Electron Shuttles in Redox Processes: Characterization, Quantification and Remediation Optimization

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Redox (reduction-oxidation) processes direct the ultimate success of *in-situ* remedial processes in an aquifer. As redox processes progress, electron acceptors are consumed and, ultimately, depleted. Electron shuttles may be used to extend the available electron acceptors to include ferric iron that may otherwise be biologically unavailable. Electron shuttles have two forms: one oxidized and one reduced. The role of these shuttles is catalytic. As the microbial flora oxidizes the organic substrates, it reduces oxidized electron shuttles. These shuttles then react with ferric iron in the aquifer matrix, passing the electron on to the ferric iron and re-oxidize themselves.

The use of electron shuttles in microcosm studies has been applied to sewage treatment, to the remediation of ground water contaminated with chlorinated ethenes, hexavalent chromium or uranium. Further, the microcosm studies have provided detailed accounts of the role of electron shuttles in these processes. Unfortunately, most of the work that has been done has utilized AQDS (anthroquinone-2,6-disulfonate). While AQDS is a "model" electron shuttle that is easily obtained and simple to use, it is considerably more soluble than most electron shuttles and has atypical electrochemical properties, limiting the applicability of the microcosm studies in situations where the electron shuttle is very different from AQDS.

Electron shuttles are typically found in humic substances. At field scale electron shuttles have been used to enhance biological reductive dechlorination of chlorinated ethenes and to promote anaerobic oxidation of vinyl chloride. The electron shuttles used in field remediations are often indirectly administered (*e.g.* as bark mulch). Such applications are likely to produce a variety of shuttles. Further, while these studies have presented invaluable information and significantly advanced our understanding of the role of electron shuttles in groundwater remediation, key information has been missing from the field studies regarding the quantity and type of electron shuttles present in the groundwater.

It would require development of several analyses to measure all of the possible electron shuttles. To develop those analyses would be costly and the price of the analytical suite necessary to characterize the electron shuttles present at a site would also be very costly. To avoid that problem, but still provide information about the quantity and type of electron shuttle in the groundwater, we have developed a Total Electron Shuttle (TES) test in which all electron shuttles are measured and reported versus a standard response that AQDS would generate.

The method relies upon pre-treating the sample to isolate the humic fraction, reducing that fraction, removing the reducing agent and then letting the reduced fraction re-oxidize by reducing ferric oxide. The final quantification relies upon measurement of the ferrous iron produced by that reduction. We present some examples of the application of TES concentrations to compare effectiveness of some potential electron shuttle amendment solutions.