



# 第14回国際土壌科学会議

Kyoto Japan  
August 12-18, 1990

Volume II : Commission II

Transactions

14th International Congress of Soil Science  
14<sup>e</sup> Congrès International de la Science du Sol  
14. Internationaler Bodenkundlicher Kongreß

KINETICS OF ION SORPTION/DESORPTION ON SOIL CONSTITUENTS  
USING PRESSURE-JUMP RELAXATION

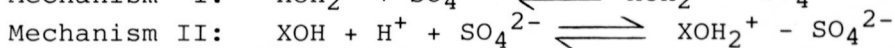
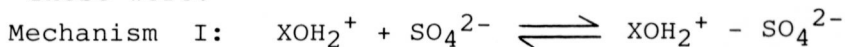
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One of the major considerations in studying the rates of reactions on soils and soil constituents is the method one uses. Batch and flow techniques have primarily been used for such systems; both have inherent advantages and disadvantages. With both techniques, one is usually studying apparent rate laws since mass transfer and chemical reaction phenomena are occurring simultaneously. Moreover, many ion sorption/desorption reactions occur on time scales of seconds or less and cannot be measured with traditional flow and batch techniques. This is particularly true of many metal sorption and ion exchange phenomena on soils and soil constituents. For such systems, relaxation techniques such as pressure-jump must be used. Such techniques are novel to soil chemistry investigations. Theoretical aspects of pressure-jump relaxation will be briefly discussed.

In this paper, we have employed the pressure-jump relaxation technique with conductivity selection to study the kinetics and mechanisms of molybdate and sulfate sorption/desorption on goethite. For molybdate, a postulated reaction mechanism consisting of two consecutive elementary steps was examined and verified through kinetic and equilibrium studies. The first step is the formation of an ion-pair complex through the electrostatic attraction between the protonated surface and the  $\text{MoO}_4$  anion. The second step involves a ligand exchange process, whereby one mol of  $\text{H}_2\text{O}$  is replaced by one mol of adsorbed  $\text{MoO}_4$  from the surface. It is much slower than the first step. The forward and backward intrinsic rate constants for steps 1 and 2 are:  $k_1^{\text{int}} = 4019.2 \text{ mol}^{-1} \text{ L s}^{-1}$ ,  $k_{-1}^{\text{int}} = 391.5 \text{ s}^{-1}$ ,  $k_2^{\text{int}} = 1.888 \text{ mol}^{-1} \text{ L s}^{-1}$ , and  $k_{-2}^{\text{int}} = 42.34 \text{ s}^{-1}$ . A slightly modified triple layer model (TLM) was employed to calculate the distribution of ionic species on the goethite surface, in the  $\alpha$  and  $\beta$  layers, and in the bulk solution at equilibrium, and electrical parameters for the charged surface. Both equilibrium and kinetic data fit the postulated mechanism for the reaction steps and the modified adsorption model well.

For sulfate, a single relaxation was observed and reciprocal relaxation times ( $\tau^{-1}$ ) increased with increasing pH. Using the modified TLM to obtain equilibrium parameters and pressure-jump relaxation to get  $\tau^{-1}$  values, several reaction mechanisms were evaluated. Two electrostatic mechanisms best fit the data. These were:



where  $\text{XOH}_2^+ - \text{SO}_4^{2-}$  represents a surface complex of a positively charged surface site with adsorbed sulfate occurring as an outer-sphere complex (electrostatic attraction).

Equations relating  $\tau^{-1}$  to forward and backward intrinsic rate constants ( $k_1$  and  $k_{-1}$ ) and the equilibrium parameters were developed for both mechanisms and tested. Linear relationships resulted for both mechanisms indicating they were operational for sulfate adsorption on goethite. Using calculated  $k_1$  and  $k_{-1}$  values,  $K^{int}$  parameters were calculated for both mechanisms. These were  $K^{int} = 107.55$  and  $K^{int} = 109.14$ . Comparing the  $K^{int}$  value of  $109.6$  calculated from equilibrium studies to those calculated kinetically, it would appear that Mechanism II is the most plausible mechanism for sulfate adsorption on goethite.

In summary, the p-jump technique appears to be a valuable method to use for elucidating the kinetics and mechanisms of ion sorption on soil constituents.