

REDUCING THE UNDERGROUND MIGRATION OF URANIUM

Although uranium (U) has been widely used for over 70 years in a variety of military and commercial roles, the safe disposal and remediation of this toxic, radioactive element remains a challenge. Waste uranium comes from multiple sources, including tailings from mining operations, the spent fuel rods of fission power plants, and decommissioned nuclear weapons. Regardless of the source, waste uranium often ends up below ground where it can contaminate groundwater, so scientists continue to search for strategies to slow the underground migration of this toxic, radioactive hazard. One strategy involves introducing substances below ground that retard the formation of highly-soluble uranium compounds. In this study, scientists exposed uranium oxides to calcium and phosphate as a means of keeping the uranium in a low-solubility mineral form. The researchers tracked the chemical changes associated with this process using several techniques, including x-ray spectral measurements performed at the APS. Their observations confirmed that calcium and phosphate slow the transition from less-soluble uranium compounds to more-soluble ones. While the protective effects of the chemical treatment eventually faded under real-world oxidizing conditions, the processes employed and the data gathered will substantially contribute toward the goal of reducing subsurface uranium hazards.

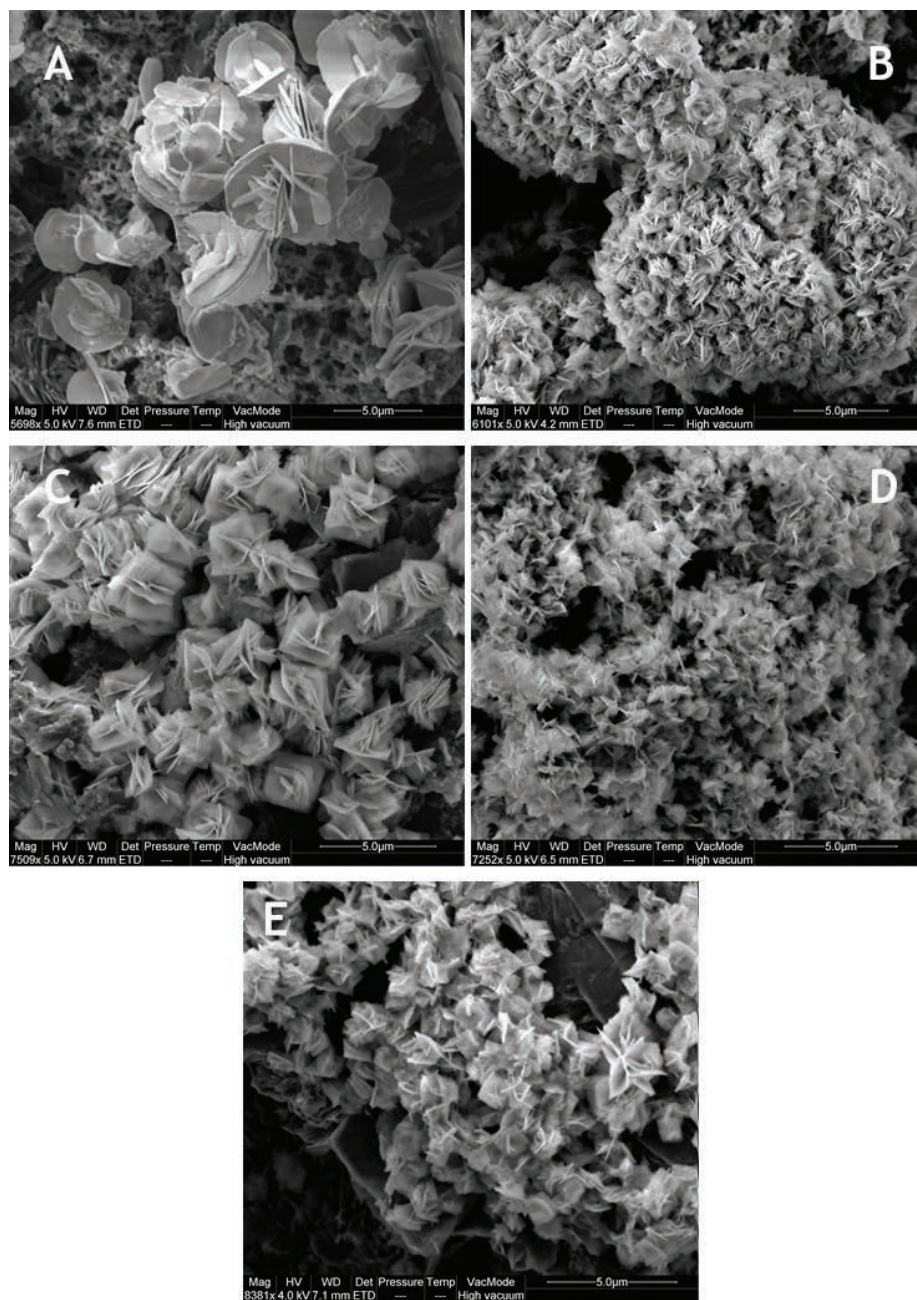


Fig. 1. Micrographs obtained with a scanning electron microscope (SEM). The images show the results of U^{IV} solids oxidized over three days (72 hours). The top two panels compare oxidized UO_2 with (a) no added Ca or PO_4 , to (b) 400 micromoles/L (400 μM) of added Ca and PO_4 . The middle and bottom panels compare oxidized $U^{IV}-PO_4$ that had (c) no added Ca or PO_4 , to (d) 100 μM of added Ca and PO_4 , and (e) 400 μM of added Ca and PO_4 . (5- μm scale bars are located at bottom right of each micrograph; other data at bottom of each picture displays SEM magnification, etc.)

Uranium is naturally present at low concentrations in soil and rocks, where its inherent radioactivity contributes to normal background radiation levels. However, ground contaminated with higher-than-normal concentrations can pose serious environmental and health-safety risks. When removal of subsurface uranium is impractical, scientists attempt to restrict its underground movement. The chief culprit in uranium migration is groundwater: this heavy metal readily forms compounds that can dissolve in water. By inducing uranium to form compounds with low solubility, its migration can be considerably reduced.

The researchers in this study, from Argonne, the Illinois Institute of Technology, and the Bulgarian Academy of Sciences, tracked the chemical evolution of two important uranium compounds. The first was uranium dioxide, UO_2 , a major constituent of uranium ore. The second was a more complex uranium/phosphate compound produced naturally by subsurface bacteria, denoted $U-PO_4$. (In both cases, the oxidation state of the uranium was +4, so that these compounds are more precisely labeled as $U^{IV}O_2$ and $U^{IV}-PO_4$.) The $U^{IV}O_2$ formed nanoparticles, while the $U^{IV}-PO_4$ exhibited an amorphous (non-crystalline) structure. In soil, both compounds will combine with subsurface oxygen to form new compounds. These chemical reactions can change the original oxidation state of the uranium, from +4 to +6 (denoted U^{IV} and U^{VI} , respectively). This change in oxidation number is important since compounds containing U^{IV} are generally less water soluble than U^{VI} compounds.

Initially, $U^{IV}-PO_4$ and nanoparticulate $U^{IV}O_2$ were placed in neutral water solutions (pH 7.0) containing dissolved oxygen and carbon dioxide. Experiments were performed with and without the addition of calcium (Ca) and phosphate (PO_4) to the solutions. Adding calcium and phosphate significantly altered the ensuing chemical reactions. This difference can be seen in the micrographs of Fig. 1, which compare the uranium compounds after three days in their oxygenated solutions, both with and without exposure to Ca/PO_4 . The morphological differences between the oxidized uranium solids are dramatic.

The chemical species present in the solutions (some with Ca/PO_4 , others without) were tracked with several distinct measurement techniques, including x-ray absorption near-edge spectroscopy (XANES), performed at the MR-CAT 10-BM-A,B x-ray beamline at the APS. XANES was used to observe the oxidation states of the uranium compounds present in each of the solutions.

Figure 2 is a plot based on the XANES data showing that the addition of calcium and phosphate reduced the oxidation rates of the $U^{IV}O_2$ and $U^{IV}-PO_4$ compounds, thereby slowing the conversion from the less-soluble U^{IV} state to the more-soluble U^{VI} state. While the addition of calcium and phosphate lowered the oxidation rate 10-fold, the two compounds eventually oxidized completely. Nevertheless, this finding indicates that subsurface uranium exposed to sufficient calcium/phosphate levels, whether naturally from the surrounding environment or artificially by injection into the waste site, is one possible strategy for slowing uranium migration.

Another important observation was an observed build-up of a $Ca-U^{VI}-PO_4$ coating on the $U^{IV}O_2$ nanoparticle surfaces, which served to limit further oxidation. Additionally, the researchers expect that the chemical reaction rates determined from these experiments will be used to improve the numerical modeling of actual subsurface uranium migration. — Philip Koth

See: Drew E. Latta^{1*}, Kenneth M. Kemner¹, Bhoopesh Mishra^{1,2}, and Maxim I. Boyanov^{1,3}, "Effects of calcium and phosphate on uranium(IV) oxidation: Comparison between nanoparticulate uraninite and amorphous U^{IV} -phosphate," *Geochim. Cosmochim. Acta* **174**, 122 (2016).

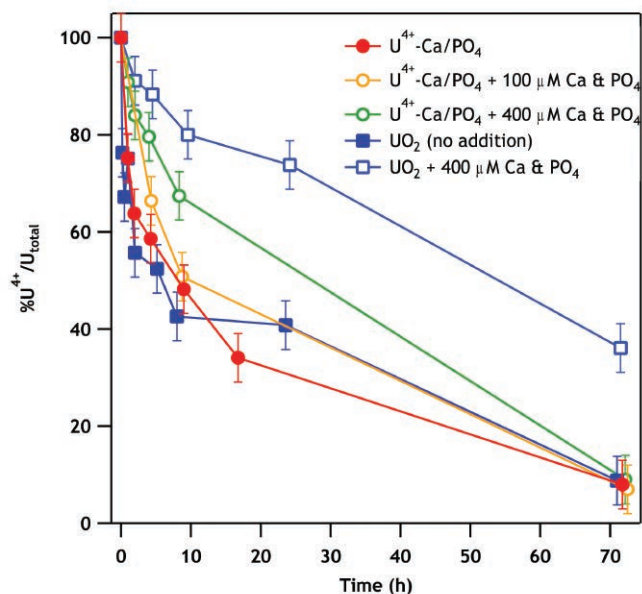


Fig. 2. Plot of oxidation rates of uranium compounds U^{IV} -phosphate and uranium dioxide, UO_2 . Data derived from XANES x-ray spectroscopy. Squares represent oxidation data for UO_2 , while circles are oxidation data for U^{IV} -phosphate. Legend at top-right indicates whether or not calcium/phosphate was added to solution. Note how adding 400 μM of calcium and phosphate significantly slows oxidation of both UO_2 and U^{IV} -phosphate. (" U^{4+} " and " U^{IV} " both indicate uranium possessing an oxidation state of +4.)

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