

REMEDIATION OF SOILS FROM RADIOACTIVE CONTAMINATION

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Soils have been contaminated with radionuclides in Australia and other parts of the world through the testing of atomic weapons and through mining. Significant contamination exists in the USA. Leaching from tailings dams can contaminate soils through long distances as the radionuclides may be transported through the soils via groundwaters. Such contamination is difficult to remove. The addition of phosphates and the formation of autunites may offer a mechanism for removal of the radioactive contamination. This group of minerals is "clay-like" and has been termed the uranyl micas. These minerals are secondary minerals and are formed from solutions. The implication of such a phenomenon is that the minerals are soluble and will pass into groundwater systems and hence will be transported long distances. This provides the reason for the remediation of soils. Autunite solid-state and solution chemistry plays one of the most important roles in the actinide chemistry, mineralogy, geochemistry and "environmental chemistry" with regard to uranium(VI) migration in natural waters. Actinide autunite complexes inclusive those of uranium are to be reflected in migration from a nuclear waste repository or in accidental site contamination. To gain an understanding of the geochemical behaviour of such materials, a fundamental knowledge of actinide carbonate chemistry and mineralogy seems to be needed (Clark et al., 1995). The study of the uranyl carbonates has been undertaken for an extended period of time (Huang and Kerr, 1960; Neumann and Bryn, 1958). There are a significant number of compounds containing the uranyl ion (Whittle, 1955). Contaminated wastes may also offer a source of radionuclides for terrorism and hence the easy detection of such uranyl minerals is imperative and leads to a new branch of chemistry which might be titled "Nuclear Forensics".

The autunite group of minerals are tetragonal uranyl arsenates, phosphates and vanadates. The minerals have a general formula $M(\text{UO}_2)_2(\text{XO}_4)_2 \cdot 8-12 \text{H}_2\text{O}$ where M may be Ba, Ca, Cu, Fe^{2+} , Mg, Mn^{2+} or $\frac{1}{2}$ (HAl) and X is As, or P or V. The minerals have a layer-like structure (Locock and Burns,

2003). These minerals are often known as uranium micas (Cejka et al., 1985; Cejka et al., 1984). A characteristic feature of the minerals is their layer structure in which uranium is bound in uranyl-phosphate layers. The cations and water are located in the interlayer space. The mineral autunite has the formula $\text{Ca}[(\text{UO}_2)_2(\text{PO}_4)]_2 \cdot \text{H}_2\text{O}$. Autunite is amongst the most abundant and widely distributed of the uranyl phosphate minerals, yet because of its pseudotetragonal symmetry and rapid dehydration in air, the details of its symmetry and structure are uncertain. The structure contains the well known autunite type sheet with composition $[(\text{UO}_2)_2(\text{PO}_4)]$ resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra. The calcium in the interlayer is coordinated by seven H_2O groups and two longer distances to uranyl apical O atoms. Two symmetric independent H_2O groups are held in the structure only by hydrogen bonding (Locock and Burns, 2003). This paper will show the application of electron microscopy, X-ray diffraction and Raman spectroscopy to the identification of the autunite mineral group and other secondary uranyl minerals.

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