Fe^{2+}-Fe^{3+} Transformations in Clay and Resin Ion-Exchange Systems

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Abstract: The pH, Eh, electrical conductivity (EC), and the amounts and valency of replaceable iron were measured periodically on Fe^{2+}- and Fe^{3+}-saturated montmorillonite and cation-exchange resin at three temperatures. Differences in the pattern of change of pH, Eh, and EC with time appear to be related more to the histories and modes of preparation of the systems than to intrinsic differences in the hydrolysis of the iron in them. Electron transfer reactions involving crystal components of the clay can cause oxidation of adsorbed Fe^{2+} ions; the activation energy (Ea) for oxidation on the clay's surface was 6 kcal/mole, less than a third of the activation energy reported for Fe^{2+} oxidation in solution. In the Fe^{2+}-resin, where Ea = 10.7 kcal/mole, perturbed surface-water molecules may act as electron acceptors enhancing Fe^{2+} oxidation.

Polymerization and precipitation of the adsorbed iron is affected by the necessity to maintain electroneutrality, the ability of the iron-hydroxy ions and small polymers to move about in the voids of the ion exchanger, and the steric hindrance posed by the matrix of the ion exchanger to the formation of large polymers. In resin, little or no iron precipitates, probably due both to steric hindrance and the inability of the resin to release ionic components to maintain electroneutrality. In clays, steric hindrance is small, and Al and Mg are released from the crystal to maintain electroneutrality, thus the precipitation of iron is abundant and is controlled by the rate of release of Al and Mg from the crystal.

Key Words: Adsorption • Electron transfer • Ion-exchange resin • Iron • Oxidation • Smectite

Clays and Clay Minerals; October 1980 v. 28; no. 5; p. 335-345; DOI: 10.1346/CCMN.1980.0280503

Clay Minerals Society (www.clays.org)