Evaluation of Reactive Cap Amendments to Sequester Dissolved Manganese in Upwelling Groundwater

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Background/Objectives. Elevated dissolved manganese (Mn) concentrations have been detected in sediments in an area of groundwater discharge to surface water at a tributary and backwater site located along the Delaware River in New Castle, Delaware. To meet the site-specific cleanup levels for sediment, the discharge of groundwater with elevated Mn concentrations through sediment will be addressed by installing an innovative reactive cap layer. A series of laboratory treatability tests were conducted to evaluate reactive amendments for Mn removal. The objectives of this study were to: 1) provide empirical bench-scale data to aid in reactive amendment selection for in-situ Mn removal from site groundwater; 2) develop data needed to estimate reactive media lifecycle in the field; 3) assess the irreversibility and stability of the sequestered Mn; and 4) provide information necessary to iterate cap design thickness and amendment dosing.

Approach/Activities. Representative site groundwater samples were collected from monitoring wells at the site for a series of preliminary batch tests with reactive media selected because dissolved Mn removal from groundwater can be achieved by adsorption on iron oxides and/or precipitation as Mn carbonate (e.g., rhodochrosite) under reducing conditions and alkaline pH. The media tested includes zero-valent iron (ZVI), granular ferric hydroxide (GFH), iron oxide coated sand (IOCS), calcite ($CaCO_3$), crushed limestone (rock calcite), siderite ($FeCO_3$), and an iron oxide rich granular slag material beneficially sourced from a former mining site in Tennessee. Batch tests investigated the rate and extent of Mn removal as a function of initial Mn concentration, reaction time, and liquid-to-solid (L/S) ratio. Initial batch test results revealed that the extent of Mn removal was highest for ZVI, which also increased the pH of the weakly acidic groundwater, but removal rates were limited by the relatively slow anaerobic ZVI corrosion kinetics. Subsequent testing identified granular magnesium oxide (MgO) as an effective additional amendment for pH buffering to enhance Mn removal, because both Mn adsorption and precipitation of Mn carbonate are generally more favorable at higher pH. Based on these results, four different combinations of the most effective reactive media were selected for laboratory-scale column testing. The column tests were carried out over 30 days in a 5-cm-diameter polycarbonate column apparatus with 20-cm reactive media layer depth using site groundwater (15 mg/L of Mn). The columns were operated at approximately 0.60 mL/min, corresponding to approximately 2.7 h of hydraulic residence time. Following completion of the column tests, the Mn-loaded column materials were recovered and analyzed by selective sequential extraction (SSE) to evaluate Mn sequestration on the solids.

Results/Lessons Learned. Among all reactive media, ZVI was the best performing media in the batch tests in terms of Mn removal capacity and rates, followed by granular slag and calcite. A column packed with granular slag and a small amount of MgO exhibited excellent Mn removal efficiency, with the effluent Mn concentration remaining below 5 µg/L throughout the column test duration. This study suggests that the granular slag, which is readily available at low cost, mixed with a small additive of MgO for pH control, is a suitable amendment for a reactive cap layer to sequester Mn at the site.