Kinetics and Mechanisms of Cation Exchange and Dehydration of Microporous Titanium and Zirconium Silicates

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The kinetics of ion-exchange reactions of 6 minerals with heteropolyhedral framework structures [heterosilicates: sitinakite, $KNa_2Ti_4Si_2O_{13}(OH)\cdot 4H_2O$, penkvilksite, $Na_4Ti_2Si_8O_{22}\cdot 5H_2O$, zorite, $Na_6Ti(Ti,Nb)_4(Si_6O_{17})_2O(OH)_4\cdot 11H_2O$, terskite, $Na_4ZrSi_6O_{15}(OH)_2\cdot H_2O$, gaidonnayite, $Na_2ZrSi_3O_9\cdot 2H_2O$, and kuzmenkoite-Mn, $K_2Mn(Ti,Nb)_4(Si_4O_{12})_2(OH,O)_4\cdot nH_2O$], and so-called zirfesite, an amorphous product of natural hydrolysis and cation leaching from eudialyte, with aqueous solutions of salts of Cs, K, Sr and Cu was investigated by the of dynamic calorimetry method. Quantitative kinetic and thermodynamic data characterizing ion-exchange processes with natural heterosilicates have been obtained for the first time. The effect of temperature, the nature and concentration of ions in the solution, as well as preliminary modification of the sorbent (hydration/dehydration, leaching of a part of extra-framework cations, amorphization) on the kinetic low and activation energies of ion-exchange reactions was investigated. It was shown that terskite being amorphized under natural conditions can concentrate and keep fast U and Th that could have a practical use for the immobilization of these elements. Structural transformations accompanying cation-exchange processes and thermal dehydration of natural titano-, niobo- and zirconosilicates, a new class of mineral raw materials and prototypes of synthetic microporous materials for technologies of water purification, immobilization of radioactive isotopes and concentration of rare elements, have been investigated by means of single-crystal X-ray diffraction, Rietveld and full-profile IR spectroscopy methods. In particular, crystal chemistry of Rb-, Sr-, Ba-, Ca- and Pb-exchanged forms of natural hilairite are investigated using single-crystal X-ray diffraction data.

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