

## Enzymatically mediated precipitation of phosphate minerals

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Phosphate-based strategies have potential for the safe management of uranium mining wastes. Phosphate forms insoluble complexes with metals (e.g. Al, Ca, Fe, La, Pb, Ra, Th, and U) that can be used to form host materials or contaminant-phosphate phases. Natural analogues (e.g. apatite, monazite) are stable over geological timescales and across varying pH, redox, and chemical conditions [1].

Phosphate biominerals can be produced by microbial phosphatase enzymes that hydrolyse organic phosphates and release inorganic phosphate. The liberated phosphate may then form precipitates with metals such as La, or U [2].

This project has focused on phytate (C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>), sourced from plant waste products, as a phosphate donor. Phytate forms insoluble complexes with a range of metals, which could be used to provide initial immobilisation. Treatment with phytate-degrading fungal phytase enzymes to release inorganic phosphate may then further reduce the solubility of contaminants.

This has been tested for Al, Fe(II), Fe(III), La, and Pb. At pH 5.5 in single metal (5 mM) solutions, phytate was able to immobilise 60–98% of each metal. Phytase addition improved metal removal to ~90% for Al and Fe and ≥99.9% for La and Pb. XRD and chemical analyses indicated that Al, Fe, and La were incorporated into amorphous, mixed phytate-inorganic phosphate phases, while Pb precipitated as hydroxypyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH). Leaching tests of the La precipitate in artificial groundwater (pH 5.5) indicated that less than 0.01% of La was released to solution.

Additionally, phytase-producing fungi *Aspergillus niger* and *Blastobotrys adenivorans* have been investigated in liquid cultures, sand columns, and artificial mine tailings. Complete removal of La was achieved in solution and sand systems, with *B. adenivorans* producing rhabdophane (LaPO<sub>4</sub>·nH<sub>2</sub>O) and *A. niger* producing a mixture of La phosphates and oxalates. However, clays present in the artificial tailings inhibit phytase activity, and the *in situ* precipitation of phosphate biominerals in the presence of reactive solids requires further attention.

[1] Rakovan & Pasteris (2015) *Elements*, **11**, 195–200. [2] Macaskie et al. (2004) in *Phosphorus in Environmental Technologies: Principles and Applications*, 549–581.