

Field Test of Limestone as a Treatment Medium for Groundwater at the Savannah River Site

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Abstract: Groundwater downgradient from the F- and H-Area Seepage Basins at the Savannah River Site is contaminated with acids, metals, radionuclides, and tritium originally released as part of low-level waste streams from the Radiochemical Separations Areas processing facilities. To stem the flux of tritium discharged from the basin area, a series of wells was installed to extract the groundwater and re-inject it upgradient of the seepage basins. Tritium is captured in an extraction-re-injection cycle that allows it to decay. To meet regulatory criteria for re-injection metals and radionuclides must be treated and removed. One method under consideration for this removal is in-situ contact with limestone. Equilibration of the groundwater with limestone raises the pH to approximately 8. At this pH, metals and radionuclides can be removed by direct precipitation, co-precipitation, and enhanced adsorption. A pilot test was performed to provide data required to assess the applicability of limestone in groundwater treatment. The demonstration unit consisted of several columns of limestone with different total column lengths and thus different residence times. Groundwater from the basins was passed through each of the columns and analyzed for metals, radionuclides, ions, pH, and conductivity. The results from both the laboratory and field tests show the limestone's effectiveness as an in-situ treatment medium.

The solutions disposed in the Savannah River Site's F- and H-Area Seepage Basins originated from processing of uranium slugs and irradiated fuel. Disposal of these solutions in the basins began in 1955 and continued through 1988. The nature of the processes resulted in low-level waste that contained a variety of actinides, activation products, fission products, and tritium. In addition, dissolved metals such as mercury, lead, cadmium, and chromium were present. The solutions were generally acidic with average pH values of 2.4 in H-area (Killian et al., 1987a) and 2.9 in F-Area (Killian et al., 1987b). A total of approximately 7.1×10^9 liters of waste solution were disposed of in the F-Area Seepage Basins and 6.0×10^9 liters were disposed in the H-Area Seepage Basins (Cummins et al., 1991). Though the seepage basins essentially functioned as designed, groundwater was contaminated with tritium, some metals, and various radionuclides. The constituents of greatest concern are tritium, mercury, strontium-90, uranium-238, iodine-129, strontium-90, curium-244, americium-241, cadmium and aluminum.

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A similar matrix, acid mine drainage, has been effectively treated with limestone as a component of the treatment system (Hedin et al., 1994). Acid mine drainage results from oxidation of pyrite (FeS_2) associated with coal and ore deposits. In addition to its acidic nature, it typically contains high concentrations of dissolved iron, aluminum, and other metals. Effective treatment of acid mine drainage can be achieved by raising the pH causing aluminum and ferric iron phases to precipitate. Removal of other contaminant metals occurs by co-precipitation or adsorption onto these phases.

This method of acid mine drainage treatment is applicable to treatment of F- and H-Area groundwater. As with acid mine drainage, pH is a dominant control on metal and radionuclide concentrations and mobility in this groundwater. Therefore, increasing pH by contact with limestone will have some of the same benefits as observed with acid mine drainage treatment.

Though limestone may be an effective treatment for some metals and radionuclides, it may enhance mobility of others. Dissolved anionic (negatively charged) species tend to become more mobile in soils as pH increases because surface charge on aquifer minerals becomes increasingly negative. Constituents such as I-129 and Tc-99 that are sorbed to minerals at pH 3 to 4 may be mobilized by the elevated pH associated with limestone treatment. Likewise, uranium and other actinides can form strong dissolved carbonate complexes that are neutral to negatively charged species (Langmuir, 1978; Ames et al., 1983; Clark et al., 1995). This highlights the need for careful consideration of the negative consequences of limestone treatment, as well as the benefits. Key to understanding the dynamics of this process is knowledge of the effect of limestone treatment on groundwater chemistry. This includes understanding the design variables, including deployment location, groundwater-limestone contact time, and limestone aggregate size, that may allow optimization of treatment and minimization of negative consequences.

The field test was designed to assess the effect of limestone treatment on the chemistry of groundwater from F- and H-Areas. Analytical measurements made over a four-week continuous test run were used to quantify the effects on pH, concentrations of metals and radionuclides, evaluate the effect of contact time between groundwater and limestone on the extent of reaction, determine longevity of limestone, and characterize sludge precipitated within the columns. The test apparatus used water from the F-Area and H-Area extraction tanks. These waters are a composite of groundwater removed from the contaminant plume by the extraction well network in each area. Thus, they are the best approximation of typical groundwater composition in each of the plumes. Identical sets of columns were deployed at the extraction tanks in both F- and H-Areas. The systems consisted of 6 columns connected by PVC and polyethylene tubing to a 525-gallon tank that will be filled with water from the extraction tank. Water was pumped with a diaphragm-metering pump into a PVC manifold with 7 outlets – one for inlet sampling and one to each column. This ensured that the feed water for all columns was of identical composition. The pumping flow rate was approximately 70 ml/minute and flow meters regulated flow into each column at 10 ml/minute. Water flowed from bottom to top in the columns and was discharge into a drain manifold that was open to

atmosphere. Outlet sampling ports were placed between each column and the drain manifold.

The columns were designed to allow evaluation of several issues associated with limestone treatment of acidic groundwater. Five of the columns consisted of 4-inch diameter PVC and one column consisted of 6-inch diameter PVC. The 4-inch columns were filled with $\frac{3}{4}$ -inch limestone aggregate. To assess the effect of larger diameter aggregate, the 6-inch column was filled with 2 $\frac{3}{4}$ -inch limestone aggregate. Using measured flow rates and estimated porosity a semi-quantitative comparison of the effectiveness of the two aggregate sizes was made. The columns were constructed in four different lengths to achieve four different groundwater-limestone contact times. Pressure gauges were installed at the top and bottom of the 5-foot and 2-foot (4-inch diameter) columns to monitor pressure differentials. A 0.5-foot long column of soil was positioned down stream of column 3, so that water passing through column 3 was then passed through the soil column. The purpose of this column was to provide a qualitative assessment of the effects of interaction with limestone on sorption of various constituents.

The sampling strategy was designed to optimize data collected to meet study objectives, while minimizing analytical costs. For all samples obtained, pH was measured in the field. During the first week of operation pH was measured at all sampling ports each day and one set of samples were obtained for laboratory analyses of metals and anions. Thereafter, sampling of all sample ports was done once per week for laboratory analyses of metals and anions.

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