

## White Paper

### Aquifer pH buffering during Enhanced Reductive Dechlorination



By R. Wagenfeld *B AS*

## Aquifer pH buffering during Enhanced Reductive Dechlorination

### Introduction

Enhanced Reductive Dechlorination (ERD) of DNAPL compounds like tetrachloroethene (PCE) and trichloroethene (TCE) by organohalide-respiring bacteria is a bioremediation technology which has gained popularity during the last two decades. Especially since the discovery of bacterial species, like *Dehalococcoides mccartyi*, which can fully convert these compounds to ethene, this remediation approach has been adopted by many consultants and remediation contractors faced with chlorinated solvent contaminations in aquifers.

### pH effects of Electron Donor injection

ERD remediation approach almost always includes the injection of an organic substrate being either of soluble nature, like sodium lactate or molasses, or insoluble nature, like vegetable oil emulsions into the aquifer. In both cases however this process generates acidity, lowering the pH of the aquifer, especially when insufficient buffering capacity is available in the aquifer. This effect will be more acute with soluble substrates which generate a rapid release of hydrogen and subsequently acidity. With slow release (low solubility) substrates this effect is less dramatic as hydrogen is released over a longer period of time but its effect cannot be ignored when designing a ERD remediation program.

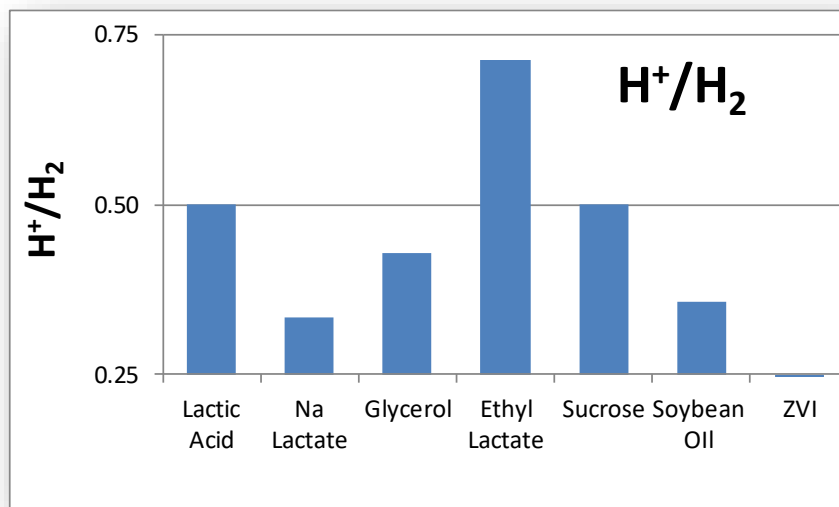


Figure 1. The amount acidity generated per released  $H_2$  equivalent from different electron donor substrates (courtesy of EOS Remediation, LLC).

The reductive dechlorination process releases acidity. For each PCE molecule, fully converted to ethene, 4 hydrochloric acid molecules are produced.

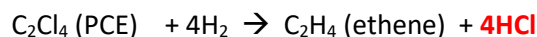
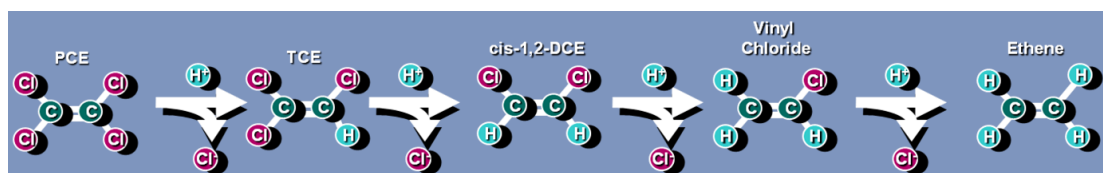


Figure 2. The reductive dechlorination pathway of PCE and the associated hydrochloric acid production reaction

### The effect of pH on microbial activity

Bacteria are sensitive to changes in their environment. A slight change in temperature and/or pH can have a dramatic effect on their activity. Temperature can be considered as a generic parameter controlling microbial activity rates. Most bacteria living in aquifers can be considered as mesophilic bacteria which operate in a temperature range between 10° C to 45° C with an optimum of 30° C to 37° C. As most shallow to moderate depth aquifer temperatures are well below this optimum, increasing the temperature could significantly increase their activity. But as the temperature of groundwater is quite steady<sup>[1]</sup> this will have little impact on bacterial activity rates during aquifer bioremediation unless the temperature is artificially adapted.

Many scientific studies have demonstrated that bacteria prefer certain pH range in which they perform optimally. Most microorganisms important for subsurface bioremediation function most efficiently in near neutral conditions<sup>[2]</sup>. Low pH can interfere with pH homeostasis or increase the solubility of toxic metals<sup>[3]</sup>. Microorganisms can expend cellular energy to maintain homeostasis, or conditions in the cytoplasm and periplasm may change in response to external changes in pH<sup>[4]</sup>. Some anaerobes have adapted to low pH conditions through alterations in carbon and electron flow, cellular morphology, membrane structure, and protein synthesis<sup>[2]</sup>.

Many of the bacteria involved in ERD aquifer remediation programs operate in a pH range of 6 to 9. *Dehalococcoides mccartyi* has a pH range between pH 6 and 8, with highest activity measured between pH 6.9 and 7.5<sup>[5]</sup>.

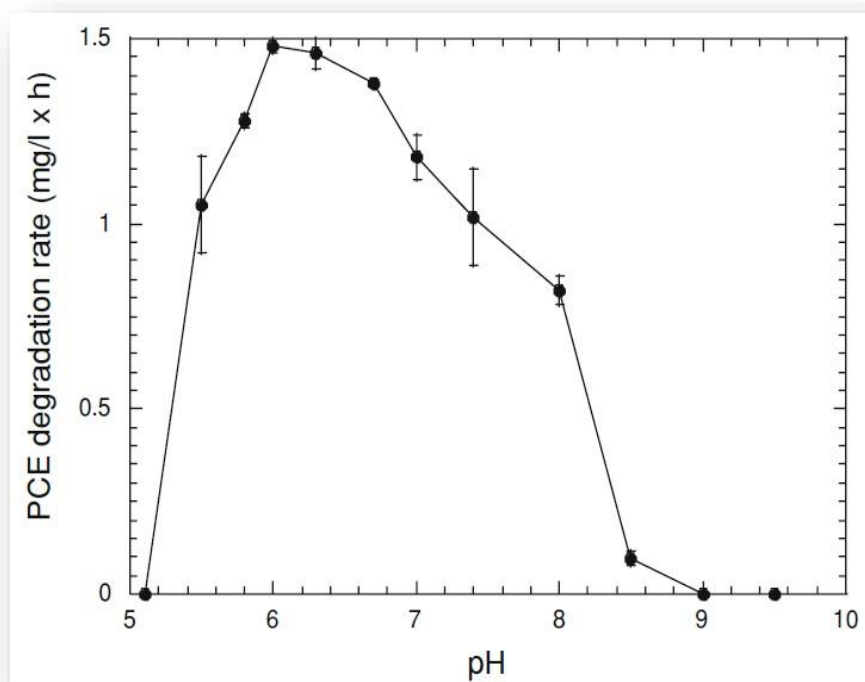


Figure 3. PCE degradation in relation to pH of a commercial bioaugmentation culture <sup>[6]</sup>

Acids are produced during ERD that can cause pH to decline, inhibiting further dechlorination. Whilst reduction of PCE to *cis*-DCE can occur at pH down to 5.5 or possibly lower, the rates of *cis*-DCE reduction to VC to ethene are reduced below a pH of 6.0. For efficient dechlorination to non-toxic end products, the aquifer pH should be maintained above 6.0 during ERD<sup>[7]</sup>.

### Aquifer pH buffering

Buffering of pH – the resistance to pH change – in groundwater systems can be an important control on contaminant attenuation or degradation processes. This happens when aquifer buffering capacity is sufficient to counteract pH changes resulting from contaminants entering the aquifer and/or *in situ* remediation processes. Buffering capacity can occur naturally or be engineered by addition of amendments to the groundwater system<sup>[8]</sup>.

### Engineered pH buffering

If the natural buffering capacity is insufficient to maintain the pH within the optimum for bacterial activity, buffer injection should be considered to avoid stalling of the biodegradation.

Although many alkaline compounds could be applied to buffer the pH in aquifers, their applicability is limited either by the amount of hydroxide (OH<sup>-</sup>) provided by kilogram of injected base, the solubility or the effect on the pH in case of overdosing. Caustic soda (NaOH) for example has a high solubility, which makes it easy to dose, it will have a strong effect on the pH as it has a high pH but as it only provides one hydroxide per mole the amount needed can be high. There is also a serious risk of overshooting the desired pH range as itself is high in pH and is very soluble.

Base	Formula	MW	Solubility	Saturated solution pH	pH at Alkalinity of 100 mg/L CaCO <sub>3</sub>	Concentration of Total Salt to Achieve Alkalinity of 100 mg/L CaCO <sub>3</sub>
		g/mole	g/L			
Caustic Soda	NaOH	40.0	1,100	>13	11	40
Caustic Potash	KOH	56.1	1,200	>13	11	56
Soda Ash	Na <sub>2</sub> CO <sub>3</sub>	106	300	~11.7	10.3	53
Baking Soda	NaHCO <sub>3</sub>	84	78	~8.3	8.3	84
Hydrated Lime	Ca(OH) <sub>2</sub>	74.1	1.85	>12	11	37
Milk of Magnesia	Mg(OH) <sub>2</sub>	58.3	0.01	~10.3	N/A	N/A

Table 1. Physical properties of common basic salts used to raise pH in groundwater<sup>[8]</sup>.

Magnesium hydroxide is a “sparingly” soluble base and occurs in nature as the mineral brucite. The solubility of brucite is controlled by the pH of the system even to a degree that brucite can re-mineralize at higher pH’s.

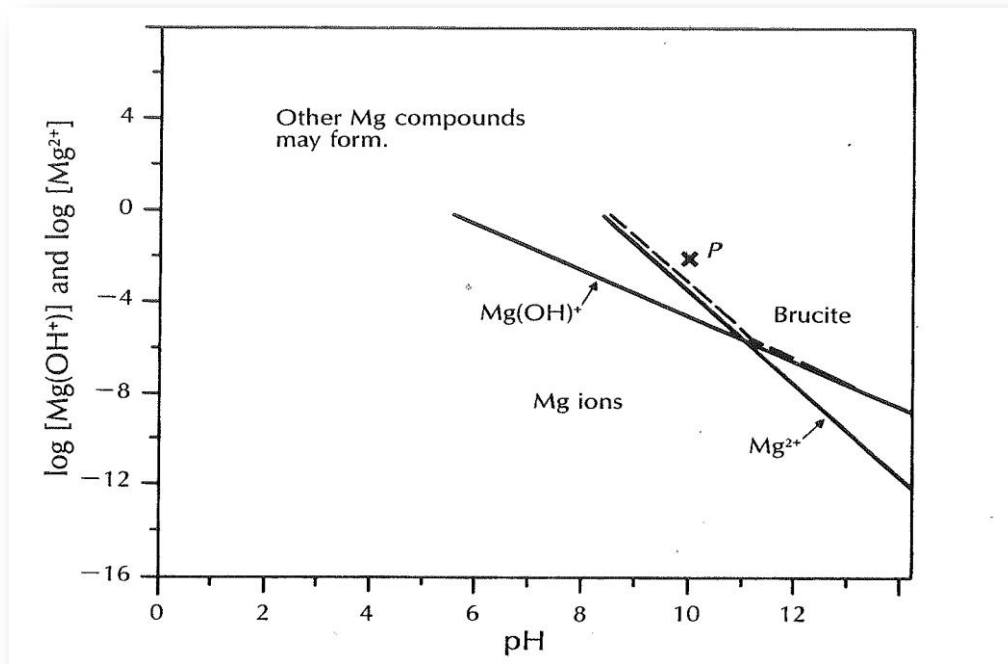


Figure 4. Brucite solubility in relation to the pH<sup>[9]</sup>

As can be seen in the graph in figure 4 the solubility of brucite increases at lower pH's. When used to buffer the pH brucite will solubilize when the pH drops, releasing OH<sup>-</sup> ions and neutralizing acidity created by the H<sup>+</sup> ions which are released during the reductive dechlorination process.

Brucite, in its natural form, is not injectable. A proprietary process has created a colloidal suspension of the Brucite which has a mean particle size of ~1 μm, similar or smaller to non-soluble organic electron donor substrate emulsions. It has a bulk density of ~1,4 mg/l and a pH of 9-10. This product is commercially available under the name CoBupHMg.

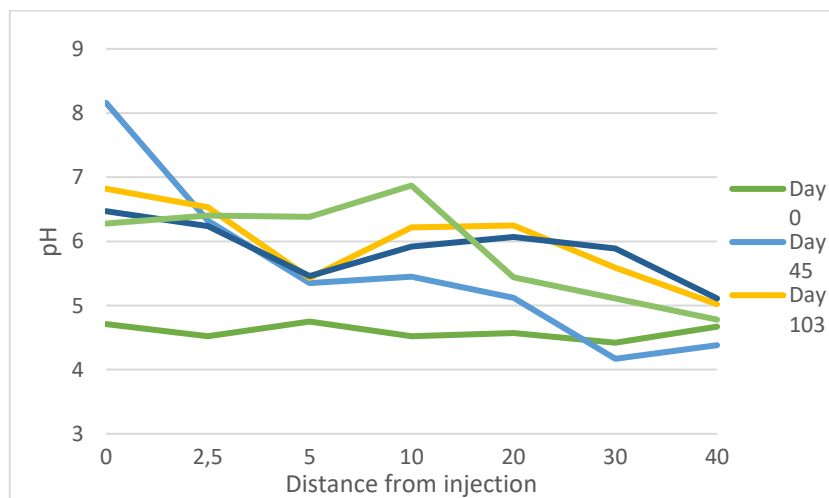


Figure 5. The effect of CoBupHMg on the aquifer pH in time and distance of injection point (Data courtesy of APTIM and EOS Remediation, LLC)

### Estimating Amendment Dosage

When manipulating and buffering pH during remediation, it is important to know the dosage of amendment required to achieve the desired results. The goal is to keep groundwater pH within the optimal range. Dose amount is based on an estimate of mass of acid produced during the remediation process and the acid buffering capacity of the aquifer solids. Dr. Robert Borden, Emeritus Professor of Civil, Construction and Environmental Engineering North Carolina State University, created a new buffer tool for SERDP/ESTCP that calculates a variety of buffers and can be used to calculate the required buffer to adjust pH<sup>[10]</sup>. This tool is provided free of charge for use in developing preliminary estimates of the amounts of base or alkali required to maintain a target pH during anaerobic bioremediation.

Important factors to know before inject a buffer into an aquifer are;

- Soil acidity
- Groundwater acidity
- Concentrations of chlorinated volatile organic compounds (CVOC's)
- Substrate selection and if already applied how much was injected.

### Summary

Aquifer pH lowering during ERD remediation programs, which is related to the use of soluble or insoluble organic substrate, has a potential negative effect on biological degradation rates. When insufficient natural buffer capacity in the treatment zone of the aquifer is available it is advisable to introduce buffering capacity by injecting a alkaline product in order to prevent stagnation of the biological degradation of the chemicals of concern. The use of milk of magnesium in the form of the natural mineral Brucite offers adequate buffering capacity avoiding risks of overshooting the desired pH range as its solubility is controlled by the pH itself. Proper remedial design will identify the need for buffering prior or during the ERD program.

## Literature

- [1] [microbewiki.kenyon.edu/index.php/Groundwater](http://microbewiki.kenyon.edu/index.php/Groundwater)
- [2] Lowe, S.E., Jain, M.K. and Zeikus, J.G., 1993. Biology, ecology, and biotechnological applications of anaerobic bacteria adapted to environmental stresses in temperature, pH, salinity or substrates. *Microbiological reviews*, 57(2), pp. 451-509.
- [3] Slonczewski, J.L., 2009 Stress Responses: pH, In *Encyclopedia of Microbiology* (3rd Ed.), Editor-in-Chief: Schaechter, M., Academic Press: Oxford Vol 5. pp. 477-484
- [4] Foster, J.W., 1999. When protons attack: microbial strategies of acid adaptation. *Current opinion in microbiology*, 2(2), pp.170-174
- [5] Löffler, F.E., Yan, J., Ritalahti, K.M., Adrian, L., Edwards, E.A., Konstantinidis, K.T., Müller, J.A., Fullerton, H., Zinder, S.H. and Spormann, A.M., 2013. Dehalococcoides mccartyi gen. nov., sp. nov., obligately organohalide-respiring anaerobic bacteria relevant to halogen cycling and bioremediation, belong to a novel bacterial class, Dehalococcoidia classis nov., order Dehalococcoidales ord. nov. and family Dehalococcoidaceae fam. nov., within the phylum Chloroflexi. *International journal of systematic and evolutionary Microbiology*, 63(2), pp.625-635. doi: 10.1099/ijs.0.034926-0
- [6] 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.
- [7] [www.enviro.wiki/index.php?title=Low\\_pH\\_Inhibition\\_of\\_Reductive\\_Dechlorination#Summary](http://www.enviro.wiki/index.php?title=Low_pH_Inhibition_of_Reductive_Dechlorination#Summary)
- [8] [www.enviro.wiki/index.php?title=PH\\_Buffering\\_in\\_Aquifers](http://www.enviro.wiki/index.php?title=PH_Buffering_in_Aquifers)
- [9] Faure; 1998, *Principles and Applications of Geochemistry*, Figure 9.2, pg123
- [10] [www.eosremediation.com/estimating-base-requirements-for-enhanced-reductive-dechlorination/](http://www.eosremediation.com/estimating-base-requirements-for-enhanced-reductive-dechlorination/)