

## Laser induced breakdown detection (LIBD): Quantification of colloid formation of tetravalent actinides and homologues

### Abstract

The aim of the present work is the use of laser induced breakdown detection (LIBD) to investigate the colloid generation of tetravalent actinides and their homologues. LIBD is a very high sensitive method to determine the particle size and concentration of aqueous colloids. The method is based on the dielectric breakdown in the matter through light absorption from a laser beam. In the focus of the laser beam, the energy density is so high, that a plasma results. Colloidal particles which diffuse in the focal region are detected by setting an appropriate laser energy. The generated plasma is detected through its expansion-generation shockwave.

Three principal LIBD applications are presented:

The agglomeration of  $ZrO_2$  colloids is investigated by LIBD at particle concentrations typical for natural systems (range of particle concentrations between  $2.6 \cdot 10^6$  -  $3.4 \cdot 10^8$  particles/cm<sup>3</sup>). A linear correlation is found up to  $2.6 \cdot 10^6$  particles/cm<sup>3</sup> between aggregation rates and particle concentrations at  $pH_{IEP}$  8.20 (isoelectric point) and an ionic strength of 0.1 M NaClO<sub>4</sub>. The results agree with the simple diffusion limited aggregation (fast aggregation) model of Smoluchowski.

The generation of Th(IV) colloids through hydrolysis and polynucleation is investigated in 0.5 M NaCl by LIBD. The investigation of long-time stability of Th(IV) colloids is also performed at total concentrations of Th(IV) between  $10^{-5}$  and  $10^{-2}$  M in  $pH_c$  range 3 – 5. A dilution of Th(IV) suspension at constant pH below the solubility limit of Th(OH)<sub>4</sub>(am) downgrades colloids to ionic species. A dilution of Th(IV) suspension with 0.5 M NaCl of neutral pH causes an increased oversaturation and colloid generation, leading to a steady state, where Th(IV) colloids are in equilibrium with ionic species. The generated Th(IV) colloids are found to remain stable up to 490 days with respect to particle concentration and size.

The hydrolysis and colloid generation of Pu(IV) is investigated in 0.5 M HCl / NaCl by LIBD and UV/Vis/NIR absorption spectroscopy. Dilution titration experiments are performed by variation of  $pH_c$  value in range 0 - 2.4 and the total concentration of Pu in range  $1.2 \cdot 10^{-3}$  -  $5.3 \cdot 10^{-7}$  M. Exceeding the solubility of Pu(OH)<sub>4</sub>(am), the generation of Pu(IV) colloids can be detected by LIBD. The obtained solubility curve has a slope of -2. This can be explained through the generation of dihydroxo complexes Pu(OH)<sub>2</sub><sup>2+</sup> as dominant species in this range of  $pH_c$  and Pu concentration. The derived solubility product is  $\log K_{sp}^0 = -59.26 \pm 0.30$  and is lower than the value calculated with literature solubility data. Dihydroxo species undergo the colloid generation and an equilibrium is reached between the Pu(OH)<sub>2</sub><sup>2+</sup> species and Pu(IV) colloids. This equilibrium is analog to that observed between colloidal and ionic Th(IV) species but, contrary to the metastable Th(IV) colloids, a decrease of particle size and concentration is observed in the case of Pu(IV) with increasing time. The combination of spectroscopic and LIBD measurements show how the competing reactions of plutonium – the hydrolysis and polynucleation with colloid generation, and on the other hand the disproportionation of Pu(IV) to Pu(III) and Pu(VI) as well as the complexity of mechanisms, complicate the thermodynamic assessment.