

Mechanisms of uranyl sequestration by hydrotalcite

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To date no studies have been made to determine how hydrotalcite, a Mg-Al subclass of permanently positively charged layer double hydroxides, sequester uranyl cations (UO_2^{2+}) and specifically the uranyl tris-carbonate ($\text{UO}_2(\text{CO}_3)_3^{4-}$) complex. Coprecipitation and adsorption experiments (MgSO_4 , $\text{Al}(\text{NO}_3)_3$, $\text{UO}_2(\text{NO}_3)_2$) in CO_2 -rich and CO_2 -poor environments were conducted at pH 9.5 and 7.0 to observe the amount U sequestered, the effects from the presence of UO_2^{2+} on phase formation (powder XRD) and the specific bonding environment (U L_{III} XAFS) by which UO_2^{2+} becomes incorporated into the hydrotalcite structure and/or adsorbs to its external surfaces. Uranyl did not inhibit the formation of hydrotalcite, and the absence of carbonate ions from the systems (CO_2p) promoted expansion of the interlayer spacing from ca. 8.4 Å (CO_3 -interlayer) to ca. 8.6 Å consistent with a mixed sulphate-nitrate interlayer and possibly incorporating some $\text{UO}_2(\text{CO}_3)_3^{4-}$. In all cases, Mg^{2+} ions were deficient in the structure reducing the ideal Mg:Al of 3:1. Theoretical negative charge occurred when the Mg:Al ratio dropped below 2.5 – the case of two samples prepared at pH 7.0. The absence of increased UO_2^{2+} or Al sequestration suggested that neither Al nor UO_2^{2+} occupied the vacant Mg sites. *Preliminary analysis* of the U L_{III} edge XAFS data showed that the first shell coordination environment was dominated by carbonate ligands in CO_2 -rich environments, whereas carbonate ligands were absent from uranyl's first shell in CO_2 -poor environments. In the latter environments, uranyl was coordinated by four O atoms in the equatorial plane at ca. 2.3 and 2.5 Å. The higher shell environment is dominated by signal from the O-U-O-U MS path near 3.68 Å in CO_2p and CO_2r samples. In both environments, we observed Mg and Al at ca. 3.20 and 3.35 Å, respectively. Interatomic distances suggest that UO_2^{2+} binds to Mg sites as an edge-sharing complex and as a bidentate binuclear surface complex to Al atoms. The magnitude of the CN (ca. 0.3 U-Mg and ca. 0.9 U-Al) suggest that one third of U atoms bond as edge-sharing complexes, one half bond as bidentate binuclear complexes and ca. 20 % is held in the positively charged double layer as outer-sphere complexes. The *preliminary conclusions* are that UO_2^{2+} and $\text{UO}_2(\text{CO}_3)_3^{4-}$ adsorb via an inner-sphere mechanism to hydrotalcite, which would involve ligand exchange of carbonate moieties in CO_2r environments, which is supported by reduced U-C coordination numbers in CO_2r samples.