## REACTIONS OF POLYNUCLEAR HYDROXYALUMINUM CATIONS WITH MONTMORILLONITE AND THE FORMATION OF A 28-Å PILLARED COMPLEX: COMMENT

Key Words-Aluminum, Anion deficiency, Hydroxy-Al, Montmorillonite, Pillared interlayer complex.

The paper by Singh and Kodama (1988) makes a valuable contribution to our knowledge of reactions between clays and hydroxy-aluminum compounds. There are things about this paper, however, that cannot be allowed to go unchallenged.

The authors quote three references to justify the assumption that the difference in Al concentration between 0 and 30 min shaking, before extracting with chloroform, always measures the concentration of Al in the form of polynuclear hydroxy-Al cations, referred to here as polynuclears. One of the three references quoted makes this claim, if the solution is filtered through a 25- $\mu$ m Millipore filter (Turner, 1969)—the company that made these filters first claimed that the pore size was 10  $\mu$ m. The only other reference quoted, that deals directly with measuring the Al in the polynuclear form was published much later (Turner, 1976b). In the later publication, the Al in the form of polynuclears was assumed to be that which was released at the first-order rate of 0.16 min.

An examination of the results in Table 2 of Singh and Kodama (1988), inasmuch as the pH of the solution was 4.18 (Figure 1), shows a deficiency of anions, i.e., Cl<sup>-</sup>, of about  $1.7 \times 10^{-3}$  mole ions per liter to balance the cations. An excess of OH<sup>-</sup> ions added also exists of about 11% over that accounted for in the products of the reactions, which is equivalent to about  $1.7 \times 10^{-3}$  mole ions per liter. Why these discrepancies occurred cannot be answered, but either a large error exists in the values presented in the Table or, and what is more likely, some noncrystalline aluminum hydroxide was precipitated when the NaOH was added to the AlCl<sub>3</sub> solution. Only a fraction of such a solid would be measured with the 30-min shaking (Turner, 1971).

The reason for Table 1 in Singh and Kodama (1988) is obscure. It may have been included to indicate that no hydroxy-Al compound precipitated during the partial neutralization of the AlCl<sub>3</sub> solution and/or that the polynuclears were not transformed to a more stable

form of polynuclears during aging. Whatever the reason, 90 days is far too short a time to determine whether such a system is at equilibrium, or even in a metastable condition, if Cl<sup>-</sup> is the anion present (Tsai *et al.*, 1984, 1985; Ross *et al.*, 1971; Turner, 1976a, 1976b).

R. C. TURNER<sup>1</sup>

233 Third Avenue Ottawa, Ontario K1S 2K2 Canada

## REFERENCES

- Ross, G. J. and Turner, R. C. (1971) Effect of different anions on the crystallization of aluminum hydroxide in partially neutralized aqueous aluminum salt solutions: *Soil Sci. Soc. Amer. Proc.* 35, 389-392.
- Singh, S. S. and Kodama, H. (1988) Reactions of polynuclear hydroxyaluminum cations with montmorillonite and the formation of a 28-Å pillared complex: *Clays & Clay Minerals* 36, 397–402.
- Tsai, P. P. and Hsu, P. H. (1984) Studies of aged OH-Al solutions using kinetics of Al-Ferron reactions and sulfate precipitation: Soil Sci. Soc. Amer. J. 48, 59-65.
- Tsai, P. P. and Hsu, P. H. (1985) Aging of partially neutralized aluminum solutions of sodium hydroxide/aluminum molar ratio = 2.2. Soil Sci. Soc. Amer. J. 49, 1060– 1065.
- Turner, R. C. (1969) Three forms of aluminum in aqueous systems determined by 8-quinolinolate extraction methods: *Can. J. Chem.* 47, 2521–2527.
- Turner, R. C. (1971) Kinetics of reactions of 8-quinolinolate and acetate with hydroxyaluminum species in aqueous solutions, 2: Initial solid phases: Can. J. Chem. 49, 1688– 1690.
- Turner, R. C. (1976a) A second species of polynuclear hydroxyaluminum cation, its formation and some of its properties; *Can. J. Chem.* 54, 1910–1915.
- Turner, R. C. (1976b) Effect of aging on properties of polynuclear hydroxyaluminum cations: *Can. J. Chem.* 54, 1528– 1534.

(Received 8 December 1988; accepted 17 March 1989; Ms. 1860)

<sup>&</sup>lt;sup>1</sup> Retired from Soil Research Institute, Agriculture Canada, Ottawa, Ontario, Canada.