

Incorporation of molybdate into the Ca-Al-hydrotalcite lattice

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Layered double hydroxides (LDHs) are lamellar mixed hydroxides abundantly studied for their uptake of anionic contaminants (e.g., As, Se, Cr, etc.) from polluted water[1], due to their positively charged surface and exchangeable intercalated anions. AFm phases are minor phases present in hydrated cement and also in hydrated coal fly ash (CFA) that belong to the Ca-Al LDHs family[2]. The objective of this project is to better understand the MoO_4^{2-} sorption mechanisms on AFm- SO_4 and AFm- Cl_2 and therefore the capacity of these minerals to retard Mo mobility.

Anionic exchange in the AFm interlayer was studied using wet chemical methods. Total aqueous concentrations of Mo indicate that the removal rates of Mo oxyanions by AFm- Cl_2 from the solution are higher than for AFm- SO_4 . Compared to the average K_d value of $0.03 \text{ m}^3 \text{ kg}^{-1}$ for AFm- SO_4 , a value of $10 \text{ m}^3 \text{ kg}^{-1}$ for AFm- Cl_2 was obtained in $[\text{Mo}]_{\text{initial}}$ range of 0.001 to 0.02 mM, suggesting that the uptake capacity of AFm- Cl_2 is larger than that of AFm- SO_4 .

Mo K-edge XANES spectra showed different uptake mechanisms as $[\text{Mo}]_{\text{initial}}/[\text{Cl}_2]_{\text{intercalated}}$ ratio increased from 2×10^{-4} to 1 (in absence of CaMoO_4 precipitate) in AFm- Cl_2 . Mo symmetry evolves from tetrahedral to octahedral and back to tetrahedral coordination with increasing surface coverage. Three sorption mechanisms are proposed: edge surface site complexation, structural co-precipitation/incorporation (confirmed by EXAFS with a second shell of Ca and O), and interlayer anion exchange (confirmed by in situ XRD with a shift of the (001) reflection to lower angle). In contrast, MoO_4^{2-} interactions with AFm- SO_4 at stoichiometric concentrations of total exchange lead to formation of a CaMoO_4 precipitate.

These results show different Ca-Al LDHs' affinity for MoO_4^{2-} and an interplay of different sorption mechanisms.

[1] Goh *et al.* (2008) *Water Res.* **42**, 1343-1368.

[2] Matschei *et al.* (2007) *Cem. Concr. Res.* **37**, 118-130.