

Thermodynamic modelling the sorption of heavy metals and actinides onto clay minerals by Gibbs energy minimization approach

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One of the major aims in the development of sorption models was to set up the simplest chemically reasonable model with the least number of variable parameters capable of describing and predicting sorption over a wide range of conditions. In this study we have investigated the sorption of heavy metals and actinides onto montmorillonite, illite and kaolinite in aqueous solutions by applying the Gibbs energy minimization computer code "HCh" (Yu.V. Shvarov, Moscow State University) via a non-electrostatic model. The emphasis is made on the named clay minerals because of their importance in terrestrial weathering processes and designed industrial applications. The thermodynamic model combines cation exchange at a permanent negatively charged sites and pH-dependent surface complexation at the amphoteric edge-type sites. Site types, their individual capacitance and the acidity constants associated with them, were considered to be non-adjustable parameters and were fixed in all of the calculations: the cation exchange capacity (CEC) is 0.9, 0.25 and 0.05 equiv/kg and equal to concentration of exchangeable sites NaX; the aluminol ($>AlOH$) and silanol ($>SiOH$) edge-type sites are responsible for the surface complexation, and their total density is a part of a CEC (0.09, 0.1 and 0.05 mol/kg). The equilibrium constants for the adsorption and ion exchange reactions could be found due to correlations with the aqueous hydrolysis constants.

The calculated sorption models showed good approximation of experimental distribution coefficients of majority sorbates onto named three clay minerals. We note that the model parameters discussed here are closely dependent on the decisive variables, namely the surface site capacities. Indeed, the value of the CEC and the density of edge sites directly control the metal uptake by considered clay minerals. It allows to show that: a) the influence of ionic strength and pH of solutions on the metal sorption is differentiated depending on the crystallochemical type of clay mineral. The more sorption capacity of a phase, the influence of concentration of electrolyte is more strongly revealed. As a result, kaolinite could be successfully used in the solutions with $I > 0.1$ and $pH > 5$ instead of montmorillonite, which exhibits the highest exchange capacity; b) the sorption show a higher difference in selectivity of the cations in the pH range 4-8, where it is greatly affected by the element chemical properties (affinity to the hydrolysis in solutions and the surface-binding complexation); c) on the contrary, at weakly acidic pH of diluted solutions (low ionic strength), selectivity coefficients K_c could be accepted the same for analogous type of cations, if was not determined exactly. Usually, K_c values for bivalent-monovalent exchange are ~ 3 to 4 and for bivalent-bivalent exchange around unity.

The Bicaz lake (Romania): Hydrodynamics and trace element behaviour

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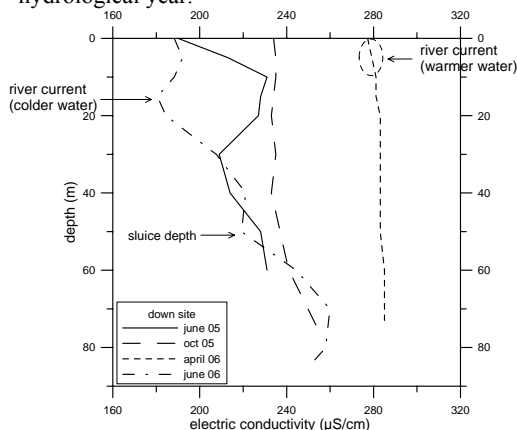
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The dammed lake of Bicaz (East Carpathians, Romania), presents the following physical characteristics: 31.1 km length, 2 km wide, water volume of $1.150 \cdot 10^9$ m³. The Bistrița river is the main tributary with a mean water contribution of $1.721 \cdot 10^9$ m³/year and a mean suspended matter flow of 291,000 tons/year. This river drains a catchment rich in formerly mined mineralizations of polymetallic sulfides.

Three locations, an upper, a middle, and a down site as well as the main tributary river were sampled for one hydrological year.



The electric conductivity and the concentration of major ions allow to evidence a water layer whose position varies along the lake and according to season (water temperature and lake depth). This current which originates from the Bistrița river is intensified by the sluice drawing off. The distribution of Fe between dissolved and particulate forms, along the lake and for each season, and the distribution of Mn, excepted in some cases, show the lake is mainly oxidizing. In the dissolved phase, the concentration of Fe and Mn is smaller than in the river. Some trace elements such as Cr and V occur mainly in the particulate form, and are enriched in the dissolved phase compared to the Bistrița. On the contrary, Ni, As and U are found mainly in the dissolved phase: Ni is enriched compared to the river whereas As and U are similar. The distribution of Co between particulate matter and solution is variable and does not follow Mn. The concentration of Co in the dissolved phase is smaller than in the river.

Thus, stratification of the water column within the lake is disturbed by the river current and by the sluice. The weak relationship between Fe and Mn and analyzed trace elements may be linked to hydrodynamics of the lake.