

Speciation of Alkaline Earth Adsorption on the Surfaces of Oxide and Hydroxide Minerals in Salt Solutions

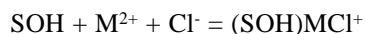
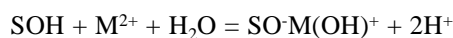
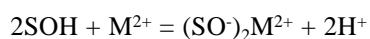
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Most experimental studies of adsorption and surface charge development, as well as most surface complexation models, have focussed on the mineral-water interface immersed in 1:1 electrolytes. However, Ca(HCO₃)₂ or NaCl+CaCl₂ are the main electrolytes in most river waters, shallow groundwaters, and higher temperature groundwaters. Consequently, the application of experimental results and existing models to natural waters is highly questionable. As a first step towards addressing this situation, a comprehensive analysis of the adsorption of alkaline earths is being undertaken. Experimental data from batch adsorption studies of alkaline earths, surface titrations of proton consumption in the presence of alkaline earths with alkali salts and with alkaline earth salts as background electrolytes, zeta potentials, and X-ray adsorption and surface diffraction techniques are being integrated with the aid of the Extended Triple Layer Model (ETLM; Criscenti et al., 1999). This approach helps to establish a framework for the prediction of alkaline earth adsorption and surface speciation on oxide and hydroxide surfaces over a wide range of pH and ionic strengths.

Analysis of batch adsorption and surface titration data for the systems Ca/rutile/NaCl, Ca/goethite/NaCl, Ca/quartz/NaCl, Ca/quartz/KNO₃, Ca/silica/NaCl, and Mg/silica/NaCl has established that the following three reactions are of importance in the context of the ETLM:



where M represents an alkaline earth metal. The surface species produced in these reactions can be termed (respectively): a bidentate-binuclear metal surface species (BB); a metal hydroxide species (MH); and a metal chloride complex (MCl). Of these species, the BB and the MH species represent complexing on the beta-plane of the ETLM and are common to all the systems studied. They also appear to be important (based on preliminary analysis) in the systems Sr/silica/NaCl and rutile/Mg(NO₃)₂. The relative abundances of the alkaline earth surface species vary substantially. For example, the BB surface species predominates at low values of pH, ionic

strength and surface coverage. However, the MH species predominates at high pH values and surface coverages. At high ionic strengths (e.g. I>0.1 molar), the MCl and the MH surface species are both relatively abundant.

The results of the above analysis are also consistent with surface X-ray diffraction and absorption studies. On rutile, Sr and Rb are adsorbed close to the surface (Fenter et al., 2000), probably as inner-sphere complexes. If Ca adsorbs to rutile similarly, then the BB and MH surface species for Ca on rutile probably also represent inner-sphere complexes, even though the Ca in these species is adsorbed at the beta plane. This suggestion agrees with analyses of the electric capacitances of rutile showing that alkali electrolyte cations form dehydrated, inner-sphere complexes on rutile at the beta-plane (Sverjensky, 2000). Furthermore, if the Ca on rutile forms a tetradentate species like the Sr (Fenter et al., 2000) then the (110) plane will contain two bridging and two terminal functional groups. These should be Ti₂(OH)^{1/3} and O₅Ti(OH)^{-1/3} (Koretsky et al., 1998). Adsorption of Ca on these functional groups can be expressed by reactions that are thermodynamically and electrostatically equivalent to the formation of either the BB or the MH surface species. Consequently, for adsorption of alkaline earths on rutile, the results of the ETLM analysis are consistent with the X-ray studies. For other solids, the ETLM analysis may also be consistent with the X-ray studies. For example, based on EXAFS studies, Sr forms outer-sphere complexes when adsorbing from alkali chloride solutions on goethite and silica (O'Day et al., 2000; Sahai et al., 2000). On goethite and silica, the background electrolyte cations form hydrated, outer-sphere complexes at the beta-plane of the ETLM (Sverjensky, 2000). Consequently, if the Sr is adsorbed at the beta-plane as BB and/or MH species, it too will be an outer-sphere complex, in contrast to the situation with rutile.

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