PHYSICAL-CHEMICAL TREATMENT OF METALS AND RADIONUCLIDES IN THE SATURATED ZONE USING COLLOIDAL BUFFERS - 12515

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Abstract

There are numerous acidic plumes throughout the DOE complex and the nation as a whole. Low aquifer pH is a major concern since many important radionuclides (Pu, Ra, Sr, Tc) and metals (Cd, Co, Cs, Mn, Ni, Pb, Zn) strongly sorb to iron hydroxides and aluminosilicates under neutral to alkaline conditions, but are mobile in acidic plumes. To effectively use natural and enhanced attenuation (NEA) for management of these contaminants, we must be able to raise aquifer pH and maintain it at background levels until the external acid loading to the aquifer has dissipated.

Geochemical modeling showed that a permeable reactive barrier (PRB) formed by injection of colloidal $Mg(OH)_2$ would last much longer than colloidal Ca(OH)2 due to the much lower solubility of $Mg(OH)_2$. Assuming a 1,000 meq/L suspension of colloidal Mg(OH)2 could be effectively distributed, the PRB could last over twenty years before rejuvenation was required.

Preliminary bench-scale treatability studies were conducted to demonstrate the efficacy of increasing the aquifer pH using a colloidal pH buffer. Laboratory studies demonstrated that three different colloidal $Mg(OH)_2$ suspensions (concentration varied from 1,000 to 1,250 meq/L) could be transported through the columns packed with aquifer sand without significant permeability loss. The time before suspension breakthrough into the column effluent varied with surface treatment, indicating the $Mg(OH)_2$ retention and PRB longevity could be controlled by varying the suspension surface treatment.

Introduction

There are numerous acidic plumes throughout the DOE complex and the nation as a whole. Low aquifer pH is a major concern since many important radionuclides and metals (Cd, Co, Cs, Mn, Ni, Pb, Sr, Zn) strongly sorb to iron hydroxides and aluminosilicates under neutral to alkaline conditions, but are mobile in acidic plumes. To effectively use natural and enhanced attenuation (NEA) for management of these contaminants, we must be able to raise aquifer pH and maintain it at background levels until the external acid loading to the aquifer has dissipated.

When acidic water enters the subsurface, the pH decline is limited by a series of processes including dissolution of carbonate minerals, proton (H^+) adsorption, and slow dissolution of certain minerals (Fe and Al hydroxides, aluminosilicates, and feldspars).

Carbonate minerals are absent in many southeastern aquifers, but these aquifers do contain substantial amounts of iron hydroxides ($Fe(OH)_3$) and clay minerals with potential for pH buffering by H^+ adsorption. However, much of the $Fe(OH)_3$/clay buffering capacity may be concentrated in lower permeability zones and may not be accessible to the mobile groundwater. In addition, the ambient pH in many aquifers is relatively low (4 – 6) due to extensive leaching by infiltrating rain water and much of the $Fe(OH)_3$/clay buffering capacity has already been consumed by prior loading with H^+. In these aquifers, acidic plumes migrate rapidly due to the low buffering capacity of the aquifer material. Once acid addition ends, the aquifer pH will rise very slowly due to the low neutralizing capacity of the infiltrating rain water, and the large amount of H^+ sorbed to the aquifer material.

Natural and Enhanced Attenuation (NEA)

Natural Attenuation (NA) relies on naturally occurring physical, chemical and biological processes to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. Enhanced attenuation (EA) is the use of low-energy, long-lasting technologies to reduce contaminant loading and/or increase the natural attenuation capacity of a formation (SRNL, 2006; ITRC, 2008, ITRC, 2008b). Reducing long-term maintenance costs are extremely important for metal and radionuclide contamination, since these contaminants must be immobilized for very long time periods.

Between 1955 and 1988, approximately 7 billion liters of predominantly acidic solutions were discharged into three unlined basins in the F-Area of the Savannah River Site (SRS) generating a roughly 1 km^2 metals/radionuclides plume. In 1997, a plume containment system was installed where contaminated groundwater was extracted from the aquifer, treated by chemical precipitation, reverse osmosis and ion exchange then then reinjected back into the aquifer. The system had high operating costs ($1 million per month) and created 5000 ft^3 per year of radioactive solid waste.

DOE is evaluating the use of natural and enhanced attenuation processes to more sustainably manage the F-Area Seepage Basins at the Savannah River Site (SRS). Sr-90 and uranium are important contaminants at the site and are known to sorb to the aquifer material under ambient pH (>5) conditions. However, nitric acid addition to the seepage basins has generated a low pH (~3.2) plume where Sr-90 and U sorption are very limited.

To take advantage of the natural attenuation capacity of the aquifer, a modified funnel-and-gate system was installed that directs the more highly contaminated groundwater towards gates where alkaline solutions are injected to raise the aquifer pH. As acidic contaminant-bearing groundwater enters this zone, its pH is neutralized, causing Sr-90 and uranium to adsorb to treatment zone minerals. Downgradient monitoring indicates the system is effective in reducing Sr-90 and uranium migration.

SRS currently uses a mixture of sodium hydroxide (NaOH) and sodium bicarbonate ($NaHCO_3$) for pH adjustment. The materials are very soluble, so they are easy to inject. However, their high solubility also results in rapid washout from the treatment zone. Currently, the treatment zone must be regenerated every 12 - 18 months as acidic water migrates into the treatment zone from upgradient, causing the pH to drop, and contaminant mobility to increase. This requires extracting contaminated groundwater, amending with base, and reinjecting water, resulting in long-term operating costs and worker exposure. Other disadvantages of this approach include: (a) elevated levels of Na can mobilize clays, reducing formation permeability; (b) carbonate addition can increase uranium mobility through formation of uranyl (UO_2) carbonate complexes; and (c) carbonate addition can result in CO_2 degassing with associated formation blocking.

Technical Approach

An alternative approach for management of the F-Area plume would be to form a permeable reactive barrier (PRB) by distributing colloidal $Ca(OH)_2$ or $Mg(OH)_2$. As the $Ca(OH)_2$ or $Mg(OH)_2$ dissolves over time, it will raise the pH, providing a long-term, sustainable solution with lower costs and lower worker exposure. Since $Ca(OH)_2$ and $Mg(OH)_2$ are less soluble in water, they will last longer, reducing the frequency of base addition.

The potential longevity of PRB for treatment of the F-Area plume was evaluated using the PHREEQC geochemical model (Parkhurst and Appelo, 1999). For illustrative purposes, we have assumed a 500 m wide PRB would be installed downgradient of the F-Area seepage basins consisting of 55 wells installed 9.1 m (30 ft) on-center. Assuming a 9.1 m long well screens, each well would be injected with approximately 75 m^3 (20,000 gallons) of suspension per well containing 1,000 meq/L of either $Ca(OH)_2$ or $Mg(OH)_2$. Assuming an injection rate of 19 L/min (5 gpm) per well, the total injection time would be 1-2 months. The influent water entering the barrier is shown in Table I and was selected to approximately match the in situ chemical composition of the F-Area plume at the SRS. Groundwater flow velocity was assumed to be 100 m/d (328ft/d) and effective porosity to be 0.25.

Figure 1 shows the simulated pH vs time, immediately downgradient of a PRB formed by injection of colloidal $Ca(OH)_2$ or $Mg(OH)_2$. $Mg(OH)_2$ is much less soluble than $Ca(OH)_2$ so it does not result in as large a pH increase and lasts much longer. Assuming a 1,000 meq/L suspension of colloidal $Mg(OH)_2$ could be effectively distributed, the PRB could last over twenty years before rejuvenation was required. If several barriers were installed through the length of the plume, it might be possible to provide sufficient alkalinity to permanently neutralize the plume.

Table I – Influent Groundwater Composition

Parameter	Concentration	
	mg/L	mM
pH	3.2	
Sodium (Na)	110.0	4.8
Potassium (K)	2.0	0.05
Calcium (Ca)	14.0	0.35
Magnesium (Mg)	4.0	0.16
Aluminum (Al)	27.0	1.0
Iron (Fe)	0.1	0.002
Manganese (Mn)	4.0	0.07
Nitrate (NO_3^-)	547.0	8.83
Sulfate (SO_4^{-2})	9.0	0.09
Chloride (Cl^-)	25.0	0.7
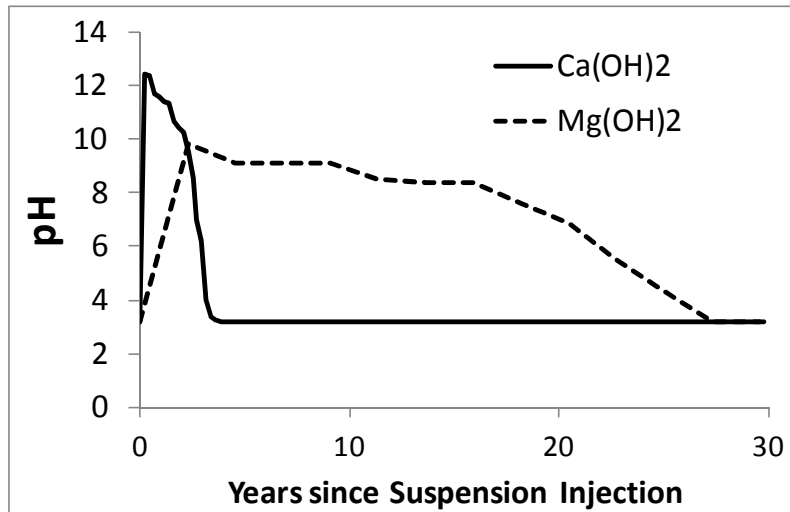
Figure 1. Simulated - pH vs time, immediately downgradient of PRB formed by injecting colloidal $Ca(OH)_2$ or $Mg(OH)_2$.

Colloid Transport Studies

While $Mg(OH)_2$ addition could be very effective for long-term pH adjustment, distributing colloidal $Mg(OH)_2$ can be challenging. $Mg(OH)_2$ has a net positive charge under typical

aquifer conditions (zeta potential of $Mg(OH)_2$ = + 25 mV at pH=10,(Pokrovky and Schott, 2004). As a result, untreated colloidal $Mg(OH)_2$ is strongly retained by negatively charged aquifer sediments.

Over the past several years, we have been working to develop methods for distributing colloidal buffers in aquifer. As part of this work, we have developed suspensions of solid alkaline materials where the particle size, surface charge, degree of flocculation and settling rate are controlled to enhance transport and distribution throughout the treatment zone.

A series of column experiments were conducted to evaluate the effect of different surface treatments on the transport and retention of $Mg(OH)_2$ suspensions in laboratory columns. The suspensions were all prepared to meet the following objectives: 1) median particle size of the suspension was 0.6 μm, which is much less than the median pore size of the sediment; 2) the particles surface charge is controlled to manage particle capture by negatively charged surfaces; 3) non-flocculating suspension to prevent formation of large flocs which could become trapped in the pores, and 4) slow settling rate to reduce separation during injection and enhance transport in the subsurface. Samples suspensions have a shelf-life of over 2 months to allow manufacture and shipping to the site.

Results and Conclusions

Figure 2 shows the results of three column experiments where 2.5 cm x 28 cm laboratory columns were packed with field sand (D_{50} = 0.38 mm, D_{10} = 0.17 mm) and then flushed with several pore volumes of three different $Mg(OH)_2$ suspensions with varying surface treatments (A, B and C).

All of the suspensions were effectively transported through the columns after injection of 1 – 3 pore volumes (PV) of suspension. There was no significant permeability loss in any of the columns, indicating large volumes of suspension can be injected without clogging the aquifer. For some of the suspensions, there was a modest decline in effective permeability during the actual suspension injection due to the somewhat higher viscosity of the suspension. However, permeability recovered to preinjection values when chase water was injected.

The results presented in Figure 2 demonstrate that the time before breakthrough into the column effluent and amount of $Mg(OH)_2$ retained in the column varied with surface treatment.

Treatment A was the most strongly retained, requiring injection of 3 pore volumes (PV) of suspension before high concentrations of $Mg(OH)_2$ suspension were discharged in the effluent. In comparison, high concentrations of $Mg(OH)_2$ suspension were discharge within 2 PV for Treatment B and within 1 PV for Treatment C.
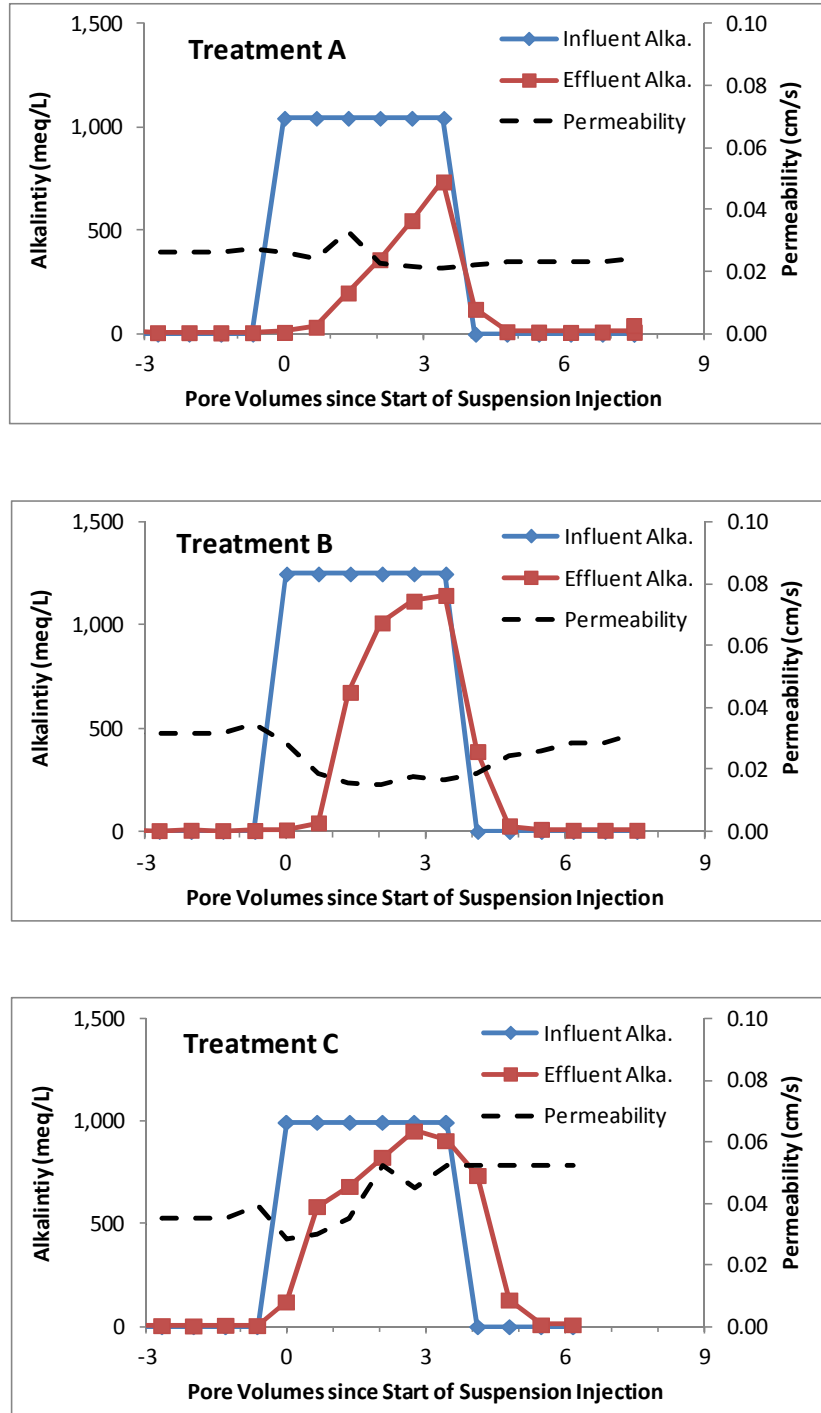
Figure 2. Effect of surface treatment on transport of colloidal $Mg(OH)_2$ suspensions in laboratory columns packed with sand.

The fraction of injected $Mg(OH)_2$ retained within the column varied from 61% for Treatment A, to 38% for Treatment B, and 18% for Treatment C.

When groundwater acidity is very high, Treatment A might be preferred, since the higher $Mg(OH)_2$ retention would generate a very long lasting barrier. However when groundwater acidity is lower, Treatment C might be preferred since the $Mg(OH)_2$ suspension could be transported farther with less injection water and fewer wells.

Follow-on work, if funding becomes available, will include a small pilot- scale demonstration of the technology at a DOE complex location, the calibration of commercially available geochemical models, and comparison of their ability to simulate the performance of the pilot-scale system.

Acknowledgement

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