

# Detection of uranium colloids under anoxic conditions by Laser-Induced Breakdown Detection (LIBD)

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**ABSTRACT.** Freshly prepared colloidal particles of U(IV) are detected by LIBD. The pH at the onset of colloid detection is used to re-evaluate the solubility product of U(IV) hydroxide.

Uranium, among other actinides, plays an important role in the long-term safety assessment of nuclear waste repositories. Furthermore, it is naturally present in former uranium mines and might contaminate aquifers when these mines are flooded. The correct determination of the thermodynamic solubility of uranium is essential for the geochemical modeling of these scenarios.

**EXPERIMENTAL.** The preparation of the U(IV) colloids and the sampling method are described in detail in [1]. A uranium concentration of  $10^{-4}$  M was chosen. The basics of LIBD are explained in [2], the LIBD setup established at the IRC is presented in [3]. Sample solutions were investigated at laser pulse energies of 1.5 mJ. One thousand laser pulses were applied three times on each sample. The mean value of the measured breakdown probability at each pH was calculated and used to detect the onset of colloid formation.

The distribution of breakdown events in the focal area of the laser beam was also determined by LIBD to evaluate the mean size of the formed colloids [cf. 2].

**RESULTS.** Fig. 1 shows the dependency of the breakdown probability on the pH of the solution. The colloidal impurities in ultrapure water cause a background of the breakdown probability of some 4 %, this level is marked by a dashed line. The breakdown probability remains below the background level up to a pH of 2.55. It shows a steep slope at this point, *i.e.* a significant amount of colloids was generated and the solubility product of uranium(IV) hydroxide had been exceeded.

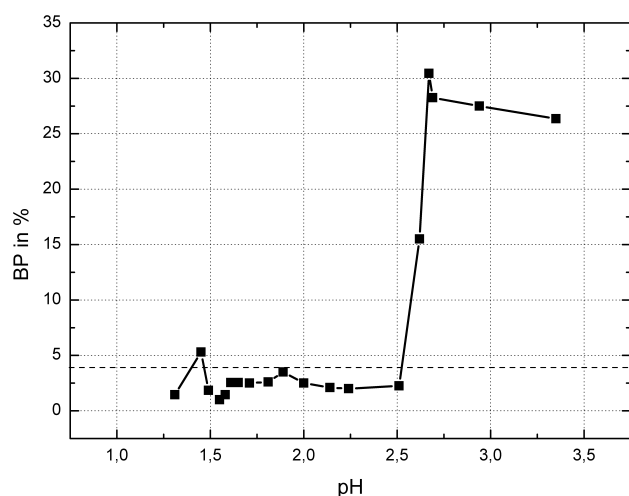


Fig. 1: Dependency of breakdown probability on pH in a  $10^{-4}$  M U(IV) solution.

The solubility product of  $U(OH)_4$  under the given conditions is calculated by equation (1).

$$K'_s = [U^{4+}][OH^-]^4 \quad (1)$$

To obtain a value which is comparable to published solubility products, the following facts have to be taken into account:

- U(IV) has a strong tendency to hydrolyse. Therefore not all U(IV) is in solution as  $U^{4+}$  but in the form of U(IV) hydroxo complexes. This is corrected by calculating the speciation of U(IV) using the respective hydrolysis constants from a recent review by Neck and Kim [4].
- The investigations were carried out in a solution containing 0.2 M  $HClO_4/NaClO_4$ . The calculated solubility product under these conditions has to be corrected to  $I=0$  using the specific ion interaction theory (SIT) described in the NEA-TDB [5].

Under these circumstances,  $\log K'_s$  for uranium(IV) hydroxide is calculated to be  $-54.3$  at zero ionic strength. This value is in good agreement with the value of  $-54.5$  published in the review by Neck *et al.* [4]. Data in [4] are based on the results of solubility experiments but the contribution of colloids was not quantified in these experiments.

A similar study on thorium colloids [6] indicated a dependency of the solubility of the actinide on the particle size. The colloidal phase is better soluble than the bulk of the solid. In the case of thorium, a shift of the solubility product by about one order of magnitude resulted. Our focal lengths obtained by LIBD indicate that the formed colloids have a particle size that also needs to be taken into account when calculating the solubility product. Such corrected calculations are under way.

Presently it is assumed that the formed colloids consist of amorphous uranium(IV) hydroxide. The existence of other solids, e.g. microcrystalline  $UO_2$ , is also imaginable and has to be examined by other methods (XRD, EXAFS).

Furthermore, it is necessary to repeat the measurements for different concentrations of U(IV) to confirm the independence of  $K'_s$  on the selected uranium concentration.

## REFERENCES

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