



In situ removal of Pb and As(V) from multi-element aqueous solutions by precipitation of mixed apatites

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Several technologies employing apatites have been developed for cleanup of contaminated soils and wastes (Clara et al. 2007). Apatites are characterized by relatively high stability, low solubility and very flexible structure allowing for many substitutions, particularly Ca-Pb and P-As. It is not fully understood, however, how the dissolution-precipitation processes of their formation compete in the case of precipitation from the multi-element solutions. The purpose of these experiments is precipitation of apatites by the reaction of aqueous solutions containing simultaneously Ca^{2+} , Pb^{2+} , phosphates, arsenates and F^- , Cl^- , Br^- and I^- at various pH. It is hypothesized that a single phase isostructural with apatite (a complicated solid solution containing all of these elements) precipitate at the conditions of the experiment. Formation of such a phase is also anticipated in the real system in the field.

Three portions of 400 mL of solutions have been added using peristaltic pump to 1000 mL of redistilled water: 1 - dissolved $\text{Pb}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$; 2 - dissolved K_2HPO_4 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$; and 3 - dissolved NH_4F , NH_4Cl , NH_4Br and NH_4I (at the pH of 4.5, 7.0, and 10 controlled with 1M HNO_3 and 1M KOH ; 25°C, 1 atm.). The molar concentrations of the reagents correspond to the molar stoichiometry of apatite: 3:2 Ca:Pb or 2:3 Ca:Pb; 1.5:1.5 P:As; 0.2:0.2:0.2:0.2 F:Cl:Br:I. This corresponds to the precipitation of $\text{Ca}_3\text{Pb}_2(\text{PO}_4)_{1.5}(\text{AsO}_4)_{1.5}\text{F}_{0.2}\text{OH}_{0.2}\text{Cl}_{0.2}\text{Br}_{0.2}\text{I}_{0.2}$ solid solution or $\text{Ca}_2\text{Pb}_3(\text{PO}_4)_{1.5}(\text{AsO}_4)_{1.5}\text{F}_{0.2}\text{OH}_{0.2}\text{Cl}_{0.2}\text{Br}_{0.2}\text{I}_{0.2}$ isostructural with apatite. The products were syringe sampled after 7 days, washed with water, dried at 60°C and analysed using powder X-ray diffraction XRD and electron microscopy SEM-EDS.

The experiment resulted in the precipitation of very fine, white, crystalline powders. SEM imaging reveals one population of homogeneous aggregates of crystals in the form of elongated rods or needles (up to 1 μm) in each sample. The XRD patterns clearly show a well crystalline, monomineral apatite phase. The reaction of solutions containing 3:2 Pb:Ca or 2:3 Pb:Ca at pH 4.5 result in precipitation of halogenated pyromorphite – mimetite solid solution member. At higher pH (7.0 and 10.0), diffraction patterns fit closer to hydroxylpyromorphite or hydroxylmimetite with limited substitution of Ca^{2+} .

The results show that the single phase isostructural with apatite solid solution forms at all pHs. The chemical composition of the solid does not perfectly represent the concentrations in the solution. Pb is preferable substituted into the apatite structure while P:As molar ratio is in agreement with starting composition. The results suggest that Pb and As can be immobilized by coprecipitation of composite apatite in presence of Ca^{2+} , PO_4^{3-} , Br^- , Cl^- , F^- and I^- . This work is funded by NCN research grant No. 2017/27/N/ST10/00776. MM is partially funded by AGH research grant No 11.11.140.158.

Clara, M., Magalhaes, F., & Williams, P. A. (2007). Apatite group minerals: solubility and environmental remediation. In *Thermodynamics, solubility and environmental issues* (pp. 327-340).