

# Coprecipitation of Ce with lead phosphates

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There is growing interest in alternative pathways for recovery of REE, especially from apatite sources, as modern technologies require a steady supply of critical elements. Phosphates have strong affiliation with metals, including REE and Pb. It was hypothesized that, similarly to Ca-apatites, also Pb-apatite (pyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ) can embed significant amounts of REE in the structure. A series of model experiments were carried out for coprecipitation of Ce with Pb-phosphates leading, among others, to formation of pyromorphite-Ce (PYM-Ce).

Synthesis of PYM-Ce were conducted at ambient conditions, at pH 1-11, by mixing solution containing relatively high concentrations of Pb and Ce (~15000 and ~1700 ppm, respectively) with solutions containing stoichiometric concentrations of  $\text{PO}_4$  and Cl. In control experiments, phosphates were precipitated in absence of: a) Ce, b) Pb, or c) Cl.

In all experiments, phosphate precipitation results in the removal of almost all Ce from solution. PYM-Ce precipitation reduces Ce concentrations from 1700 ppm to 2,5 and 1,2 ppm at acidic and alkaline pH, respectively. In the absence of Cl, concentration of Ce also drops down to ~2 ppm.

In the entire pH range, PYM-Ce was precipitated (with a small admixture of another phosphate phase) in the form of needles, 10 – 1  $\mu\text{m}$  in size. Crystal size decreases with increasing pH. In the presence of Ce, PYM crystals are longer and thinner. In the absence of Pb, fibrous rhabdophane-Ce (RHA-Ce) is formed, aggregating in alkaline pH. In the absence of Cl, a new Pb-Ce phosphate phase, not quite identified at this stage of the study, is formed with a composition approximated by SEM/EDS, FTIR, and thermal analysis as  $\text{Ce}_2\text{Pb}_3(\text{PO}_4)_4 \cdot 3,3\text{H}_2\text{O}$ . PXRD patterns indicate low degree of crystallinity. Nanometer crystallites form globular aggregates ~0,5  $\mu\text{m}$  in diameter.

Coprecipitation of Ce with Pb phosphates in the presence of Cl is advantageous because it results in the recovery of almost all Ce from solution in the form of a crystalline PYM-Ce that is easily separated from suspension. This works over a wide range of pH and concentrations.

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