Cr(VI) adsorption on γ-alumina

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Cr (VI) is a toxic contaminant that has been introduced into numerous surface and subsurface systems through industrial activities such as electroplating, leather tanning and steel manufacturing. In solution, it forms anionic complexes (CrO_4^{-2}, $HCrO_4^-$), and as such, may bind to the surfaces of positively charged solids. High surface area, synthetic γ-alumina is often used as an analog for aluminum oxides found in soils and sediments. It has a high point of zero charge (~5.5-8.9), and thus may bind Cr (VI) even at relatively high pH. However, few studies have investigated Cr (VI) sorption on γ-alumina.

In this study, Cr (VI) sorption on γ-alumina (N_2 BET SA = 233 m^2/g) was measured as a function of pH (3-10), ionic strength (0.1 to 0.001 M $NaNO_3$), and pCO_2 (0, atmospheric, 2.5%). A large batch slurry of 2 g/L γ-alumina with 10^{-5} or 10^{-6} M Cr (VI) was titrated from pH 3 to 10, with aliquots removed at ~0.5 pH intervals. Individual aliquots were further equilibrated for 4 hrs, after which the supernantant was removed by centrifugation and syringe-filtration and analyzed for Cr (VI) by UV-vis spectrophotometry (diphenylcarbazide method) or for total Cr by ICP-OES using matrix-matched calibration standards.

Cr (VI) sorption is rapid, reaching equilibrium within 15 minutes, and is reversible, with 100% desorption occurring within 24 hrs. As expected, sorption decreases with increasing pH. For a given solution condition, more Cr (VI) uptake occurs in the 10^{-6} M compared to the 10^{-5} M Cr (VI) experiments. Adsorption edges show little dependence on ionic strength or pCO_2, except that Cr (VI) sorption is suppressed at low pH in experiments with high ionic strength and high pCO_2.

The measured adsorption edges were individually modeled using constant capacitance, diffuse double layer and triple layer surface complexation models. For each model, multiple site density, protonation/deprotonation stability constants, Cr (VI) reaction stoichiometries and capacitances were tested. In each case, good fits could be produced for individual edges. However, none of the models tested resulted in satisfactory fits over the complete range of measured pH, ionic strength, sorbate/sorbent, and pCO_2 conditions. The best fits were obtained using a constant capacitance model, because stability constants for this model are ionic-strength dependent.

Timing of denudation, erosion and surface uplift of the Hunza Karakoram – A case study of combined thermochronological and geomorphological approaches

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Geomorphological records of extreme surface uplifts of the Hunza Karakoram in the late Cenozoic are correlated with thermochronological history of relevant crystalline rocks during active collision orogeny. A set of studied samples dated by apatite fission-track (AFT) technique come from the SW-NE transect in the Hispar and Gharesa regions of the Hunza Karakoram. Variable lithological types of crystalline rocks were collected from 2 400 to 5 600 m a. s. l. and yielded ages between 3.9 ± 0.2 Ma to 9.7 ± 0.4 Ma. Our results confirmed effective denudation, erosion and transport of near-surface rock masses during the late Cenozoic.

Time-temperature modeling of AFT samples from the Hunza Karakoram shows a similar thermal history style, involving a period of total thermal annealing and a subsequent period of cooling corresponding to considerable denudation and erosion processes. Two dominant trends of cooling rate have been observed: (1) the Upper-Miocene to Pliocene period of a slow rate about 0.1 km/Ma followed by (2) the Quaternary period of a relatively rapid rate about 2.6 km/Ma. The later period of cooling can be associated with an approaching of (sampled) rock assemblages nearby late Cenozoic denudation and/or erosion surfaces.

Measured track-lengths vary from 10.3 ± 2.8 μm to 12.1 ± 2.2 μm with a negative skewness. The track-lengths-frequency histogram demonstrate a bimodal distribution with a short peak representing the higher temperature tracks and also with longer peaks derived from final cooling. These data give evidence of mixed ages as a result of (at least) two-stage cooling history of studied crystalline rocks.

Denudation and erosion of rock masses in the Hunza Karakoram estimated by a combination of current elevations of samples and depths of fossil apatite partial annealing zones reached up to 4 km from the Upper Miocene to the present.