efficiently monitoring regions of stimulated bioremediation, an emerging approach for sequestration of toxic metals and radionuclides. Specifically, we have shown that the accumulation of metabolic end products near an electrode surface during biostimulation creates electrochemical changes that are directly detectable using the electrochemical potential method under field conditions. We have resolved spatiotemporal changes in open-circuit potentials resulting from variations in the onset, location, and sustenance of sulfate reduction, as well as those resulting from the accumulation of Fe2+ associated with iron reduction or its release accompanying FeS oxidation. EP measurements using robust, inexpensive, and widely deployable metallic electrodes may thus be useful for evaluating the sustenance of redox conditions favorable for the long-term stability of reduced precipitates, better enabling the postclosure management of contaminated sites.

[45] Acknowledgments. Funding was provided by the Environmental Remediation Science Program, Office of Biological and Environmental Research, U.S. Department of Energy (DE-AC02-05CH11231 to LBNL; cooperative agreement DE-FG02ER63446 to PNNL). We thank Qusheng Lin (University of Oregon) for his assistance with constructing the Eh-pH diagram for the Cu-S-O system.

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