Dense Brines as Sources of Groundwater Contamination by Perchlorate and Chromate

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Background: In the late 1990's, Region IX of the US EPA approached Dr. Martyn Smith, Program Director of the University of California at Berkeley Superfund Basic Research Program, concerning the recently discovered perchlorate contamination of groundwater throughout the western region. Ammonium perchlorate, the major component of solid rocket fuel, was used extensively in the aerospace industries. Because perchlorate was not a regulated contaminant, wastewaters were frequently released to the environment.

The situation encountered with perchlorate is not unique. There are numerous other instances of subsurface contamination caused by the release of concentrated brines containing contaminants at levels that far exceed water quality guidelines. Acid mine drainage, landfill leachates and nuclear fuel reprocessing solutions are some of the industrial brines that are known to impact groundwater resources.

Dr. James Hunt at U.C. Berkeley initiated research to understand the processes that control the movement of brines, such as perchlorate, in the subsurface. He demonstrated that the density contrast with ambient groundwater will cause concentrated perchlorate solutions to sink through an aquifer until pooling on a lower-permeability confining layer. Density differences will then cause the brine to migrate and diffuse into the lower-permeability confining layer. Perchlorate then slowly diffuses into the flowing groundwater leading to the creation of a long-term source zone. This scenario mirrors the formation of concentrated source zones that are common in aquifers contaminated with dense nonaqueous phase liquids (DNAPLs) and both situations represent difficult remediation challenges.

Advances: A fundamental understanding of brine transport and recovery is needed in the design of optimal remediation systems using technologies that involve the injection of dense water-miscible fluids into the subsurface to accomplish contaminant destruction, isolation, or removal. Brines are miscible with water - but are more dense and more viscous than ambient groundwater. These property differences can dominate (a) transport in the subsurface, (b) release of contaminants associated with brines into groundwater, or (c) delivery and recovery of remedial fluids. While the freshwater-seawater interface in groundwater systems has been extensively studied, the brines identified in this work have much greater contrasts in density and viscosity than encountered at freshwater-seawater interfaces.

Dr. Hunt’s group compiled previously published data on vertical transport of brines in porous media and compared these with a generalization of an existing stability analysis. The available data were not sufficient to test the stability analysis and quantify brine dispersion during one-dimensional vertical displacements. The researchers conducted additional one-dimensional
laboratory-scale experiments to examine the downward displacement of water by brine and brine displacement by water. Under downward flow conditions, gravitational and viscous forces work against each other and these tests were specifically designed to examine the mixing processes. The researchers conducted nearly 400 tests, using calcium chloride and potassium chloride as experimental brines. The resulting data set and analysis demonstrate the applicability of the stability analysis to predict conditions under which brine dispersion will be enhanced by unstable displacements and suppressed by stable configurations.

**Significance:** Brines have not been fully appreciated as source terms for groundwater contamination or for constraining the delivery and recovery of remediation solutions. Because brines are completely miscible with water, the initial expectation is that brines could be displaced by groundwater flow. On the other hand, brine density and viscosity dominate the transport of the brines and associated contaminants within aquifers and into less accessible subsurface environments. Brine dispersion as quantified during vertical transport in this research can be used to approximate brine emplacement in aquifers. Dr. Hunt provided the first synthesis of existing data for one-dimensional vertical displacements, either upwards or downwards. Quantification of these transport processes is essential in understanding the long term source of contaminants that will be present in groundwaters requiring treatment and in the design of delivery and recovery systems for in situ remediation fluids.