	Experiment title: EXAFS investigation of U(IV) precipitates	Experiment number: 20-01-691
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Report:

Mobility and migration of actinides in the environment is an important issue to predict appropriate construction aspects of nuclear waste repositories. Because uranium(IV) has a very low solubility at pH ~7, it is considered as immobile under the redox conditions of a nuclear waste repository. The same is valid for uranium mining areas. However, the U(IV) precipitate may occur as nano-sized colloids which are very mobile in the environment. Nuclear waste and uranium mining with open shafts and tunnels contain under oxic conditions uranium predominantly in oxidation state VI. The reduction process of such U(VI) to U(IV) may result in U(IV) colloids as observed in the laboratory especially in low pH. Similar colloids appear with Th(IV) and Pu(IV). Such colloids are meta-stable and may migrate out of the retaining barriers. Anoxic water with a certain amount of carbonate and silicate is usually present in geological formations used for uranium waste disposal. We found

meta-stable colloids of U(IV) and Th(IV) at near-neutral pH, especially in presence of silicate. The structure of these colloids is recently under discussion. It is known that tetravalent oxyhydroxy colloids undergo over time ordering processes and form sequences of AnO_2 structures. The question raises, if such ordered domains occur also in $An(IV)$ silica colloids. Subsequently we compare the EXAFS spectrum of ThO_2 with the spectrum of a Th/Si colloid sample.

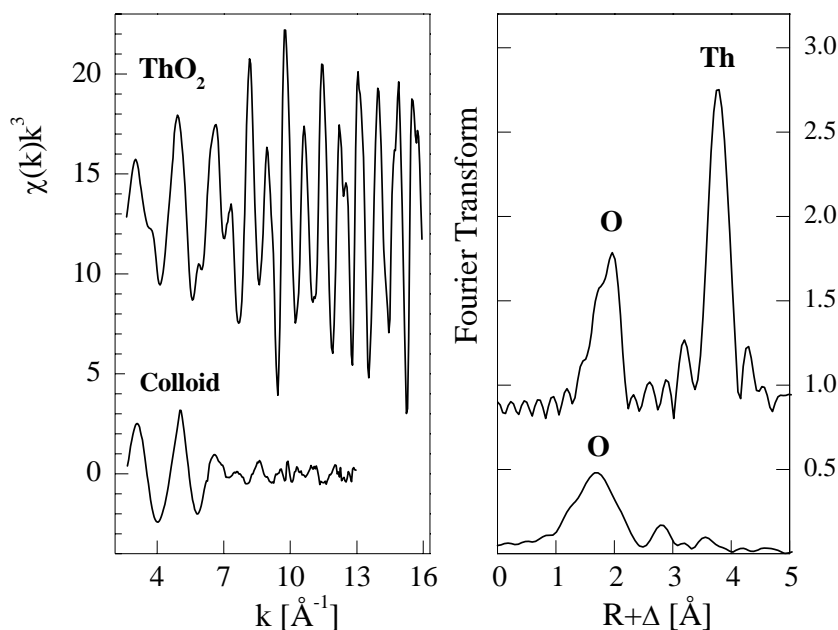


Figure 1. Th L_3 edge EXAFS (left) and the corresponding Fourier Transformation (left) of ThO_2 and a Th/Si colloid sample.

ThO_2 crystallizes in the space group Fm-3m. Each Th atom is directly coordinated by 8 oxygen atoms and is surrounded in the next coordination sphere by 12 Th atoms. The EXAFS spectrum of ThO_2 in Fig. 1 shows 8 identical Th-O distances at 2.42 \AA and 12 Th-Th distances of 3.96 \AA . The spectrum of the colloid sample shows clear differences. The first peak, corresponding with the oxygen shell is broadened, indicating a variety of oxo and hydroxo bonds in the coordination sphere of thorium. A peak representing the Th-Th interaction is completely missing, indicating that the structure is either completely changed, e.g. by replacing Th-O-Th bonds by Th-O-Si bonds, or at least highly disordered. There is also no structural similarity with the crystalline $ThSiO_4$ polymorphs. Thus, so far we could not identify any ordered domains in such colloids.