

## Characterizing Unsaturated Diffusion in Porous Granular Tuff

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Evaluation of chemical diffusion in unsaturated media is very important in the investigations of contaminant transport and remediation, risk assessment, and waste disposal (e.g., the potential high-level nuclear waste repository at Yucca Mountain, Nevada). For a porous aggregated medium such as granular tuff, the total water content is comprised of surface water and internal water components. The surface water component (water film around grains and pendular water between the grain contacts) could serve as predominant diffusion pathways. Innovative approaches are needed to investigate and characterize these unsaturated diffusion processes.

In this work, we present two experimental approaches (an electrical-conductivity diffusion analog and direct micro-profiling diffusion measurement using laser ablation–inductively coupled plasma–mass spectrometry) to examine unsaturated diffusion processes in porous granular tuff. Using electrical conductivity and the Nernst-Einstein equation, we have measured the diffusion coefficient of potassium chloride in 2–4 mm granular tuff at several water contents. Using the micro-profiling approach, diffusion measurements of contact treatments of different tuff grain geometries (cube-cube, cube-sphere, and cube-tetrahedron) inside several relative-humidity chambers (43, 76, 93, 98, and nearly 100%) were conducted for nonsorbing and sorbing tracers. These treatments were to investigate the influence of contact points and the presence of surface water films on unsaturated diffusion. Results show the critical role of both water-film continuity and pendular water elements in controlling pathways and the magnitude of diffusion. When the surface water component is critically small, steadily decreasing diffusion coefficients occurred with very little decrease in volumetric water content. Currently used diffusion models, relating diffusion coefficients to total volumetric water content, inadequately describe unsaturated diffusion behavior.