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Formation of CeSiO4 and AnSiO4 (An = Th, U, Pu): insights coming from hydrothermal synthesis and thermodynamic issues

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Actinides are the main contributors to the long-term radiotoxicity of spent nuclear fuels. The interactions between these radioelements and silicate species in geological conditions could influence their mobility and could affect the safety of the radwaste storage facilities. Especially, the formation of actinide silicate $AnSiO_4$ has to be considered carefully, as thorium and uranium silicates are rather abundant in environmental silicate rich media and under reductive conditions. Moreover, the natural formation mechanism of coffinite $USiO_4$, which involves the alteration of UO_2 in reductive and silica rich media, rose important debates about the radionuclides' behavior under geological repository conditions. Additionally, the formation of actinide oxy-hydroxy-silicate colloids has been mentioned for thorium, uranium and neptunium in weakly basic carbonate media. Such colloids are suspected to play a huge role on the actinide mobility in environmental conditions. Therefore, the synthesis and the determination of the thermodynamic properties of $AnSiO_4$ could be a crucial issue to study the behavior of these elements in the environment.

Aiming at the synthesis of pure and single phase $AnSiO_4$ phases, multiparametric hydrothermal treatments were developed varying pH of the starting mixture, ligand concentrations (including carbonate ions), reactant concentrations, temperature and duration of the heating/hydrothermal treatment, redox conditions...). $ThSiO_4$ was first obtained through two different optimized sets of conditions: the first one in acidic media without any complexing agent and the second one in weakly basic media in the presence of large quantities of carbonate ions. In addition, the optimized conditions of formation were more specific for $USiO_4$ as only weakly basic carbonate media allowed the formation of coffinite. Pure $CeSiO_4$ (considered as $PuSiO_4$ surrogate) was successfully prepared using solid Ce(III) silicate precursors, which counterbalanced the hydrolysis of Ce(IV) and allowed the formation of pure $CeSiO_4$. This way was transposed with success to prepare $PuSiO_4$ in the hot-laboratories of the ATALANTE facility.

Thermodynamic analysis of the prepared phases was finally performed. Whereas the results obtained suggested the stability of thorite, it confirmed the metastable character of other actinide silicates like U- or Ce- end members.