

Maintaining Neutral pH in Deep Soils and Ground Water Utilizing Insoluble Colloidal Buffers

James Piegat (jpiegat@RNASinc.com) and William A. Newman (Remediation and Natural Attenuation Services, Inc., Brooklyn Center, MN, USA)

ABSTRACT: Optimal pH for most biodegradation processes falls between 6.5 and 8.5. Enhanced bioremediation in poorly buffered soils and ground water is likely to lower pH below 6.5 as the added electron donor produces carbon dioxide and organic acids. The common agricultural practice of liming soils adds alkalinity and adjusts soil pH by mixing finely divided insoluble calcium carbonate into the shallow subsurface. Conversely, delivery of an insoluble solid buffer into deeper soils and ground water aquifers presents a formidable technical challenge. The principal challenges include: 1) keeping particles in suspension during storage and transportation; 2) moving the buffer solids a useful distance through the soil or aquifer; 3) retaining sufficient buffer in the soils that will not be washed out by advective ground water flow after injection; and 4) minimizing changes to soil permeability. Soluble buffers are commonly lost within relatively short periods of time as a result of advective ground water flow. Colloidal buffer systems can be transported significant distances in the subsurface, yet can also have substantial retention in the soil or aquifer after injection. Suspensions of micro- and nano-scale insoluble buffer particles are explored in soil columns. Subsurface mobility of the diluted suspensions is enhanced by careful control of particle size and treatment with selected additives to produce a negative surface charge. Stable suspensions of insoluble buffer solids containing more than 500,000 mg/Kg of total alkalinity (as CaCO₃ equivalents) were produced through the use of optimal particle size and proprietary additives (U.S. patent pending). These suspensions were stored for more than six months without significant settling, agglomeration or cementing of buffer particles. The concentrated suspensions can be easily diluted with water in the field by gentle mixing for injection into deep soils or ground water. Column studies using sandy soils indicated the effective transport of more than five pore volumes of a suspension containing more than 20,000 mg/L total alkalinity (as CaCO₃ equivalents), with significant alkalinity retained in the soils, and less than 10% loss in permeability. The commercial product developed from this research is being tested in field trials and will be marketed under the trademark *Neutral Zone*TM.

INTRODUCTION

The need for a relatively neutral pH for biodegradation of chlorinated solvents is generally accepted, although it appears that some strains of bacteria have developed a tolerance for naturally low pH conditions (Singletary, et. al., 2007). However, reductive dechlorination at poorly buffered, pH neutral sites can be slowed or halted if pH should drop as a result of bioremediation activities, but can be improved at sites that are only mildly acidic if pH is raised (Leahy, et. al., 2007).

A variety of soluble buffers, such as potassium hydroxide (Cline, et. al., 2007) and sodium bicarbonate (Santos-Ebaugh, et. al., 2007) have been used to raise pH and thereby enhance reductive dechlorination. However, the effect is generally short-lived (Santos-

Ebaugh, et. al., 2007). Advective ground water flow can quickly remove a soluble buffer, requiring continual reinjection to maintain pH over time.

High pH can be as detrimental to bioremediation as low pH. Some soluble buffers such as the strong base potassium hydroxide, a toxic corrosive, can rapidly neutralize large amounts of acid. But they can also raise pH as high as 12 and kill all of the microbes in the treatment area. Distributing such a buffer throughout a treatment zone can be problematic as it is easy to have a concentration adversely high around injection points, and yet ineffectively low in other areas remote from the injection points. An insoluble solid buffer can avoid such problems as the base is not liberated by dissolution in water, which could raise pH too high, but is largely liberated by the very acid it will neutralize.

Hence, the desire is to create an ideal buffer for enhanced bioremediation sites or for sites where acidity itself is the contaminant. The ideal buffer would have a high buffering capacity to offset high acidity, yet be relatively insoluble in water to have a long service life and to avoid the problem of adversely high pH. It would have no cations that could create an adverse environment or that would be considered a contaminant. It would be easily injected into and distributed within an aquifer, yet would become immobile after injection ended when the higher pore water velocities of injection returned to ambient conditions. It would not decrease permeability. It would have a long shelf life and be easily handled in the field. It would not be toxic, corrosive, or otherwise hazardous to those who ship, handle, or dispose the material. Finally, it would consist entirely of food-grade ingredients, yet be inexpensive.

The principal challenges to creating such a buffer include: 1) keeping particles in suspension during storage and transportation; 2) moving the buffer solids a useful distance through the soil or aquifer; 3) retaining sufficient buffer in the soils that will not be washed out by advective ground water flow after injection; and 4) minimizing changes to soil permeability. RNAS has met these challenges with a product that will be marketed under the trade name Neutral Zone™.

METHODS

Test specimens consisted of 1-1/2" diameter x 12" long columns of beach sand obtained from Park Point in Duluth, MN. This sand was chosen because of its uniform size distribution ($D_{50} = 0.25$ mm, $D_{90} = 0.37$ mm) and lack of inherent alkalinity. The average column had a mass of 622.1 g, porosity of 43.2%, and pore volume of 169.2 cc.

Three permeameter tests were run on each test specimen to establish the initial permeability. Next, 800 ml, approximately five pore volumes, of a diluted sample of a Neutral Zone™ prototype was injected through the specimen. Dilutions to 0.5%, 2%, 5%, and 10% solids by weight were tested for each prototype. Each specimen was then flushed with 800 ml of deionized water followed by three permeameter tests.

Hydrometer Tests. Several different materials that could serve as insoluble solid buffers were obtained from different sources. The particle-size distribution for each material was certified by its manufacturer and independently confirmed with a Horiba™ Laser Scattering Particle Size Distribution Analyzer. However, particles of micron or sub-micron size will commonly aggregate into much larger particles during handling and manufacturing processes. Therefore, all prototype formulas of Neutral Zone™ were

analyzed for particle size distribution using the hydrometer analysis specified by ASTM Standard D 422 with some modifications.

The hydrometer test of Standard D 422 begins with 50 g of an air-dried sample. As drying a prototype would significantly increase clumping in a way that would not occur during product use, a volume of the prototype suspension that would include 50 g of solid material was tested. The Standard calls for dispersing the solids in a solution of sodium hexametaphosphate to prevent aggregation. However, this step would mask the effectiveness of the dispersants used for the manufacture of Neutral Zone™, and was not followed.

Initial test suspensions were mixed with Apparatus A that uses a stirring paddle rotated at 10,000 rpm, followed by hand turning the sedimentation cylinder upside down and back for a period of one minute, as specified in the ASTM Standard. To understand how easily any particles that might settle during storage could be resuspended, hydrometer tests were repeated mixed only by the hand turning the sedimentation cylinder and without the mixing with Apparatus A.

Permeability Tests. All prototype formulas of Neutral Zone™ were analyzed for their effect on permeability using the test method specified by ASTM Standard D 5856. The hydraulic system was constant head and used deionized water. A rigid-wall, compaction-mold permeameter was constructed with 1-1/2" o.d. x 12" long clear PVC tubing and custom end plates that prevented swelling of the test specimen.

Three runs of 500 ml each of deionized water were conducted on each specimen prior to injection of a Neutral Zone prototype and three more runs of 500 ml each following the flushing of columns with deionized water.

Buffer Retention. Eight aliquots of 100 ml each were collected during both prototype injection and flushing. All aliquots and the 500 ml discharge from each of the three final permeameter tests were titrated to measure the movement of the buffer in each specimen. Finally, each column was cut into ten equal sections and titrated to measure the amount of buffer that remained. Columns were cut into ten equal samples and oven-dried. A ten-gram sample was extracted from each sample and titrated with 1.600 N sulfuric acid to determine alkalinity, which was measured as calcium carbonate equivalent. The pH end point was 4.5.

RESULTS AND DISCUSSION

Buffer Suspension. Choice of buffer materials is critical to developing a product that will have a useful shelf life, where the high concentration of solid particles tends to keep them suspended, and a useful life during mixing and injection in the field, where the diluted concentration of particles tends to allow them to settle. The buffer material in all prototypes was the same chemical substance and had the same purity. However, differences in particle size and method of manufacture made a significant difference in the suitability of a particular material.

Figure 1 shows the difference between perhaps the best and the worst of the different buffer materials that were tested in the hydrometer. As the hydrometer uses a dilute sample (0.5% solids by weight), these tests reflect what will happen in the field as the user dilutes the shipped product for injection.

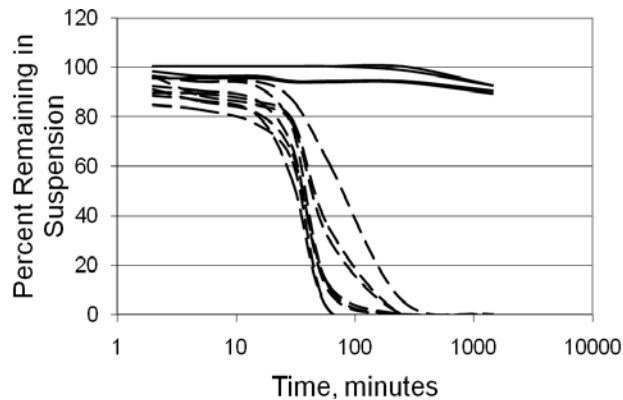


FIGURE 1. Hydrometer tests of 6704 series (solid lines) and 6814 series materials (dashed lines).

In five of the six formulations of the 6814 series prototypes, the hydrometer indicates that virtually all of the solid buffer will settle within two hours. Using 6814 material would require the frequent mixing of small batches of dilute buffer and the disposal of any diluted material remaining if injection is shut down for any reason.

Settled buffer particles must be avoided in any finely-divide solid buffer material. They will aggregate into either a viscous gel or a hard, clay-like layer. Field methods may break up settled buffer into particles small enough to be entrained in an intake hose, but particle sizes will be much larger than the original material with the likely result being clogged well screens and aquifer pores.

Choice of additives. Unlike the kinetically stable droplets of a sub-micron emulsion, raw particles of a solid buffer will settle even if they are sub-micron in size. To create a stable suspension, additives must be included to prevent aggregation of small particles during storage and to retard settling after dilution. Figure 2 shows hydrometer test results for six different additive formulations as applied to prototype material 6950. In the worst example, one-third of the solid material fell to a level below the hydrometer within only two minutes of the start of the test.

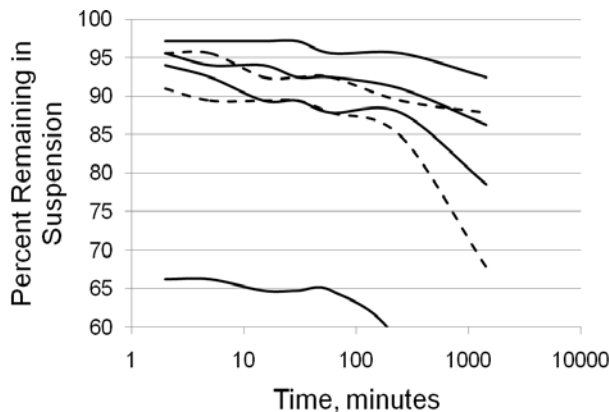


FIGURE 2. Hydrometer tests of material 6950 with six different additive formulations.

Effect of high-shear vs. hand shaking sample preparation. Dispersion of the particles of solid buffer and mixing in additives requires a high-shear mixing process during manufacture. The ASTM standard hydrometer test also uses high-shear mixing of a diluted sample to accurately determine particle size distribution. However, high-shear mixing equipment would not be available in the field when the concentrated product is diluted for injection. Therefore, hydrometer tests were repeated without high-shear mixing for the more promising prototypes. Dispersing the concentrated product in water was accomplished by simply hand turning a mixing cylinder upside down and back as per the ASTM standard to duplicate the relatively gentle mixing that would occur during dilution in the field. Happily, the better prototypes showed no significant difference in particle size distribution between the high-shear and gentle mixing, and hence showed no significant particle aggregation occurred during dilution (Figure 3).

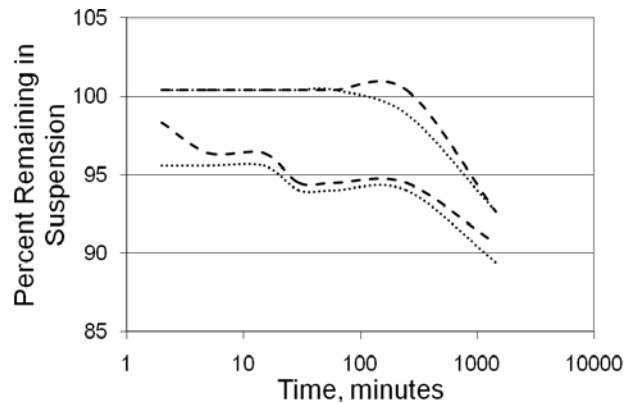


FIGURE 3. Two prototypes of material 6704 comparing high-shear mixing (dots) and hand shaking (dashes) during sample preparation.

Buffer Mobility. An insoluble solid buffer would have no value if it cannot be moved a significant distance from injection wells into an aquifer. The basis of the desired mobility of Neutral Zone™ prototypes is a sub-micron average particle size and additives that maintain a negative zeta potential on the particles. Mobility was tested by injecting diluted concentrations of prototype buffers into the same columns used for permeameter testing. Concentrations of 0.5%, 2%, 5%, and 10% solids were used for each material and were injected at a rate equivalent to a ground water velocity of 50 feet per day. This is a much higher velocity than would be encountered in ambient ground water flow conditions, but does reflect the velocities near a well during injection.

Breakthrough of the maximum concentration of buffer occurred after the injection of approximately 3.5 pore volumes (Figure 4). Injection ceased after five pore volumes. Subsequent flushing with 1,500 cc of deionized water for permeameter tests removed essentially all mobile buffer. Hence, the better prototypes showed excellent mobility.

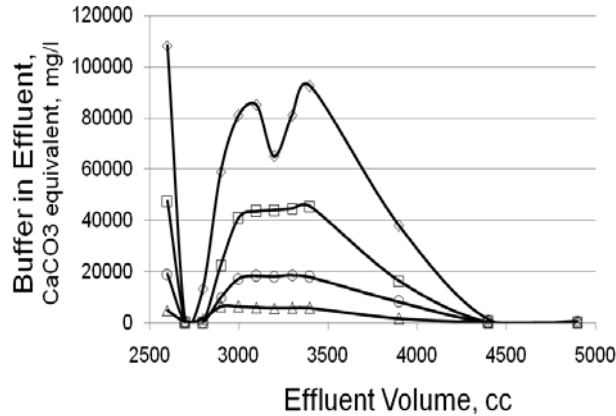


FIGURE 4. Breakthrough curves for material 6704 at 0.5%, 2%, 5%, and 10% solids. Values at 2,600 cc are the buffering capacities of the influent. Values from 2,600 cc to 3,400 cc represent buffer injection. Values from 3,900 to 4,900 cc represent flushing with deionized water during the final permeameter tests.

Buffer Retention. The effective movement of the insoluble solid buffer through columns during injection and flushing raised the concern that it might be too mobile and suffer from the same drawback as soluble buffers. Most specimens were injected with five pore volumes of diluted buffer, flushed with five pore volumes of deionized water moving at 50 ft/day, and then permeameter tested three times with three pore volumes each moving at 130 ft/day. In most cases this flushing removed nearly all the buffer (Figure 5).

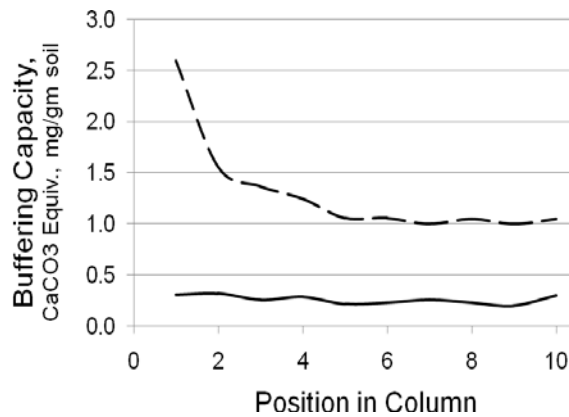


FIGURE 5. Buffering capacity retained after flushing with deionized water. Higher flushing velocity (>50 ft/day) removed nearly all buffer (solid line). Significant buffer was retained at lower velocities (8 ft/day; dashed line). Injection flow was from position 1 to position 10.

A second series of tests that eliminates high velocity flushing is currently being conducted. Flushing velocities are reduced to 8 ft/day, similar to the fastest ground water flow that might be encountered. Preliminary results indicate that useful amounts of Neutral Zone™ can be retained at even the fastest ambient ground water flow velocities.

Changes in Permeability. Initial permeameter tests (numbers 1-3) for each individual specimen generally showed a slight decline in permeability with each successive test (Figure 6). In general, permeameter test 4, the first following injection of a buffer prototype, showed a distinct drop in permeability (Figures 6, 7a). However, permeabilities measured in tests 5 and 6 recovered essentially to the values that would be expected by extrapolating the results from the first three tests (Figures 6, 7b).

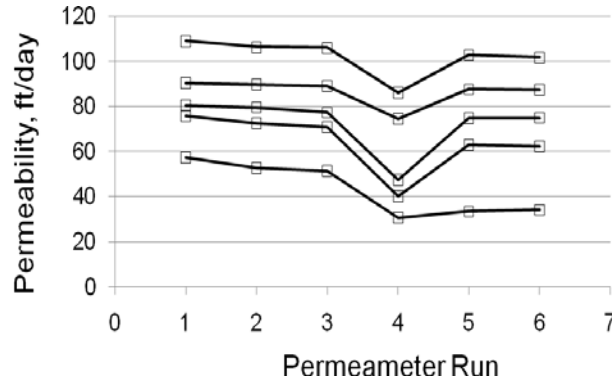
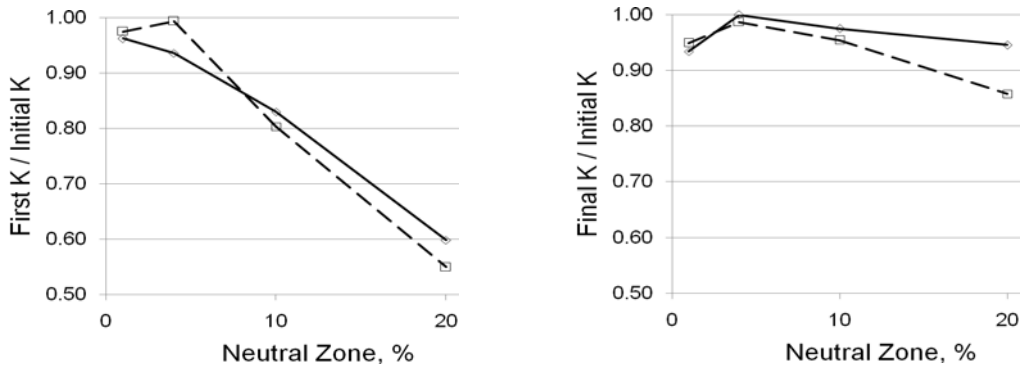


FIGURE 6. Permeameter test results for five selected column studies. Runs 1 through 3 were performed prior to buffer injection; runs 4 through 6 were performed after injection.



FIGURES 7a and 7b: Initial loss of permeability (left) and ultimate loss of permeability (right) compared to the concentration of Neutral Zone™ that was injected. In all cases, Neutral Zone™ was 50% solids by weight. Solid line is material 6904; dashed line is material 6978.

It should be noted that the initial decrease of permeability immediately after injection of even the highest concentration of the buffer is less than the variation in initial permeabilities of the otherwise identically prepared specimens used in the hydrometer tests.

CONCLUSION

Careful selection of materials and specific manufacturing methods have allowed the development of an insoluble solid buffer. The buffer consists of sub-micron sized calcium carbonate particles (50% by weight), additives that make for a stable product, and water. All ingredients except the dispersant are food grade. The U.S. Food and Drug

Administration allows the dispersant to be used as a secondary direct additive in food for human consumption. The buffer has a useful handling time after dilution in the field because of the slow settling rate seen in the better prototypes. When diluted, the buffer was easily pumped through the test medium. Initial drop in permeability was low and recovered after flushing with additional water. This buffer will be marketed under the trade name Neutral Zone™.

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