

New Insights into the Speciation of Trivalent Chromium Exchangeable Pools at Particle Surfaces: An Isotopic Exchange Kinetic Model

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Chromium is one of the most (eco)toxic heavy metals, posing significant environmental and ecological risks. A comprehensive understanding of its bioavailability and mobility is therefore essential, beyond the simple quantification of its total concentration in soils and waters. In natural environments, chromium occurs primarily in ultramafic systems in two oxidation states: trivalent (Cr(III)) and hexavalent (Cr(VI)). Its mobility and availability are largely controlled by interactions with mineral particles and colloids in soils and surface waters.

To investigate the role of Cr-bearing phases in regulating Cr mobility, we applied the Stable Isotopic Exchange Kinetics (SIEK) approach, a robust method for quantifying the time-dependent exchangeable fraction of Cr in environmental matrices. This study aimed to develop and apply appropriate isotopic exchange kinetic (IEK) models to characterize the exchangeable Cr(III) fraction (ECr(III)) and its kinetic parameters for a range of typical Cr scavengers, including goethite, hematite, pyrolusite, kaolinite, montmorillonite, chromite, fuchsite, amphibole, chlorite, serpentine, and humic acids in ultramafic soils.

IEK modeling revealed the presence of one to three distinct exchangeable Cr(III) pools at the surfaces of these phases. The fast-exchange pool exhibited rate constants that were two to four orders of magnitude higher than those of the slow-exchange pools. The fast-exchange pool was attributed to outer-sphere complexation mechanisms, such as electrostatic interactions or cation exchange, whereas the slow-exchange pools were linked to inner-sphere complexation involving surface-reactive functional groups. The relative proportions of fast versus slow exchangeable pools varied across mineral phases, providing insight into their role in chromium retention and mobility.

Additionally, redox transformations of Cr(III) to Cr(VI) were observed at pyrolusite surfaces, adding complexity to the exchange mechanisms. This highlights the need for further investigation into the coupled processes of Cr exchange and oxidation, particularly in environments where manganese oxides are present.