

Ion adsorption by metal oxides under hydrothermal conditions

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Werner Stumm and his collaborators have guided the geochemical community's understanding and conceptualization of mineral-water interfacial reactions for the past 25 years. Our research has been focused on extending their seminal contributions into the hydrothermal regime, where experimental data are scarce. To this end, we have been employing stirred hydrogen electrode concentration cells (SHECCs) to measure hydrogen ion adsorption by various metal oxides to 250°C. The relatively inert oxide rutile (TiO_2), has received the most attention to date, and aspects of this work dealing with hydrogen

ion adsorption by the rutile surface in NaCl and tetramethylammonium chloride media have been published (Machesky *et al.*, 1994; Machesky *et al.*, 1998).

This presentation will focus on our recent efforts to quantify and rationalize (i.e. model) the adsorption of cations by the rutile surface from 25 to 250°C. In these experiments, we are following surface charge development in the presence and absence of divalent cations (e.g. Ca^{2+}) added to the background monovalent electrolyte test solutions (e.g. NaCl + HCl) with SHECCs. In complementary experiments,

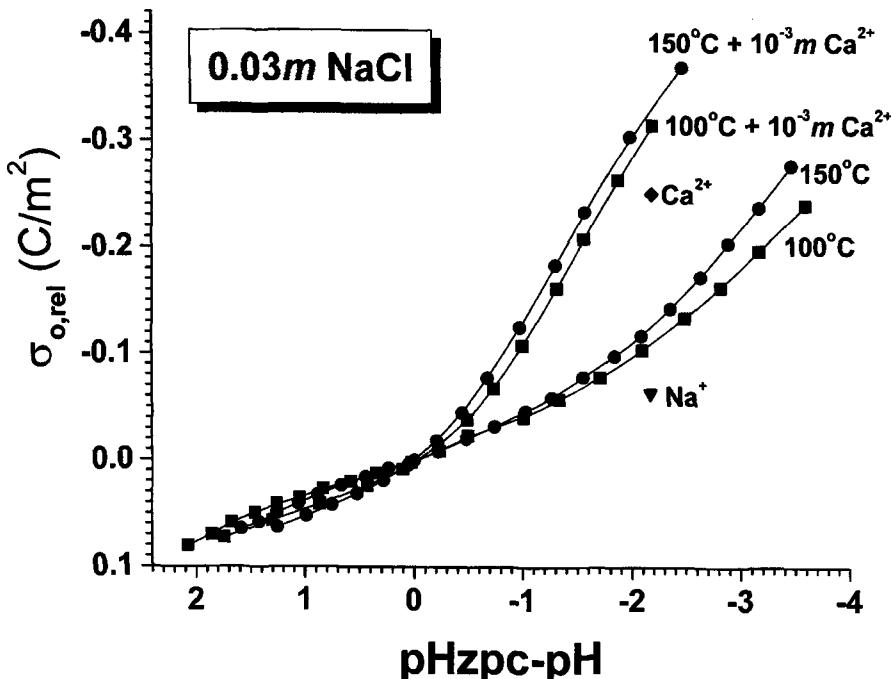


FIG. 1. Relative surface charge data ($\sigma_{0,\text{rel}}$, C/m²) referenced to the pHzc (pHzc-pH) at 100 and 150°C in 0.03m NaCl with and without added Ca^{2+} ($10^{-3} m$). The measured Ca^{2+} (◆, in C/m²) and calculated Na^+ (▼) contributions to the total negative charge compensation for the last titration point of the 100°C titration (■, upper curve) are also included.

the concentrations of divalent cations remaining in solution are determined on subsamples of our test solutions that are withdrawn during a titration.

Results for several titrations (in 0.029m NaCl + 0.001m HCl) at 100 and 150°C are presented in Fig. 1. Here, the results have been normalized to the point of zero charge (pHzpc) at these temperatures (4.9 at 100°C and 4.4 at 150°C). The origin of the plot corresponds to the pHzpc and '0' surface charge, while positive and negative coordinates signify positive and negative surface charge, respectively. The addition of 10^{-3} m Ca²⁺ to 0.03m NaCl greatly enhances negative surface charge development on the rutile surface relative to that without added Ca²⁺. Figure 1 also includes the measured amount of Ca²⁺ adsorbed, and the inferred contribution of Na⁺ to the total negative surface charge compensation (total negative charge–Ca²⁺ compensated negative charge) for the final pH value of the 100°C titration. At this pH (7.07) 80% of the total negative surface charge is compensated (screened) by adsorbed Ca²⁺, with the remainder satisfied by Na⁺.

Within the context of the 1 pKa description of surface charge development (Machesky *et al.*, 1998), negative charge compensation can be described as,



where Ti-OH^{-1/2} represents a negatively charged surface hydroxyl group site on the rutile surface, and Mⁿ⁺ is a cation of charge, n. Negative surface charge

compensation occurs as a result of cation adsorption in the interfacial region. Moreover, divalent cations are more effective at screening negative surface charge development than monovalent cations because of their higher charge and smaller size. Precisely how this charge compensation (or adsorption) varies with temperature and ionic strength is a principal focus of our research.

To our knowledge, these results are among the first direct measurements of cation adsorption coupled with surface charge determination under hydrothermal conditions. Moreover, once a complete data set is obtained, Surface Complexation Theory (championed by Stumm and collaborators) will be used to rationalize the results. It is anticipated that direct measurements of cation adsorption will greatly aid these modelling efforts since the contribution of these cations to negative charge compensation will be explicitly known. Consequently, associated model parameters will be more tightly constrained. Our modelling efforts will be summarized in this presentation.

References

- Machesky, M.L., Palmer, D.A. and Wesolowski, D.J. (1994) *Geochim. Cosmochim. Acta*, **58**, 5627–32.
 Machesky, M.L., Wesolowski, D.J., Palmer, D.A. and Hayashi, K.I. (1998) *J. Coll. Interf. Sci.*, **200**, 298–309.