

# This Week's Citation Classic

CC/NUMBER 14  
APRIL 5, 1982

Hingston F J, Posner A M & Quirk J P. Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23:177-92, 1972.

[Institute of Agriculture, University of Western Australia, Western Australia]

Adsorption of anions on goethite and gibbsite is determined by pH, surface area, surface charge, and the  $pK_a$  of the conjugate acid of the anion. At a constant pH, anion adsorption resulting in ligand exchange makes the surface charge more negative. [The SCI® indicates that this paper has been cited over 120 times since 1972.]

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December 16, 1981

"My research on reactions of anions at interfaces between aqueous solutions and oxide minerals began in the 1960s in the regional laboratory of CSIRO, Division of Soils, Perth, Western Australia. At that time, understanding of reactions of ions in soils seemed much less satisfactory for anions than for cations. Although surface reactions in soils and sediments had long been known to be important for studies of plant nutrition, soil mineralogy, and pollution, the mechanisms of anion adsorption seemed very complex.

"It occurred to me that the most useful model of ionic reactions at aqueous/solid interfaces should include adsorption by chemical forces, coulombic forces, and interactions. As pH determined surface charge and the species of ions in solution, it should have a controlling role in the reactions.

"My first attempt to unravel the mechanism of the reactions was made using boric acid/borate adsorption on soil clays.<sup>1</sup> Then during a year at the headquarters of the

Division of Soils, Adelaide, South Australia, the work I did with Max Raupach on kinetics of adsorption and desorption of silicic acid/silicate on synthetic aluminium hydroxide reinforced my ideas about the significance of ion size, steric factors, surface charge, and pH.

"On my return to Perth I commenced a PhD study of adsorption of a range of anions on synthetic iron and aluminium oxides, at the soil science department, University of Western Australia, with J.P. Quirk and A.M. Posner as my supervisors. I am indebted to them for their patience in discussions and help with concepts.

"Most difficulties I encountered were concerned with my conceptions of the nature of oxide surfaces and their reactions. Among these were the meaning of equilibrium and reversibility in the aqueous solution/oxide interface systems, effects of crystal morphology, the significance of surface coverage for anions and oxide surfaces, and the distinction between adsorption and precipitation. Even now some aspects of these difficulties are not clearly resolved.

"Probably the reason for the frequent citation of the paper is that we made a first attempt to put some order into understanding mechanisms of adsorption of anions on oxide minerals, taking into account the role of pH in surface complex formation through ligand exchange, surface charging reactions, and species in the aqueous phase. The hypotheses developed have formed a basis for subsequent investigations by many researchers. Deservedly, some concepts and approximations have been seriously questioned and modified, but in essence the original ideas have been incorporated in more formal mathematical models of interactions at aqueous solution/oxide interfaces.<sup>2</sup>

"More detailed discussion of up-to-date ideas on anion adsorption and applications of the studies are outlined in a recent review."<sup>3</sup>

1. Hingston F J. Reactions between boron and clays. *Aust. J. Soil Res.* 2:83-95, 1964.

2. Bowden J W, Posner A M & Quirk J P. Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. *Aust. J. Soil Res.* 15:121-36, 1977.

3. Hingston F J. A review of anion adsorption. (Anderson M A & Rubin A J, eds.) *Adsorption of inorganics at solid liquid interfaces*. Ann Arbor, MI: Ann Arbor Science Publishers, 1981. p. 51-90.