Analysis of breakthrough curves of Np(V) in clayey sand packed column in terms of mass transfer kinetics.

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The transport properties of Np(V) were studied in a column packed with a mixture of silica sand and natural clay minerals (8% w/w), essentially montmorillonite and kaolinite with goethite (6.5% of clays fraction). The clayey sand packing is 1.6 cm in diameter and 7 cm in length; the pore velocity is 3.6 m/day. Np(V) was injected as a concentration pulse of 8.0 10^{-6} mole/l in a solution containing sodium perchlorate and sodium carbonate at a given pH. Np(V) was detected at the outlet and the distribution coefficient, K_D,was measured from the first moment of peaks. The curve log(K_D) vs pH displays a characteristic shape : Log(K_D) firstly decreases from 1.5 at pH 8.2 to 0.5 at pH 9.8, value for which a minimum is observed. Then, when pH increases from 10.0 to 11.8, log(K_D) value increases to 1.3. The theoritical interpretation of equilibrium properties as a function of pH takes into account $Na^+/H^+/NpO_2^+$ cation exchange on a specific site of clay minerals. Analysis and modelling of peak shapes show that the stronger the retention, the higher the reduced variance of the Np(V) peaks. This behaviour is interpreted in the framework of linear chromatography theory, which leads to attribute the evolution of reduced variance of peaks vs pH to external and/or internal mass transfer limitations. Introducing the characteristic times of a first order kinetics allows one to determine the nature of mass transfer kinetics and the characteristic length of clayey sand aggregates.