



TIME AS A CHALLENGING CONSTRAINT OF EXPERIMENTAL STUDIES IN APPLIED MINERALOGY OF APATITES

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Introduction

Lead apatites with a general formula: $Pb_5(XO_4)_3Z$ (where $X = P, V, As$ and $Z = Cl, OH, F, Br, I$) are particularly significant in the field of environmental protection. Induced precipitation of these phases is the fundamental concept of the *in situ* immobilization of Pb and As in contaminated soils and wastes. Optimization of this treatment method requires extensive research on apatite phases in the field of their identification, crystallization, transformation, structure, and thermodynamic stability (Flis et al., 2011;). The research indicates the limitations of soil remediation treatments with the use of apatites. Most of the studies on the implementation of apatites as sequestration agents are based on the methods typical for experimental mineralogy, which beyond a number of undoubted advantages, are limited by laboratory conditions, including the duration of the experiment. Research on the applicable properties of apatite phases is mainly about synthesizing crystals with parameters similar to those in the environment and then dissolving them with a chosen method to determine the stability and reactivity. In this regard, the key parameter stating on the reliability of laboratory results and the possibility of referring them to field conditions is the equilibrium between solids and solutions at the stage of synthesis as well as during thermodynamic studies.

In this paper, we share selected observations on the role of time in long-term research in the field of mineral-water interaction: thermodynamics of dissolution of Pb-apatites in aqueous solutions, based on Vanadinite ($Pb_5(VO_4)_3Cl$). Particular emphasis was placed on the methods to determine the equilibrium of the systems in the context of designing the duration of experiments.

Samples and methods

Synthesis and dissolution of vanadinite.

Synthesis of vanadinite was carried out at 90°C by dropwise mixing of the aqueous solutions of $Pb(NO_3)_2$, KCl and NH_4VO_3 in molar proportions based on the stoichiometry of the vanadinite ($Pb:V:Cl = 5:3:1$ molar ratio). The synthesis yielded yellowish, homogenous precipitate. The phase was identified as pure vanadinite by the scanning microscopy and the X-ray diffraction analysis.

Dissolution experiments were performed in triplicates in 250-mL polycarbonate bottles immersed in a closed water bath with thermostatic control at 25 °C. Equal portions (150 mg) of synthetic vanadinite were washed thoroughly with redistilled water and introduced as a suspension to the bottles containing 250 mL of 0.05 M KNO_3 solution. Totally, there were 7 sets of the experiment with the pH adjusted using 0.1 M HNO_3 to: 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 6.0. The dissolution was carried out for 8 months. During this time, the bottles were manually stirred at least two times a week, and the solution samples were periodically withdrawn and filtered using a 0.2 μm polycarbonate filter. The [Cl] evolution patterns from the dissolution experiments were observed to determine the equilibrium in the suspensions. Cl concentration was measured using turbidimetric method with silver nitrate. The system was considered in equilibrium when at least three consecutive samples showed identical [Cl], with an experimental error expressed as standard deviation of triplicate results. The residual solids were sampled, washed with acetone, air-dried, and characterized with SEM-EDS. Additionally, the residuum from the experiment at pH = 3.0 was examined with XRD. After this stage of dissolution experiment, the bottles with the suspensions were transferred to a room temperature of 22 °C ± 2 °C and left for 9 years. The reactors were occasionally mixed and checked for leaks. At the end of the



experiments, the concentration of Cl in solutions was measured by turbidimetric method with silver nitrate and the residual solids were analyzed with a use of SEM-EDS (A FEI QUANTA 200 FEG, at 15 kV).

Results

Figure 1 shows the evolution of Cl concentration in experimental solutions of vanadinite dissolution. The figure shows the Cl concentrations in solutions with pH = 2.0, 2.5, 3.0 and 3.5; please note the break in the time scale separating the results obtained after 8 months from those after 9 years. The experiment was conducted at pH range from 2.0 to 6.0, but during the first 8 months, the concentrations of Cl in the solutions with $\text{pH} \geq 4.0$, were below the detection limit. As the graph indicates, after 8 months of the experiments the concentration of Cl indicated the equilibrium in solutions: the samples collected in 2200 h, 3200 h and 4000 h of the experiment yielded values identical within the experimental error. Then, the experimental suspensions were kept for a period of 9 years. The reactors were sealed, occasionally mixed, and the temperature was reduced from 25 °C to room temperature $\sim 22 \text{ °C} \pm 2 \text{ °C}$. This had ensured a quality of the long term experiment, so that after 9 years the effect of potential evaporation was negligible. The last points in the graph presented in figure 1 show the concentration of Cl in the samples collected after 9 years of research. The concentration of Cl increased in all solutions. The increased amount of Cl in the solutions with pH 2.0 and 2.5 indicated that, contrary to the assumptions, dissolution of vanadinite under these conditions had not been completed after 8 months. Similarly, solutions at pH = 3.0 and 3.5 were not in equilibrium. Cl also appeared in the solutions with an initial pH of 4.0 - 6.0, for which after 8 months of the experiment it was below the detection limit. After completing the research (9 years), the concentration of Cl in these solutions equaled to (in mM): for pH = 4.0: 0.031 ± 0.004 , for pH = 5.0: 0.021 ± 0.01 and for pH = 6.0: 0.013 ± 0.006 .

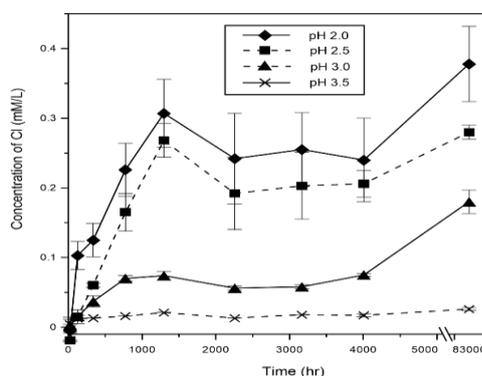


Figure 1. The evolution of Cl concentration in the dissolution experiment of vanadinite. Data points represent the average of triplicate experiments, error bars are two standard deviations.

Conclusions

In this work we have shown that the rate of transformation and recrystallization in the apatite group may be so slow that, with faulty assumptions on the duration of experiment, the metastable state can be evaluated as equilibrium. One of the means to avoid mistakes is to run parallel precipitation and dissolution experiments for the same conditions, as presented in one of our papers (Flis et al., 2011). Failure to perform the controls on equilibrium in experiments may lead to misinterpretations.

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References

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