Optimizing short- and long-term dechlorination through *in situ* pH adjustment

An Executive White Paper

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Enhanced reductive dechlorination (ERD) is a proven approach to groundwater remediation of chlorinated ethene and ethane contamination. However, remediation professionals can achieve greater immediate and sustainable results by using a product like **EOS® AquaBu*pH*™** which:

- Provides organic carbon substrate to stimulate bioactivity;
- Provides buffering capacity to adjust pH and promote rapid dechlorination;
- Sustains optimal pH range and extends dechlorination activity for three years and beyond with a single injection; and
- Avoids the various downsides associated with some ERD applications.

Optimal pH for Site Dechlorination

Studies have demonstrated that the optimal pH range for microbial dechlorination is 5.5-7.5. For example, Vainberg et al. (2006) tested BAC-9™, a commercially available bioaugmentation culture containing a mixture of sulfate-reducing bacteria, *Dehalobacter spp*., and *Dehalococcoides spp.,* to determine the optimal range for PCE degradation. Figure 1 shows the dramatic conclusions of the Vainberg study. The PCE reduction rate was greater than 1 mg/L x hr between pH 5.5 and 8.1, with the highest degradation rate (1.5 mg/L x hr) being achieved between pH 6.0 and 6.5. PCE degradation was almost non-existent below pH 5.0 or above 8.6.

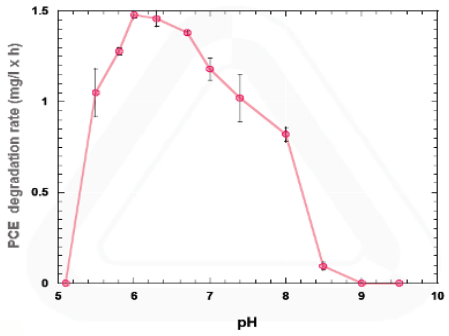

Figure 1
Source: Vainberg et al. (2006)

Eaddy (2008) evaluated the effect of pH on the conversion of vinyl chloride (VC) to ethene on the US Department of Energy's Savannah River Site culture. Figure 2 shows that a pH of 7.0 was optimum for VC degradation with some inhibitory effects at pH 6.5. VC degradation was strongly inhibited at pH of 6.0 and completely inhibited at a pH of 8.5 and 5.5.

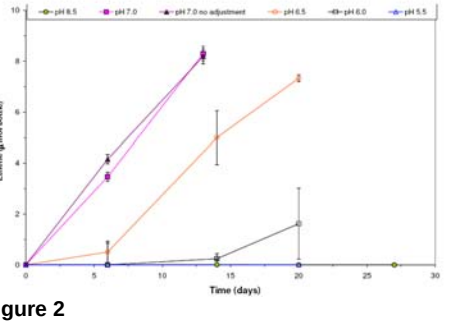

Figure 2
Source: Eaddy (2008)

ERD and pH Adjustment Techniques

ERD achieves dechlorination rates by stimulating specific dechlorinating bacteria in contaminated sites, such as *Dehalobacter spp* and *Dehalococcoides spp*. However, these bacteria are pH sensitive and are ineffective in groundwater with a pH below 6. ERD treatments frequently incorporate inorganic buffering compounds such as sodium

bicarbonate ($NaHCO_3$) or caustic soda (NaOH) to increase pH levels above 6, but these approaches entail repeat applications, ongoing maintenance effort and handling hazards. In addition, these compounds can significantly increase the sodium (Na) content of the aquifer, which can create regulatory challenges in States with groundwater standards for sodium.

Commonly employed buffering agents can yield the following negative effects:

- Calcium Carbonate ($CaCO_3$) – With a pH of 8.3, calcium carbonate (limestone) is a relatively weak buffer and has low solubility, which limits its ability to disperse into the site effectively.
- Baking Soda ($NaHCO_3$) or Soda Ash (Na_2CO_3) – With a relatively weak pH of 8.3, baking soda falls short of providing a long-term solution for pH adjustment. In the presence of acidic groundwater, both baking soda and soda ash are associated with CO_2 degassing, especially if needed in large quantities. CO_2 degassing can clog pore spaces, leading to reduced permeability. Major concerns with both baking soda and soda ash are the need to reapply and the potential of increasing the sodium concentrations in groundwater, resulting in associated violations of ground water quality standards.
- Caustic Soda (NaOH) – Given its high pH (14), an excess of caustic soda added to the aquifer may cause the pH to overshoot and inhibit dechlorination. Even dilute solutions of caustic soda pose health and safety concerns for those handling the product.

pH Adjustment with AquaBu*pH*™

AquaBu*pH*™ is a proprietary bioremediation product available through EOS Remediation. Along with providing highly effective immediate- and long-term pH optimization and site dechlorination, **AquaBu*pH*™** delivers numerous other advantages over typical ERD remediation processes and products.

AquaBu*pH*™ is a pre-mixed emulsion combining soybean oil with a suspension of a particulate alkaline pH buffering material. With a pH of ~9, **AquaBu*pH*™** is safe to handle and delivers better buffering capacity than calcium carbonate or baking soda, without the risk of overshooting optimal pH inherent in caustic soda. Also, because of its low sodium content, **AquaBu*pH*™** does not risk the regulatory challenges of buffering materials with higher sodium content.

AquaBu*pH*™ is manufactured through a special blending process that encapsulates buffering particles within oil droplets. The result is that buffering particles can be distributed throughout the aquifer with the emulsion without reducing permeability of the aquifer at the injection site. Within a short period of time, the droplets attach to the aquifer solids, providing an ideal environment not only for reductive dechlorination but also for sequestration of the chlorinated solvents.

The buffered oil droplets provide an organic carbon source and long-term pH stabilization with a single application. Studies have shown that **AquaBu*pH*™** lasts in the environment for more than three years without replenishment, delivering both organic

carbon substrate to stimulate bioactivity and extended buffering capacity superior to other pH adjustment chemicals and approaches.

Key Benefits

- A stable soybean oil emulsion with known ability to stimulate ERD;
- Product pH of ~9 resulting in pH adjustment of groundwater to a more favorable range for bioactivity;
- Small particle size for effective distribution into the aquifer without reducing permeability at the injection site;
- Long-term pH adjustment to sustain complete reductive chlorination of many chlorinated solvents to nontoxic end products;
- Immediate and sustained benefits from a single application;
- No health and safety, environmental or regulatory challenges related to high-sodium buffering agents or caustic agents; and
- Effective treatment for chlorinated solvents, energetic materials (perchlorate, RDX, TNT, etc.), and nitrate.

Case Study: Naval Weapons Station, Charleston, SC

Initial analysis showed the site to be located in clayey sand (8 to16 ft bgs) in a moderately reducing swamp deposit with shallow groundwater, a very low gradient (0.0024 to 0.0146 ft/ft) and an average groundwater pH of 5.9. TCE concentrations ranged between 10,000 and 28,000 µg/L; *cis*-DCE concentrations ranged from 200 to 400 µg/L.

The pilot area consisted of a 20 x 20 ft grid with 16 injection points. An initial injection was performed with an emulsified oil substrate that resulted in some conversion of TCE to *cis*-DCE, with little degradation of *cis*-DCE after 100 days and no significant vinyl chloride (VC) or ethene production. After 2+ years, groundwater in the treatment grid showed an average pH of 4.7 to 6.8. Microcosm studies demonstrated that low pH prevented the complete reduction of *cis*-DCE to VC and ethene.

At that point – Day 866 of the study – **AquaBu*pH*™** was injected at 19 points throughout the grid. The groundwater pH immediately and dramatically increased to 8.8. Aquifer sediment pH also increased immediately, bringing 80% of the aquifer thickness to a pH of 6.4 to 7.7 from a pre-injection pH of 4.9 to 5.3.

Over the next year, the pH stabilized in test wells between 7.1 and 7.5. By Day 1,248, pH levels were ~7, and *cis*-DCE and TCE were below detection. Although some VC remained, the concentration was substantially reduced, and 50 to 200 µg/L ethene were measured.

Microbial populations were measured after both the initial substrate injection and the **AquaBu*pH*™** injection. Background data suggested that *Dehalococcoides spp.* were present in the aquifer. In the test cell, after exposure to the lowered pH, the *Dehalococcoides spp.* population decreased to below detection. After the **AquaBu*pH*™** injection, the groundwater and aquifer pH increased to 6.0 to 8.5, resulting in a large

increase in both the *Dehalococcoides spp.* population and the population of microbes containing the TCE reductase enzyme.

Conclusion

The process of ERD creates an anaerobic environment conducive for microbially-mediated biodegradation of chlorinated solvents. When aquifer pH is too low or too high, these microbes do not function effectively. Buffering the groundwater and aquifer increases microbial activity and results in higher dechlorination rates. The application of common buffers can develop high concentrations of sodium in the aquifer, leading to some regulatory challenges. **AquaBu*pH*™** provides a long-term buffering capacity as well as a carbon source in one, easily injectable substrate for optimal immediate and long-term dechlorination.

About EOS Remediation

The use of emulsified oils for groundwater bioremediation is a significant advancement in the treatment of groundwater contaminated with chlorinated solvents, energetic materials, nitrates, oxidized heavy metals, and radionuclides. The proven **EOS®** technology substantially reduces the cost to restore contaminated aquifers. **AquaBu*pH*™** enhances **EOS®** bioremediation technology by adding long-term pH adjustment capabilities to the existing product for applications where adjustment is necessary to optimize results.

EOS Remediation uses sustainable green chemistry in its family of groundwater bioremediation products. The addition of emulsified vegetable oils provides food for the microorganisms and stimulates biodegradation activity. The **EOS®** technology has successfully turned land once deemed unusable into productive and safe real estate. The company annually completes more than 200 projects worldwide. Since first developed by Dr. Bob Borden in 1999, millions of pounds of **EOS®** have been successfully applied at sites throughout the world.

For additional information on EOS Remediation, please visit www.eosremediation.com or call 888.873.2204.

EOS® is a registered trademark of EOS Remediation, LLC.

References

Eaddy, Ashley, 2008. *Scale-Up and Characterization of an Enrichment Culture for Bioaugmentation of the P-Area Chlorinated Ethene Plume at the Savannah River Site*. M.S. Thesis, Clemson University.

Vainberg, S., R.J. Steffan, R. Rogers, T. Ladaa, D. Pohlmann and D. Leigh, 2006. *Production and Application of Large-Scale Cultures for Bioaugmentation,* The Fifth International Remediation of Chlorinated and Recalcitrant Compounds Conference, Monterey, CA.