This Environmental Management Science Program project (86598) is a collaborative effort between the University of Idaho (UI) and the Idaho National Engineering and Environmental Laboratory (INEEL) with the goal of developing a better understanding of the relationships between chemical reactivity, moisture content, and reactive transport for vadose zone porous media. The research approach relies on the use of unsaturated one- and two-dimensional conservative and reactive tracer experiments conducted at the environmental geocentrifuge facility at the INEEL. The INEEL centrifuge capabilities include an Unsaturated Flow Apparatus (UFA, model J6-UFA Beckman Coulter, Inc.) and a two-meter radius geocentrifuge (model C61-3 Actidyn Systems). In addition, to centrifuge experiments, traditional bench top unsaturated column experiments are being conducted at the UI, Idaho Falls, ID campus. A vadose zone transport model that has been modified to account for the variable acceleration found in centrifuge experiments is being used to aid interpretation of experimental results. Because the use of centrifuge approaches for reactive transport is a relatively new field, effort have focused on development/verification of theory and demonstration of experimental techniques. A conceptually powerful approach was developed to describe reactive chemistry in unsaturated media. In this approach, chemical partitioning between the solid and liquid phases is represented by the product of two functions, one dependent on interfacial processes (i.e., chemistry) and the other dependent on moisture content, but independent of chemistry. This approach allows the derivation of a relative Kd? (analogous to relative permeability) that is a function of the saturation state of the geomedium but is the same for all reactive species. Experimental validation of the relative Kd? approach using centrifuge and bench top experiments will allow the integration of saturated batch sorption experiments for species of interest with unsaturated column experiments using model tracers to define reactivity as a function of moisture content for chemical species of interest. The fundamental equations for fluid flow in a centrifuge were derived. The derivations were required because the applied acceleration along the vertical flow path is not constant as in the vadose zone, but varies with distance from the center of rotation for the centrifuge. The derived equations, which included both continuum- and pore-level derivations, suggest that the Darcy equation is not strictly valid in centrifuge experiments. The range of experimental conditions over which the Darcy equation represents a reasonable approximation of fluid flow is the subject of ongoing research. A correct understanding of the physics of fluid flow in the centrifuge experiments is critical to the interpretation of reactive transport results in the context of vadose zone settings. Unsaturated column (10 cm diameter and 30 cm lengths) experiments were conducted using the geocentrifuge at accelerations of 10 and 20 time earth’s gravity. In these experiments tracer (potassium bromide) breakthrough curves were determined by in flight electrical conductivity measurements and occurred in less than 2 hours. Breakthrough times were found to be proportional to applied centrifugal acceleration and occurred in a fraction of the time that would be required for traditional bench top experiments. The breakthrough curves were evaluated using a version of HYDRUS-1D modified for consideration of varying gravitational acceleration. The experimental results demonstrate the applicability of centrifuge approaches to evaluate unsaturated transport in significantly less time than is required for traditional approaches. These experiments have provided key information that is needed to design the more complex reactive transport experiments that are planned for the project.