

Formation of Zr(IV)-nanoparticles on Muscovite (001): effect of background electrolyte

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A hitherto unresolved question in the aqueous chemistry of Zr (IV), as well as other tetravalent cations, such as Pu(IV) and Th(IV), is how the oligo- and polymerization of their hydrolysis products proceeds on a molecular scale.[1] Recent studies show that these reactions are strongly accelerated at mineral interfaces[2], allowing for easier studies. Through CTR/RAXR modeling, we derived the electron density of Zr above the mica surface, which reveals the internal cation network in the Zr-nanoparticles. Here we propose a plausible chemical route to depict the Zr nanoparticle aggregation induced by increased concentration of background electrolyte. Without background electrolyte, the observed Zr(IV) species exists as tetramer and/or octamer as primary particles. The addition of NaCl weakens the electrostatic repulsion between primary particles to enable colloidal aggregation that evolves through several stages as confirmed by AFM images. In combination the two methods show that the pathway of the aggregation begins by connecting two or more primary tetrameric building units “head-to-head” to form rod-shaped structures (nanorod). Afterwards, the “side-by-side” aggregation becomes favored, which leads to the formation of two-dimensional nanosheets. In the end, “face-to-face” stacking leads to the nanoparticle growth to make 3D framework.

REFERENCES

- [1] Knope, K. E. et al. (2012), *Chem. Rev.*, 113(2), 944-94
[2] Schmidt, M. et al. (2013), *Env. Sci. Tech.*, 47(24), 14178-84.