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Vimala Devi Pillai-Nair

**Aluminium Species in Soil Solutions**

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## 1. INTRODUCTION

The role of aluminium in soils has long been underestimated. The first step in realizing its importance was the detection of "exchange acidity". The term denotes the process by which the addition of a neutral salt to an acid soil results in the exchange of  $\text{Al}^{3+}$  which on subsequent hydrolysis produces  $\text{H}^+$  ions. Around the year 1960, it was found that acid hydrolysis of clay minerals leads to the formation of polynucleic hydroxy-Al cations which spread out in the interlayer spaces of the three-layer silicates, finally forming a four-layer silicate called Al-chlorite. Buffering of  $\text{H}^+$  ions by clay minerals may be a step-wise process involving several solid Al-compounds. At the same time, it is difficult to explain the absence of gibbsite in most temperate soils.

Aluminium chemistry in soils is now receiving renewed attention in view of the "acid rain" problem. The acidification of non-fertilized forest soils seems to be a widespread phenomenon in the industrialized countries. The  $\text{H}^+$  ion-buffering in acid soils is almost totally related to the changes in Al bonding. The formation of solid Al-compounds should be closely connected with the binding forms of Al existing in the solution. Physico-chemical data concerning Al species in solution have been accumulating during the past few years and an analytical method to distinguish between mononucleic and polynucleic Al species has been developed. Thus, it seems necessary as well as possible to get the information regarding the Al species present in soil solutions.

## 2. REVIEW OF LITERATURE

### 2. 1. Aluminium species in pure solutions

The hydrolysis products of aluminium present in the pH range of 4 to 9 in simple systems such as aluminium hydroxide-water are still uncertain. It is generally agreed that below pH 4, all the Al exists as  $\text{Al}^{3+}$  and that above this pH, hydroxy-Al complexes are expected to be formed. Both mono- and polynuclear species have been reported and the equilibrium constants ( $K_n$ ) of some of these species have been determined. However, there is little agreement on the nature of the Al species existing above pH 4. In earlier investigations, the association of Al and hydroxide was assumed to be a mononuclear, step-wise process, the first ion formed being  $\text{Al}(\text{OH})_2^{2+}$  (Frink and Peech, 1962a). As pH increased,  $\text{Al}(\text{OH})_2^+$  was more prominent (Raupach, 1963). With still further rise in pH, a solid  $\text{Al}(\text{OH})_3$  would separate which would then partially dissolve as the anion  $\text{Al}(\text{OH})_4^-$  (Hem and Roberson, 1967). Sullivan and Singley (1968), Dezelic et al. (1971) and Dalal (1975) have pointed out the importance of the neutral species,  $\text{Al}(\text{OH})_3^0$ .

Matijevic et al. (1961) concluded from the studies on the coagulation of aqueous sols of silver halides that, between pH 4 and 7, the Al species could be defined as  $\text{Al}_8(\text{OH})_{20}^{4+}$  and at higher pH, probably as  $\text{Al}_8(\text{OH})_{22}^{2+}$  and  $\text{Al}_8(\text{OH})_{24}$ . Tanabe (1954) and Raupach (1957) suggested the existence of  $\text{Al}_3(\text{OH})_8^+$  and Kenttämäa (1955) reported the existence of  $\text{Al}_2(\text{OH})_2^{4+}$ . From infrared absorption spectra studies, Fripiat et al. (1965) suggested  $\text{Al}_4(\text{OH})_8^{4+}$  and

$\text{Al}_7(\text{OH})_{16}^{5+}$  as the possible hydrolysis species in aqueous solutions. From ultracentrifugation and acidity measurements, Aveston (1965) proposed the species  $\text{Al}_2(\text{OH})_2^{4+}$  and  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  and pointed out that his data could be explained in terms of other species also. Brosset et al. (1954) suggested  $\text{Al}_6(\text{OH})_{15}^{3+}$  as the main reaction product in the acid pH range. The possibility of the existence of  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  (Sillén, 1959) and a mixture of  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  and  $\text{Al}_7(\text{OH})_{17}^{4+}$  was also reported (Sillén, 1962).

In the studies on Al-resin (Hsu and Rich, 1960) and on Al-vermiculite systems (Hsu and Bates, 1964b), the authors found 1+ charge per Al atom, corresponding to the composition  $\text{Al}_6(\text{OH})_{12}^{6+}$ . The neutralization of  $\text{AlCl}_3$  or  $\text{Al}_2(\text{SO}_4)_3$  in the absence of resin or vermiculite resulted in a 0.8+ charge per Al atom corresponding to the composition  $\text{Al}_{10}(\text{OH})_{22}^{8+}$ . With additional results of later studies, Hsu (1977) proposed that in the absence of Dowex 50 resin or vermiculite, the hydrolyzed products were likely to be  $\text{Al}_{10}(\text{OH})_{22}^{8+}$  (double ring) or  $\text{Al}_{13}(\text{OH})_{30}^{9+}$  (triple ring) at  $\text{NaOH/Al} \leq 2.1$ . Based on structural considerations, Hem and Roberson (1967) opined that small polymerised units such as  $\text{Al}_4(\text{OH})_8^{4+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_6(\text{OH})_{12}^{8+}$  and  $\text{Al}_8(\text{OH})_{20}^{4+}$  were not likely to exist over any wide range of values of pH or molar ratio of combined hydroxide to total dissolved aluminium.

Sullivan and Singley (1968) explained the hydrolysis of aluminium on the basis of a mononuclear species model in  $10^{-3}\text{M}$  and  $10^{-4}\text{M}$  solutions and indicated the relative amounts of the different species ( $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{Al}(\text{OH})_4^-$  and  $\text{Al}(\text{OH})_5^{2-}$ ) present as a function of pH

(range 3-10) at the above solution concentrations. Their studies did not, however, reveal polynuclear species with  $\text{Al} : \text{OH} = 1 : 2.5$ ;  $\text{Al}^{3+}$  was the prominent species up to pH 4.5,  $\text{Al}(\text{OH})_3^{\circ}$  from pH 4.5 to 8, and  $\text{Al}(\text{OH})_4^{-}$  above pH 8.

The monomer model for Al suggested by Marion et al. (1976) includes the species  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_2^{+}$ ,  $\text{Al}(\text{OH})_2^{+}$ ,  $\text{Al}(\text{OH})_3^{\circ}$ ,  $\text{Al}(\text{OH})_4^{-}$  and  $\text{Al}(\text{OH})_5^{2-}$ . The distribution diagram of the relative amounts of soluble Al species as a function of pH at ionic strength 0.01 M revealed that  $\text{Al}^{3+}$  was the predominant species up to 4.5,  $\text{Al}(\text{OH})_2^{+}$  in the region pH 5 to 6,  $\text{Al}(\text{OH})_3^{\circ}$  in the region pH 7 to 8 and  $\text{Al}(\text{OH})_4^{-}$  above pH 8, the species  $\text{Al}(\text{OH})_2^{+}$  being of some importance at about pH 4.75. In the pH range 6 to 7, there was a mixture of  $\text{Al}(\text{OH})_2^{+}$  and  $\text{Al}(\text{OH})_3^{\circ}$  and above pH 9,  $\text{Al}(\text{OH})_5^{2-}$  was found.

As may be seen from the foregoing, most authors have considered pH as a main factor for discussing the relative amounts of the various hydroxy-Al species at one or two ionic strengths; the results were often explained on the basis of mononuclear hydroxy-Al species only.

According to Bache (1974),  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})_2^{+}$  were the only mononuclear ions likely to exist in appreciable amounts in dilute salt solutions, the composition of the polynuclear hydroxy-aluminium ions being very much dependent on the basicity, the Al concentration and the 'previous history' of the solution. Bache and Sharp (1976) showed that in 0.01 M  $\text{CaCl}_2$  suspensions, up to about 80% of the soluble Al in soils existed in the polynuclear form at about pH 5.

Nair and Prenzel (1978) developed a numerical model to calculate the equilibrium concentrations of a set of different hydroxy-Al species (mono- and polynuclear) in solution at a given pH and Al concentration. They pointed out the significance of polynuclear species in solution and suggested that a mononuclear model was not sufficient to explain the hydrolysis of Al under all conditions of pH, Al concentration and ionic strength.

## 2. 2. Solubility of Al present in soils and clay minerals

It has been reported by many workers (Richburg and Adams, 1970; Blancher and Scrivner, 1972; Dalal, 1975) that the  $pAl^{3+} + pOH^-$  values in soil solutions decrease with increase in pH when only mononuclear hydroxy-Al species are considered. Although Richburg and Adams (1970) implied that  $Al_6(OH)_{15}^{3+}$  was the sole hydrolysis product, they reported that the calculated activity of  $Al^{3+}$  was not altered significantly if both the monomeric and polymeric hydrolysis reactions were assumed to proceed simultaneously. This seems to agree with the findings of Turner (1968a; 1968b), who, from the studies of titration curves of Al salt solutions, found that polynuclear species were present in addition to monomeric species, particularly at high degrees of neutralization.

For laboratory prepared gibbsite, Singh (1974) reported a value of  $pK_{sp} 33.96 \pm 0.03$  at  $25^\circ C$ , and for a sample of commercial gibbsite, Kittrick (1966) found a value of  $34.03 \pm 0.05$  at the same temperature. The pH of the

equilibrium solutions of their samples were below 4; the former made corrections for  $\text{Al}(\text{OH})^{2+}$  using the first stage hydrolysis of  $\text{Al}^{3+}$  and the latter assumed all Al to be monomeric below pH 4. But it is doubtful whether it can be so assumed. As mentioned earlier, the nature of hydroxy-Al species at any pH is dependent on the total Al concentration also (Nair and Prenzel, 1978).

Dalal (1975) reported a mean  $\text{pAl}^{3+} + 3 \text{pOH}^-$  value for solution Al below pH 4 as  $35.59 \pm 0.45$  and between pH 4 and 6.3 as  $34.86 \pm 0.16$ , taking into account the neutral species  $\text{Al}(\text{OH})_3^0$  also. The  $\text{pAl}^{3+} + 3 \text{pOH}^-$  values of Richburg and Adams (1970) were all above 34.0 for the various soils they considered. These values, higher than the  $\text{pK}_{\text{sp}}$  value of approximately 34.0 reported by Kittrick (1966) and Singh (1974), could probably be due to the  $\text{pK}_{\text{n}}$  values used for the various hydrolysis products of Al and/or because some other hydroxy-aluminium species were not taken into consideration.

Ragland and Coleman (1960) reported that Al salt solutions undergo increased hydrolysis in clay suspensions than in aqueous solutions of the same pH. On the other hand, Frink and Peech (1963b) concluded that hydrolysis was suppressed in clay suspensions when compared with a solution of the same total Al concentration. But, both these hypotheses can be accepted in the light of the fact that the nature of the hydroxy-Al species present in solution is dependent on the pH, total Al concentration and the ionic strength of the medium.

Kaddah and Coleman (1967a,b) have shown that freshly prepared or aged Al vermiculites contain predominantly  $\text{Al}^{3+}$ .

However, extractions with various salt solutions induce hydrolysis to varying extents depending upon the nature of the replacing cation and its concentration. According to them, the hydrolysis product retained by the clay has a composition corresponding to  $\text{Al}(\text{OH})^{2+}$ . Studies of Kissel et al. (1971) and Rich (1970) indicate a similar salt-induced hydrolysis in montmorillonite. Aluminium interlayers may be formed in both vermiculites and montmorillonites by treating them with partially neutralized Al salt solutions, but little direct evidence of the structure of the interlayer material is available. It appears, however, that the composition of interlayer material varies from simple monomeric Al through various polynuclear species culminating in some form of  $\text{Al}(\text{OH})_3$ . According to Sawhney (1968), vermiculite fixes Al as well as hydroxy-Al ions in its interlayers, producing a stable 1.4 nm spacing. Heating the Al-interlayered vermiculite at  $300^\circ\text{C}$  produced an interstratified mixture, indicating that some interlayers collapsed while others did not. The differential collapse was attributed to different charge on the vermiculite layers. Montmorillonites, on the other hand, did not fix Al ions, but fixed appreciable amounts of hydroxy-Al ions. In addition, the stability of the interlayers in montmorillonite increased on aging in hydroxy-Al solutions and exceeded the stability of vermiculite interlayers. Sawhney (1968) postulated that the more expanded interlayer space in montmorillonite provides a favourable position for the organization of hydroxy-Al ions into gibbsite structure while the restricted expansion in

vermiculite prevents it and hence its instability in comparison with vermiculite.

### 2. 3. Influence of ligands in solution on Al hydrolysis

Studies on the hydrolytic reactions of Al at room temperature and atmospheric pressure in partially neutralized Al solutions have shown that the ionic environment in the system is important in the formation or non-formation of crystalline aluminium hydroxides. Values of  $pAl^{3+} + 3 pOH^-$  greater than that of gibbsite are indicative of more insoluble compounds governing Al solubility. According to Marion et al. (1976) gibbsite is unstable relative to kaolinite; under moderate weathering regimes, aluminosilicate minerals rather than gibbsite are of greater importance in controlling Al solubilities.

Khan (1969) investigated the interaction between certain metallic cations and humic acids isolated from soils and found that various processes such as ion exchange, surface adsorption, chelation, coagulation, and peptization are involved in the complex formation of metallic cations with humic acid and fulvic acid fractions of soil organic matter. With the exception of  $Al^{3+}$  and  $Fe^{3+}$ , the metallic cations did not precipitate humic acids when added in lower concentrations. Kawaguchi and Kyuma (1959) showed that the precipitates of Al- and Fe- humic acid complexes start to hydrolyze when the medium becomes alkaline and formed hydroxy complexes which resulted in the dissolution of the precipitates. Schnitzer and Skinner (1963) have also reported similar observations for Al- and Fe- fulvic acid complexes. Schnitzer (1969) postulated two types of reac-

tions between fulvic acid and metal ions and hydroxides: a major one in which both COOH and phenolic OH groups react simultaneously, and a minor one involving acidic COOH groups only. Kwong and Huang (1975) studied the influence of citric acid on the formation of crystalline Al hydroxides. They concluded that both the level of citric acid and the initial concentration of Al influence the formation of crystalline Al hydroxide in the system; the crystallization is hindered or delayed by citric acid apparently because coordination of carboxylate groups with Al hampers the hydrolysis of the terminal groups of Al ions. In more recent studies, Kwong and Huang (1977) showed by electron diffraction analysis that citric acid ( $1.0 \times 10^{-6}$  M and  $1.0 \times 10^{-4}$  M) hampered the formation of even microcrystalline bayerite and gibbsite at aluminium concentrations of  $1.1 \times 10^{-4}$  M and  $1.1 \times 10^{-3}$  M  $\text{AlCl}_3$ . These results indicate that organo-Al complexes are extremely important, especially in the acid pH ranges. In the alkaline ranges, these complexes will be unstable and hydroxy-Al complexes will become more important.

According to Turner and Singh (1971), chloride and nitrate ions, in the concentration found in soils, do not form soluble complexes with  $\text{Al}^{3+}$  or get involved in the reactions by substituting for hydroxide ions in the initial amorphous ions. Turner and Ross (1970) found that in the formation of gibbsite, the temperature of the systems and the chloride concentrations in solution had a marked effect on the rate of all the reactions. In all cases, gibbsite was identified as the final product,

except when the temperature was 10° C and when the chloride concentration was about 0.6 N. When the temperature was 10° C, the reactions were very slow, and they believed that given sufficient time, gibbsite would be the final product.

With sulphate ions, the situation is quite different; a number of partially neutralized or basic Al salts have been reported to precipitate from aqueous solutions and clay suspensions. Singh and Brydon (1967; 1969; 1970) identified a crystalline basic aluminium sulphate,  $\text{Al}_4(\text{OH})_{10}\text{SO}_4 \cdot 5\text{H}_2\text{O}$  with a  $\text{pK}_{\text{sp}}$  value of 117.3. Richburg and Adams (1970) studied the  $\text{pK}_{\text{sp}}$  of basaluminite in a number of soils using a monomeric hydrolysis mechanism and found it to decrease with pH. Using a polymeric mechanism, they found a constant value of  $\text{pK}_{\text{sp}} = 123$  with pH, considering the ion  $\text{Al}_6(\text{OH})_{15}^{3+}$ . Rawajfih (1975) reported the formation of basaluminites under various conditions in the laboratory. He also reported the formation of alunites,  $\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$  ( $\text{pK}_{\text{sp}} \approx 82.6$ ) and  $\text{NaAl}_3(\text{OH})_6(\text{SO}_4)_2$  ( $\text{pK}_{\text{sp}} = 76.02$  to  $76.69$ ). Another basic sulphate,  $\text{Al}(\text{OH})\text{SO}_4$  has been reported by van Bremen (1973), but no attempts seem to have been made to separate and identify or synthesize this sulphate. Hsu (1973) found that the presence of sulphate greatly influenced the crystallization of  $\text{Al}(\text{OH})_3$ . When a series of samples was prepared by adding varying amounts of  $\text{Na}_2\text{SO}_4$  to a hydroxy-Al solution, only 12% of the total Al was converted to crystalline  $\text{Al}(\text{OH})_3$  after 3 years of aging with 0.1 equivalent of  $\text{SO}_4^{2-}$ /mol Al. With 0.2 equivalent or more  $\text{SO}_4^{2-}$  per mole

of Al, the reaction products were either amorphous or crystalline basic aluminum sulphate even after prolonged aging.

Bohn and Peech (1969) studied the phosphate complexes of iron III and aluminium in dilute solutions. Although phosphato-aluminium complexes were not directly detectable, their stability constants could be estimated as  $\leq 10^3$  for  $\text{AlH}_2\text{PO}_4^{2+}$ . Over the range of ion concentrations likely to be found in soils, phosphato iron III complexes are the predominant phosphate species in solutions of  $\text{pH} < 1.3$ , phosphatoaluminium in the range of  $\text{pH} 1.3$  to  $4.3$  and aquated phosphate in the range of  $\text{pH} 4.3$  to  $7.2$ . Jameson and Salmon (1954) found evidence for  $\text{Al}(\text{HPO}_4)_3^{3-}$  in aluminium phosphate solutions with  $\text{pH}$  values between  $1.0$  and  $1.5$  and P : Al mole ratios between  $3.5$  and  $8.5$ . Salmon and Wall (1958) found the complex cations  $\text{AlHPO}_4^+$ ,  $\text{AlH}_2\text{PO}_4^{2+}$  and  $\text{Al}(\text{H}_2\text{PO}_4)_2^+$  in solutions of lower concentration and higher  $\text{pH}$  than those examined by Jameson and Salmon (1954). The presence of soluble polymeric complexes in dilute solutions ( $10$ - $30 \mu\text{M}$ ) of Al and phosphate at  $25^\circ \text{C}$  was demonstrated by White et al. (1976) by paper electrophoresis and confirmed by chemical analysis and measurements using  $^{32}\text{P}$ . The formation of aluminophosphate complexes was found to be maximum at  $\text{pH} 5$  when, at an initial P/Al mole ratio of  $1.6$ , three moles of P were complexed with four moles of Al. At  $\text{pH} 6.9$ , they found that only one mole of P was removed for every 10 of Al, suggesting that hydroxy-Al polymers predominated at higher ratios of OH ions to  $\text{H}_2\text{PO}_4$  ions.

Lindsay et al. (1959) found the  $pK_{sp}$  value of synthetic variscite,  $Al(OH)_2H_2PO_4$ , to be 30.5 at  $25^{\circ}C$ . They pointed out that the immediate reaction products of applied phosphate in acid soils were much more soluble than variscite, but upon aging, these intermediate products were slowly transformed into variscite which may coexist with gibbsite as stable solid phases.

Aluminium forms stable complexes with fluoride (Sillén and Martell, 1964; 1971), and the formation of aluminium hydroxide polymers in solution may be decreased by the presence of fluoride. However, at fluoride concentrations found in soils, the interferences may be a minimum.

The forgoing review reveals that the nature of Al species existing even in pure solutions is rather uncertain. It is therefore not surprising that the information on the species in more complicated media like the soil solutions and the reactions of aluminium in clay suspensions is far less definite. In order to predict the types of Al species found in soil solutions, a number of other factors also have to be considered. However, pH and total Al concentration of the solution are the two most important factors, and therefore, attempts to predict the types of Al species in soil solutions have to begin by taking these into consideration.

#### 2. 4. Formation of gibbsite

It has been reported that under intensive weathering conditions such as those existing in the humid tropics, much of the hydroxy-aluminium ends up as crystalline

gibbsite (Mc Lean, 1976; Ferreiro and Helmy, 1976). Hsu (1977) pointed out that gibbsite is known to occur only in acidic soils although the reaction products formed by bubbling  $\text{CO}_2$  through a concentrated sodium aluminate solution is gibbsite if the system is kept above pH 12 and bayerite if the pH is between 9 and 12. But, it is known that by adding NaOH to a chloride or nitrate solution of aluminium, crystalline aluminium hydroxides can be developed at NaOH/Al mole ratio 3 within a few hours. Clear solutions can be obtained up to NaOH/Al = 2.7 if the NaOH is added very slowly (Hsu and Bates, 1964a). Singh (1974) prepared gibbsite in acid medium by allowing a NaOH/Al = 2.4 solution to age for a year. The originally clear solution was converted to crystalline gibbsite by aging. Such experiments suggest that polynuclear hydroxy-aluminium species are metastable forms which in due course of time could be expected to become  $\text{Al}(\text{OH})_3$  (crystalline) as suggested by Frink and Peech (1963a). However, no information is available on the nature of aluminium species (if any) in equilibrium with gibbsite in natural systems.

Hsu (1977) has proposed a mechanism for the formation of gibbsite in highly weathered soils. The initial step of chemical weathering involves the displacement of the balancing bases with  $\text{H}^+$ , which is followed by the breakdown of the Al-O-Si linkage, releasing Al and Si into solution. The formation of gibbsite will be rapid once Si is separated from Al. Hence, whether the primary Al silicates weather to gibbsite directly or through a kaolinite intermediate is governed by a number of factors such as rainfall, temperature, parent rocks, ground water table,

vegetation, time and the ionic environment (sulphate, phosphate, organic complexes etc. mentioned in section 2. 3) of the region.

## 2. 5. Determination of total and polynuclear Al

Numerous procedures have been developed for the use of aluminon as a colorimetric reagent in the determination of Al (Robertson, 1950; Hsu, 1963; Frink and Peech, 1962b). It has been found (Hsu, 1963) that the precision and the accuracy in the determination of Al with aluminon are strongly affected by the original pH of the sample and the presence of phosphate and silicate. The variability in colour intensity is due to the formation of complexes with anions present in the solution under certain pH conditions. Under a preliminary acid and heat treatment, Hsu (1963) found that all Al in test solution was converted to the ionic state, after which the colour could be developed with aluminon at pH 3.7 to 4.0 at room temperature. The colour so developed is relatively stable over long periods of time (after the first one hour) and the method gives highly reproducible results. However, best results may be obtained when Al concentration is small. Hsu (1963) also related the time required for obtaining the maximum colour intensity to the concentrations of both Al and aluminon. The change in the intensity of colour is very slow after one hour, probably because within that time the mononuclear Al forms are in equilibrium with  $Al^{3+}$  under the conditions of Al concentration and pH ranges used, and the aluminon measures  $Al^{3+}$ ,  $Al(OH)^{2+}$ ,  $Al(OH)_2^+$ ,  $Al(OH)_3^0$  and polynuclear Al species if present.

Turner (1969) developed a method for the determination of  $\text{Al}^{3+}$  and mononuclear hydroxy-Al ions, polynuclear hydroxy-Al ions and the initial solid phase formed when a base is added to  $\text{AlCl}_3$  solutions based on the reaction of 8-quinolinol with these different forms. The method was modified by Bache and Sharp (1976), by which mononuclear Al is determined by shaking the sample with 8-quinolinol and extracting with chloroform. They determined total Al by shaking the sample with 5 ml reagent for 30 min and then extracting with chloroform for 30 s. Turner (1969) recommended shaking for only 10 s, but Bache and Sharp (1976) found that 30 seconds' shaking was necessary. The standard solution used in the estimation ( $10^{-4}$  M  $\text{AlCl}_3$ ) was aged at pH 3. They pointed out that organic complexed Al also reacted with 8-quinolinol. No other method has been reported for the estimation of polynuclear Al species.

### 3. MATERIALS AND METHODS

#### 3. 1. RESEARCH METHODOLOGY

The theoretical concepts underlying this study and the experimental procedures adopted to validate these concepts may appear complex. Therefore, a concise account of the research methodology is given here so that the research approach and procedures adopted could be better comprehended.

A critical evaluation of the available information (review of literature) brought out the following aspects which were taken as the starting points for this study:

- The mass action constants ( $pK_n$  values) of polynuclear hydroxy-Al species are known mostly for higher temperature ( $40^\circ\text{C}$ ) and varying ionic strengths (1M, 2M or 3M  $\text{NaClO}_4$ ), but not for the usual temperature ( $25^\circ\text{C}$ ) and low ionic strength values.
- It is possible to distinguish between fast and slow reacting Al species in solution using the method developed by Okura et al. (1962), Turner (1969) and Bache and Sharp (1976). In the solution phase of the  $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$  system, the fast reactable Al can be considered as mononuclear Al and the slow reactable Al as the polynuclear hydroxy-Al species.

Taking these as basis, the following research methodology was formulated for the study:

1. Adjustment of  $pK_n$  values of the polynuclear hydroxy-Al species to low ionic strengths on theoretical grounds.

2. Improvement of the  $pK_n$  values of the polynuclear hydroxy-Al species by an iteration procedure of comparing the experimentally determined and theoretically calculated (using a mononuclear-polynuclear aluminium species model) values of the amounts of polynuclear Al in equilibrium solutions of naturally occurring gibbsite.
3. Use of these refined  $pK_n$  values for the calculation of the concentration of polynuclear hydroxy-Al species in soil solutions and comparison of the theoretical values so obtained with the experimentally determined concentrations of the slow reacting Al species.

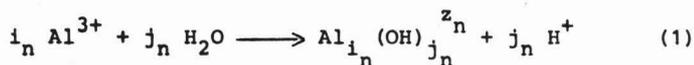
According to this research approach, systems consisting of water and the following solid phases have been investigated:

- Naturally occurring and laboratory-prepared gibbsites
- clay minerals (montmorillonite, vermiculite)
- soil samples equilibrated in the laboratory
- soil solutions collected in the field

In the case of soil systems, the solid phase contains ligands such as sulphates, phosphates and organic ligands, and the solution phase may, therefore, also contain aluminosulphate, aluminophosphate and organo-aluminium complexes. These are not considered in the theoretical calculation of the concentration of polynuclear Al species. All these complexes in solution are probably estimated as the slow reacting Al species and are referred to as polynuclear Al species throughout the text.

### 3. 2. THE MONONUCLEAR-POLYNUCLEAR AL SPECIES EQUILIBRIUM MODEL

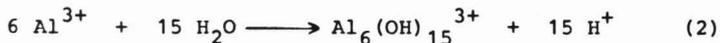
The general equation used for the model is:



$\text{Al}_{i_n}(\text{OH})_{j_n}^{z_n}$  is the general formula for the ionic species,  $A_n$ , considered,  $i_n$  and  $j_n$  are whole numbers and  $z_n$  is the charge of the species ( $z_n = 3 i_n - j_n$ ). Any number of species with specified equilibrium constant ( $K_n$ ) values can be included in the numerical model. Provision is also made for the calculation of activity of ions according to Debye-Hückel corrections. Ion diameters for the different Al species and an ionic strength,  $I_o$ , which results from the ions present in the system, but not involved in the reaction (1) may also be specified. The numerical model has been assembled into a FORTRAN programme, the details of which as suggested by Nair and Prenzel (1978) are given in Appendix I. The model is used to study the equilibria between  $\text{Al}^{3+}$  and nine hydroxy-Al species (for which the equilibrium constants were available), viz,  $\text{Al}(\text{OH})_2^{2+}$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_{13}(\text{OH})_{32}^{7+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  and  $\text{Al}(\text{OH})_4^-$ . The  $\text{p}K_n$  values of the polynuclear species  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  and  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  given in literature were as determined at varying ionic strengths (1 M, 2 M or 3 M  $\text{NaClO}_4$ ) and temperatures (25° C or 40° C). Therefore, these values will henceforth be designated as the first set of  $\text{p}K_n$  values. However, it was assumed that these values were valid for 25° C and a common ionic strength of 2 M  $\text{NaClO}_4$ .

Corrections for this ionic strength were then made according to the method of Richburg and Adams (1970) as follows:

Corresponding to the general equation (1), the equation for  $\text{Al}_6(\text{OH})_{15}^{3+}$  was considered as



$\text{pK}_{(6,15)} = 47$  for the reaction in 2 M  $\text{NaClO}_4$  at  $40^\circ \text{C}$   
 $K_{(6,15)}$  is a concentration K and is related to the thermodynamic  $K_{(6,15)}$  by the factor of  $f_{\text{H}^+}^{15} / f_{\text{Al}^{3+}}^6$ , where  $f$  denotes ion-activity coefficient. This factor can be approximated by assuming that, in solutions of equal ionic strength,  $f_{\text{Cl}^-}$  is equal in solutions of  $\text{KCl}$ ,  $\text{HCl}$  and  $\text{AlCl}_3$ ,  $f_{\text{H}^+}$  is equal in solutions of  $\text{HCl}$  and  $\text{NaClO}_4$ , and  $f_{\text{Al}^{3+}}$  is equal in solutions of  $\text{AlCl}_3$  and  $\text{NaClO}_4$ . Mean activity coefficients at  $25^\circ \text{C}$  and ionic strength of 2.0 M are:  $\text{KCl} = 0.576$ ,  $\text{HCl} = 1.009$ , and  $\text{AlCl}_3 = 0.326$ . If  $f_{\text{Cl}^-}$  is 0.576 in each of these solutions, then  $f_{\text{H}^+} = 1.76$  and  $f_{\text{Al}^{3+}} = 0.059$  and  $f_{\text{H}^+}^{15} / f_{\text{Al}^{3+}}^6$  can be calculated. Ignoring the temperature effect on  $K$  ( $25^\circ \text{C}$  vs  $40^\circ \text{C}$ ), the thermodynamic  $K_{(6,15)}$  could be calculated. Similarly, the thermodynamic  $K_{(7,17)}$ ,  $K_{(13,34)}$  and  $K_{(13,32)}$  were calculated. These  $\text{pK}_n$  values will be designated as the second set of  $\text{pK}_n$  values. Thus, two sets of  $\text{pK}_n$  values for the polynuclear hydroxy-Al species were available for use in the computer model for determining the equilibrium concentrations of mononuclear and polynuclear Al species at a given pH, total Al concentration and ionic strength.

### 3. 3. EXPERIMENTAL TECHNIQUES

#### 3. 3. 1. Aluminon method for the determination of aluminium

##### Reagents:

1. Standard aluminium solution containing 5 µg Al/ml ( $\text{AlCl}_3$  in water), prepared by dissolving 'titrisol aluminium' standard solution (Merck) containing  $1.000 \pm 0.002$  g Al in one litre water and diluting the solution 200 times.
2. 80% thioglycolic acid (Merck) diluted 100 times.
3. Aluminon acetate buffer - Diluted 120 ml glacial acetic acid to about 900 ml with water, dissolved 24 g NaOH in that, added 0.35 g aluminon (aurin tricarboxylic acid ammonium salt GR -  $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_9$ ) (Merck) and made up the solution to 1 l. The pH of this solution is 4.2, when it is diluted 5 times (as in the determinations), pH becomes approximately 3.8.

The accuracy in using the titrisol aluminium standard as the standard aluminium solution was tested by using it for determining the Al in a  $\text{AlCl}_3$  solution of known concentration ( $10^{-4}$  M), prepared from recrystallized  $\text{AlCl}_3$ . The experimental values deviated from the actual values by less than 0.5%. Therefore, the titrisol standard was used as the standard Al solution for all further determinations by the aluminon method.

##### Procedure (modified from Hsu, 1963):

Added 3 ml N HCl each to 0 (blank), 1, 2, 3, 4, 6 and 8 ml of standard Al solution (containing 5 µg Al/ml) in 50 ml standard flasks, diluted to about 20 ml, heated the solutions in water bath at 80 to 90° C for 30 min, allowed

to cool to room temperature, added 2 ml thioglycolic acid, diluted to about 35 ml, added 10 ml aluminon acetate buffer and made up to 50 ml with water. After 90 min, the Al was determined on a Zeiss PL 4 colorimeter using a 546 nm filter.

3. 3. 2. The 8-hydroxy quinoline method for the determination of mono- and polynuclear Al  
(modified from Bache and Sharp, 1976)

For determining mononuclear Al, 5 ml chloroform followed by 5 ml 8-quinolinol reagent (containing 1.4 g 8-quinolinol, 3.6 ml glacial acetic acid and 11.7 g sodium acetate per litre) are added to a test sample in a separating funnel and shaken vigorously for 15 s (this time was found to be sufficient to extract all the mononuclear Al under the experimental conditions). The mixture is allowed to stand and the chloroform layer filtered through a Schwarz Band filter paper to remove moisture, if any, in the chloroform layer. Al was determined on a Zeiss PL 4 colorimeter using a 405 nm filter and a 1 cm cell. The  $AlCl_3$  solution (containing 5 to 20  $\mu g$  Al/ml) used as a standard was adjusted to pH 3 with HCl and allowed to age. The solution is expected to contain only mononuclear Al ions at this pH and Al concentration. For determining total Al, a fresh sample of solution was shaken well with the 8-quinolinol reagent for 30 min, extracted with chloroform for 15 s, and proceeded as mentioned as earlier.

3. 3. 3. Aluminium species in gibbsite solutions

3. 3. 3. 1. Naturally occurring gibbsites and methods of their purification

Two types of naturally occurring gibbsites were used:

Tunja - Sample from Tunja, Eastern Cordillera, western rim of Sabana de Bogota, Columbia. It appeared as orange brown clusters and was easy to powder. Two particle sizes were used  $< 0.063$   $\mu\text{m}$  and  $0.063$  to  $0.20$   $\mu\text{m}$ . Samples were purified by suspending in water, the pH of which was adjusted with HCl to 3.7 or 4 depending upon the experiments to be conducted. The suspension was shaken continuously for 24 h and clarified by centrifugation. The supernatant liquid was discarded and the whole process was repeated five times. The sample is now expected to be pure and on dissolving, the solution should contain only hydroxy-Al species,  $\text{H}^+$  and  $\text{OH}^-$  ions.

Minas Gerais - Sample from Minas Gerais, Brazil. It consisted of dark brownish grey clusters of cylindrical crystals and was relatively difficult to powder. The sample could not be purified as the Tunja sample because the suspension could not be clarified even by high speed centrifugation. The  $< 0.063$   $\mu\text{m}$  particles were placed in a dialysis bag and immersed in water adjusted to pH 3.7. The water was renewed 5 times, and each time the pH was adjusted to 3.7.

X-ray diffraction analysis of the two gibbsite samples (Tunja and Minas Gerais) was done on a Philips X-ray diffraction apparatus with a Debye-Scherrer powder camera using a cobalt anode. The X-ray diagrams are identical to those reported for gibbsite (Rooksby, 1961).

### 3. 3. 3. 2. Polynuclear Al species in solutions in equilibrium with gibbsite

One g each of the purified Tunja gibbsite samples

(< 0.063 µg and 0.063-0.20 µg) was placed in two 250 ml polyethylene bottles and filled to the brim with water. The pH of the suspensions was adjusted to 3.7 with HCl and the bottles sealed air-tight to exclude all influence of the atmosphere. Another Tunja sample (< 0.063 µg) was treated similarly with its pH adjusted to 4. The bottles were shaken occasionally and allowed to stand at temperature  $25 \pm 2^{\circ}$  C. The suspensions were analysed for pH and total Al after 60, 90, 150 and 210 days and for polynuclear Al species after 150 and 210 days. After second (90 days) determination, the pH of the three suspensions were increased by 0.2 units by adding NaOH. Total Al in the first two (60 and 90 days) determinations were estimated by the aluminon method and in the second two determinations by the 8-hydroxy quinoline method.

3. 3. 3. 3. Nature of hydroxy-Al species in solution during the dissolution of naturally occurring gibbsites

One g of the Tunja sample (< 0.063 µg) was suspended in 100 ml water in a 250 ml polyethylene bottle. The pH was adjusted to 3.7 and this was taken as the 'zero' time. At intervals of about four weeks, samples were drawn from the suspension and their pH recorded. These samples were immediately clarified by high speed centrifugation and analysed for Al by the aluminon method. The total Al was considered to exist either only as  $Al^{3+}$  or to be distributed among all the mono- and polynuclear Al species. The procedure was repeated for a similar Tunja sample with its initial pH adjusted to 4, and for a Tunja sample of

bigger particles (0.063-0.20  $\mu\text{m}$ ) with its initial pH adjusted to 3.7.

The Minas Gerais sample ( $<0.063 \mu\text{m}$ ) purified as described earlier was again placed in a dialysis bag and immersed in water, pH of which was adjusted to 3.7. Thereafter, the same procedure as for the Tunja sample was followed, except that centrifugation was not necessary.

All the samples were analysed for pH and Al concentration after 150 and 210 days. The pH and total Al values measured at various times during the dissolution of the gibbsite samples were introduced into the computer programme, by which it was possible to find out the contribution of  $\text{Al}^{3+}$  to the total Al concentration at each time. The final  $\text{pK}_{\text{sp}}$  values were calculated. It was also possible to predict the nature of the species during the course of dissolution of the samples of varying particle sizes and initial pH.

#### 3. 3. 3. 4. Laboratory prepared gibbsite

Gibbsite was prepared in the laboratory by the method of Singh (1974). Dissolved exactly 13.335 g crystalline aluminium chloride in water, made up the volume to 1 l and again diluted the solution 10 times to give a 0.01 M  $\text{AlCl}_3$  solution. To 1 l of this solution in a 2 l round-bottomed flask was added 24 ml N NaOH very slowly (the whole addition took about 2 h). The solution was stirred constantly by passing through it a continuous current of  $\text{CO}_2$ -free air, obtained by allowing air to pass through a series of conc. KOH solutions. The set up was allowed to stand for a year at room temperature ( $\sim 23^\circ \text{C}$ ) with occasional measurements

of the pH of the solution. A portion of the one-year old suspension was filtered through a "Millipore" filter. The filtrate, after discarding its first portion was analysed for total and polynuclear Al, Na (atomic absorption spectrophotometer) and Cl (potentiometric titration against standard silver nitrate). The  $pK_{sp}$  value of gibbsite was calculated on the assumption that the equilibrium solution contains all the mono- and polynuclear ions (see the following section). The experimental value was compared with the theoretical value of the percentage of polynuclear Al, obtained by introducing the equilibrium pH, total Al concentration and additional ionic strength contributed by  $Na^+$  and  $Cl^-$  into the computer programme.

### 3. 3. 3. 5. Calculation of $pK_{sp}$ values of gibbsite

$$pK_{sp} = pAl^{3+} + 3 pOH^-; \quad pOH^- = 14 - pH \text{ at } 25^\circ C$$

The solubility product values for the naturally occurring gibbsite samples were calculated on the assumptions that:

- (a) All Al exists as  $Al^{3+}$
- (b) The total Al is distributed among mononuclear hydroxy-Al forms,  $Al^{3+}$ ,  $Al(OH)^{2+}$ ,  $Al(OH)_2^+$ ,  $Al(OH)_3^0$  and  $Al(OH)_4^-$ ,
- (c) The total Al is distributed among mono- and polynuclear species.

In case (a), the solubility product values were corrected for ion activity coefficients of Al according to the equation:

$$- \log f = \frac{A z_n^2 \sqrt{I}}{1 + B \frac{q_n}{a_n} \sqrt{I}} \quad (2)$$

where  $f$  is the activity coefficient of Al,  $z_n$  is the charge of the ion,  $I = \frac{1}{2} \sum (c_n z_n^2)$ ,  $I$  is the ionic strength of the solution,  $c_n$  is the concentration of the ion, A and B are temperature dependent constants and  $a_n^0$  is an ion-size parameter. The values taken were: A = 0.51, B = 0.33,  $z_n = 3$  and  $a_n^0 = 0.9$  nm (Bolt and Bruggenwert, 1976; p. 17). In cases (b) and (c), the contribution of  $Al^{3+}$  to the total equilibrium Al concentration was obtained by using the computer programme (section 3. 2). Ion activity corrections were also made in these two cases.

### 3. 3. 4. Polynuclear aluminium species in equilibrium solutions of montmorillonite and vermiculite

#### 3. 3. 4. 1. Preparation of equilibrium samples

Montmorillonite: To each of the six samples of 50 g of montmorillonite (from Hallertau, Landshut, Germany), 500 ml water was added. The suspensions were stirred with magnetic stirrers, the pH of the suspensions were adjusted with HCl to 3.2, 3.7, 4.0, 4.5, 5.0 and 5.5. It was difficult to maintain the pH at these values; therefore, repeated pH adjustments at frequent intervals were necessary and it was continued for 50 days. A total of 24 pH adjustments per sample was made during this period. The total volumes of decinormal HCl required for adjusting the pH during this period were 176, 138, 122, 104, 91 and 80 ml for the samples with pH 3.2, 3.7, 4.0, 4.5, 5.0 and 5.5 respectively. The suspensions were then (after 50 days) allowed to remain undisturbed for a further period of 6 weeks with occasional pH determinations. These are designated as the first set of

montmorillonite samples. From each container, equal amounts of the first set samples were taken out, dried, and 5 g each was then suspended in 100 ml water. The pH of the suspensions were once again adjusted to their original values, readjusted at appropriate intervals during the course of the next four weeks and then allowed to remain undisturbed (except for pH determinations) till utilized for the experiment (see section 3.3.4.2). These are designated as the second set of samples.

Vermiculite: The vermiculite flakes (from Toc mine, Loolekop (Palabora), Transvaal) were crushed (not powdered), treated similar to the montmorillonite sample and the first and second sets of vermiculite samples corresponding to the first and second sets of montmorillonite samples were prepared.

#### 3. 3. 4. 2. Analysis

X-ray diffraction: In order to find out whether the structure of montmorillonite and vermiculite had changed during the course of these treatments, X-ray diffraction analysis was done for the first set of samples of both. Took small amounts of the samples in suitable bottles, added about 3 ml each of 1 N KCl and allowed to stand for about 18 h. Then centrifuged the samples at approximately 3000 rpm for 15 min, decanted the supernatant liquid and washed the samples thoroughly with water. Treated a similar set of samples without KCl. The original samples (before pH adjustments) of montmorillonite and vermiculite were also treated with KCl and water. All samples were mounted on slides for X-ray diffraction on a 'Philips' X-ray diffraction

apparatus using a cobalt anode.

Polynuclear Al species: The pH and polynuclear Al species in the equilibrium solutions of both sets of montmorillonite and vermiculite samples were determined 26 weeks after the initiation of the experiment, i.e., 13 weeks after the first set of samples was prepared.

### 3. 3. 5. Polynuclear Al species in soil solutions

#### 3. 3. 5. 1. Equilibrium soil solutions

Two soil types were used in the studies, one from Solling and the other from Lüss. The Solling soils from the mountainous ranges of Solling District represent various horizons of 14 soil profiles which included 4 profiles of stagnogley, 2 profiles of pseudogley, 6 profiles of podsollic brown earth with indications of weak or strong pseudogleying and 2 profiles of podzolic brown earth. These profiles are developed mostly in loess material mixed with weathered triassic sandstone. Present vegetation is mainly spruce with beech only in three sampling sites.

Eight profiles of sandy soils from the Lüss area under pine vegetation were used for the studies; the depths in all profiles were 0-4, 4-10, 10-20, 20-30, 30-40 and 40-50 cm.

Detailed characteristics of both Solling and Lüss soils may be obtained from the Institute.

Took about 600 g each of the soil samples in beakers, added water to make a paste, stirred the paste well and allowed to stand for 24 h, separated the "equilibrium soil solution" by suction, and

determined its pH and Al, Na, K, Ca,  $\text{NH}_4$ , Mg, Fe, Mn, Cl,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  concentrations. These ions are expected to contribute to the total ionic strength of the equilibrium soil solutions. Air-dried the soil samples and powdered in an "Achat mill" and reserved for determination of C.

In order to find out the effect of the duration of equilibration on the amount of polynuclear aluminium in solution, saturated soil pastes were prepared using soil samples from a few selected depths and were allowed to stand with occasional stirring. After 20 days the equilibrium soil solutions were separated and analysed for all the ions mentioned above.

pH was determined with a combined electrode assembly and a digital pH meter "Metrohm Herisau E 500", calibrated to 0.01 unit with three buffers. Polynuclear Al ( = total Al - mononuclear Al ) was determined by the 8-hydroxy quinoline method as mentioned in section 3. 3. 2; Na, K, Ca, Mg and Mn by the atomic absorption spectrophotometry; Fe (phenanthroline method),  $\text{NO}_3$  and  $\text{NH}_4$  (as the N - Salicylate - DTT - complex) by colorimetry using the auto-analyser;  $\text{PO}_4$  colorimetrically by the molybdenum blue method and Cl potentiometrically by titration against standard silver nitrate.  $\text{SO}_4$  was precipitated as  $\text{BaSO}_4$  by the addition of  $\text{BaCl}_2$  and the excess Ba determined potentiometrically by titration against standard EDTA. Carbon was determined by the method of Wösthoff. Analytical details are described by Fassbender and Ahrens (1977).

### 3. 3. 5. 2. Lysimeter solutions

The water percolating below the soil layer with intensive root activity (75 to 80 cm deep) in the research sites of Beech and Spruce forests of the IBP (International Biological Program) project in Solling were used for the analysis. The water samples were collected with the help of  $\text{Al}_2\text{O}_3$  suction plates which receive continuous suction from a vacuum pump. The monthly composite samples (3 each from the Beech and Spruce sites) for the period from April to September 1977 were used in the studies.

All the samples were analysed for pH, total and polynuclear Al, and for the ions Na, K, Ca,  $\text{NH}_4$ , Mg, Fe, Mn, Cl,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$  contributing to the ionic strength of the solution. The theoretical values for polynuclear Al were calculated as described in section 3. 3. 5. 1 and compared with the experimental ones.

### 3. 3. 6. $\text{pAl}^{3+} + 3 \text{pOH}^-$ values of a population of soil solutions

The additional ionic strength,  $I_0$ , contributed by all the ions except  $\text{H}^+$  and aluminium was calculated for the Solling and the Lüss samples mentioned in section 3. 3. 5. 1, with the knowledge of the total ionic strength of the solutions of the samples equilibrated for 24 h and 20 days. Values of pH, total Al concentrations and  $I_0$  were introduced into the computer programme and the theoretical value for the polynuclear hydroxy-Al was predicted. This was compared with the experimental values of both the 24 h- and 20 days-equilibrated solutions.  $\text{pAl}^{3+} + 3 \text{pOH}^-$  values were

calculated for all the samples.

In addition, 55 samples for which the pH, total Al concentration and ionic strength values were available, were selected at random from a large number of equilibrium (24 h) soil solutions analysed at the Institute laboratory over the past many years. The samples so selected were from different places such as Escherode, Sprakensehl, Syke/Westermark, Walsrode, Lüss, Radolfhausen, Jembke and Eschwege. The additional ionic strength,  $I_0$ , contributed by Na, K, Ca,  $\text{NH}_4$ , Mg, Fe, Mn, Cl,  $\text{NO}_3$ ,  $\text{PO}_4$  and  $\text{SO}_4$ , was calculated as the difference between total ionic strength and the ionic strength due to Al and H ions. The total Al concentration, pH and  $I_0$  values were introduced into the computer programme. From the  $\text{Al}^{3+}$  concentration and its activity coefficient,  $\text{pAl}^{3+}$  values were derived and the  $\text{pAl}^{3+} + 3 \text{pOH}^-$  values were calculated for all the equilibrium soil solutions.

#### 4. RESULTS AND DISCUSSION

##### 4. 1. pK<sub>n</sub> values for polynuclear hydroxy-Al species

The different hydroxy-Al species, their ion size parameters and pK<sub>n</sub> values are given in Table 1. The pK<sub>n</sub> values from literature for the mononuclear species (and the dimer Al<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup>) mentioned in section 1 of the Table are at 25° C and zero ionic strength. Therefore, these values could be used without any corrections. For the polynuclear hydroxy-Al species, the literature values of pK<sub>n</sub> (first set values) had been determined at various ionic strengths (1M, 2M or 3M NaClO<sub>4</sub>) and at different temperatures (25° C or 40° C). Therefore, they were corrected for ionic strength according to the method of Richburg and Adams (1970) (see section 3. 2 for details). The corrected values are designated as the second set of pK<sub>n</sub> values.

When the pH and total Al concentration of the Tunja gibbsite solution (gibbsite : water = 1 : 250) were used in the computer analysis with the first set of pK<sub>n</sub> values, the theoretical value did not show any polynuclear hydroxy-Al species. But when the second set of pK<sub>n</sub> values was used, about 96% of the total Al was predicted to exist as polynuclear hydroxy-Al species at the same equilibrium conditions (additional ionic strength, I<sub>0</sub>, is zero). The experimental and theoretical values are given in Table 2. The experimental values of percentage of polynuclear hydroxy-Al species varied from 16 to 23% depending on the experimental conditions.

TABLE 1 Hydroxy-aluminium species<sup>§</sup>, their ionic diameters and pK<sub>n</sub> values

| Species | Ionic diameter (nm) | pK <sub>n</sub> values from literature (first set) | Corrected pK <sub>n</sub> values |              |
|---------|---------------------|--|----------------------------------|--------------|
|         |                     |  | xxSecond set                     | xxxThird set |

1. Species for which the pK<sub>n</sub> values were used without correction

|   |     |       |                        |  |
|---|-----|-------|------------------------|--|
| Al(OH) <sup>2+</sup>                            | 0.7 | 5.02  | (no correction needed) |  |
| Al <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> | 0.8 | 7.55  |                        |  |
| Al(OH) <sub>2</sub> <sup>+</sup>                | 0.6 | 9.70  |                        |  |
| Al(OH) <sub>3</sub> <sup>0</sup>                |     | 13.02 |                        |  |
| Al(OH) <sub>4</sub> <sup>-</sup>                | 0.5 | 23.57 |                        |  |

2. Species for which the pK<sub>n</sub> values were modified

|   |     |        |       |       |
|---|-----|--------|-------|-------|
| Al <sub>6</sub> (OH) <sub>15</sub> <sup>3+</sup>  | 0.9 | 47.00  | 35.90 | 44.17 |
| Al <sub>7</sub> (OH) <sub>17</sub> <sup>4+</sup>  | 0.9 | 48.80  | 36.00 | 45.18 |
| Al <sub>13</sub> (OH) <sub>34</sub> <sup>5+</sup> | 0.9 | 97.60  | 73.30 | 91.05 |
| Al <sub>13</sub> (OH) <sub>32</sub> <sup>7+</sup> | 0.9 | 104.50 | 80.66 | 98.65 |

§ In addition to these species, Al<sup>3+</sup> was also considered.

+ The literature values of pK<sub>n</sub> for the polynuclear species mentioned in section 2 of the Table were determined in NaClO<sub>4</sub> solution of various ionic strengths (1M, 2M or 3M) and at different temperatures (25° or 40° C).

++ The second set of values were obtained by correcting the first set of values for ionic strength on the assumption that the uncorrected values were valid for a common ionic strength of 2M at 25° C.

+++ The third set of values were obtained by correcting on the basis of comparison with the experimental data of Table 2 (see the text for details).

TABLE 2 Experimental and theoretical values of percentage polynuclear aluminium in equilibrium Tunja gibbsite solutions

| Description of sample              |            |                         | Equilibrium<br>pH | Equilibrium Al concn<br>( $10^{-4}$ mol/l) |             | Percentage of polynuclear Al species |   |         |         |
|------------------------------------|------------|-------------------------|-------------------|--|-------------|--------------------------------------|---|---------|---------|
| Particle size<br>( $\mu\text{m}$ ) | Initial pH | Gibbsite to water ratio |                   | Total                                      | Mononuclear | <sup>+</sup> Experimental            | Theoretical, using $\text{pK}_n$ values |         |         |
|                                    |            |                         |                   |  |             |                                      | 1st set                                 | 2nd set | 3rd set |
| 0.063                              | 3.7        | 1 : 250                 | 4.21              | 0.4967                                     | 0.4114      | 17.17                                | 0                                       | 95.07   | 16.92   |
| 0.063                              | 4.0        | 1 : 250                 | 4.39              | 0.2520                                     | 0.2112      | 16.19                                | 0                                       | 94.72   | 13.65   |
| 0.063-<br>0.200                    | 3.7        | 1 : 250                 | 4.24              | 0.5337                                     | 0.4114      | 22.91                                | 0                                       | 95.85   | 25.62   |

<sup>+</sup> The experimental values of percentage of polynuclear Al species at 150 days are reported here; the values at 210 days were within 1% of the values at 150 days.

This difference between the experimental and theoretical values may be due to the inaccuracy of the  $pK_n$  values used. Therefore, the second set of  $pK_n$  values of the polynuclear species mentioned in Table 1. 2 were further modified; the  $pK_n$  values for the species mentioned in Table 1. 1 were, however, assumed to be correct as they were determined for zero ionic strength and at 25° C. For each of the four polynuclear hydroxy-Al species, the  $pK_n$  values of the first set and the second set were summed up and then divided by different quotients. By trial and error, these quotients were altered until a set of  $pK_n$  values were obtained, which when used in the computer analysis of the data on the equilibrium pH and total Al concentration, gave values for total polynuclear Al species within 3% difference of the experimental values (Table 2). These modified  $pK_n$  values designated as the third set values in Table 1 are used in all further calculations, unless otherwise specified. The theoretical values of percentage of polynuclear hydroxy-Al species, calculated using this third set of  $pK_n$  values are also given in Table 2.

The experimental values of the percentage of polynuclear hydroxy-Al species at 150 days and 210 days of equilibration of the naturally occurring gibbsite samples were almost identical (difference about 1%), indicating that equilibrium had been achieved within 150 days.

#### 4. 2. Validity of the third set of $pK_n$ values

The validity of the third set of  $pK_n$  values was

confirmed by applying them to the equilibrium solutions of the laboratory prepared gibbsite.

During the preparation of the laboratory gibbsite, the solution was initially turbid when 0.1 N NaOH was added to the  $\text{AlCl}_3$  solution, but the turbidity decreased with time and the solution became clear by the end of a week. The initial turbidity may be attributed to the substitution of  $\text{OH}^-$  by  $\text{Cl}^-$  in the polymeric structure as the addition of NaOH was not sufficiently slow (Hsu, 1977). The solution then remained clear for the next three weeks and during this period, the pH decreased from 4.7 to 4.3. When the solution was 4 weeks old, the turbidity reappeared and the pH remained almost steady for the next few weeks till the 13th week when it suddenly dropped to pH 4.11. By the 15th week, pH was 4.04, and by the 16th week when pH was 3.98, there was the first appearance of crystals as observed by the naked eye. Thereafter, till the end of a year, the pH remained between 3.7 and 3.76. These changes in pH may be due to the formation of various hydroxy-Al species in solution.

Thus, the equilibrium solution of the laboratory gibbsite has a pH of 3.7; its total Al concentration was  $26.25 \times 10^{-4}$  mol/l. The mean value of its ionic strength contributed by ions other than those in equation (1) was  $4.927 \times 10^{-2}$  mol/l. Experimental value of the percentage of polynuclear Al species in the solution was 15.30% and the theoretical value 15.95%. Thus, although the values of pH and total Al of the equilibrium solutions of the

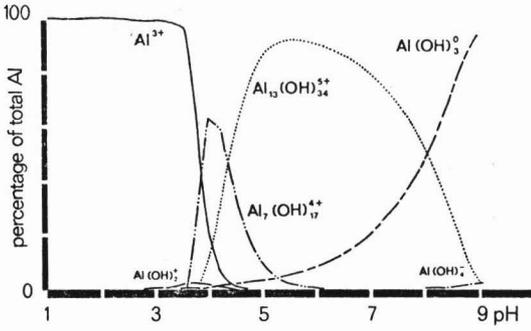
naturally occurring (Table 2) and the laboratory-prepared gibbsite are very different, there was good agreement between the experimental and theoretical values of the percentage of polynuclear hydroxy-Al in the equilibrium solution of the laboratory gibbsite. This shows that, in the  $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$  system, it is possible to predict fairly accurately, the percentage of polynuclear hydroxy-Al species at a given pH, Al concentration and ionic strength using the third set of  $\text{pK}_n$  values.

4. 3. Aluminium species in the  $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$  system at different pH and total Al values

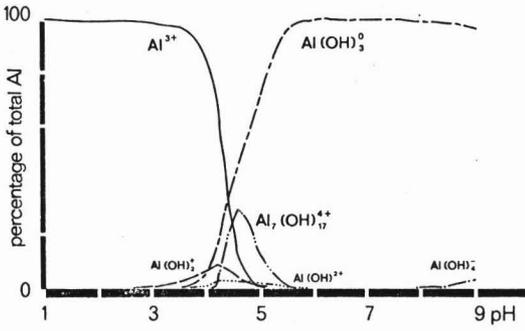
Percentages of total Al present as the different Al species at pH ranges 1 to 9 and different Al concentrations ( $10^{-3}$  M,  $10^{-4.5}$  M and  $10^{-6}$  M) likely to be found in soil solutions were calculated using the third set of  $\text{pK}_n$  values. The results are presented in Fig. 1a - 1c. The results expressed as function of pAl (pAl 0 - 6) at constant pH (pH 3, 4 and 5) are presented in Fig. 2a - 2c. For all these calculations, the additional ionic strength,  $I_0$ , was given a value of  $2 \times 10^{-3}$  mol/l.

Fig. 1a - 1c show that the trivalent Al ion is the major Al species present in the lower pH ranges. However, the actual value of pH, up to which  $\text{Al}^{3+}$  can be the major species present, depends on the total Al concentration also. In dilute solutions ( $\text{pAl} > 4.5$ ),  $\text{Al}^{3+}$  is the major species up to about pH 4, but as the Al concentration increases, the value of pH up to which  $\text{Al}^{3+}$  continues to be predominant decreases and at  $\text{pAl} = 3$ ,  $\text{Al}^{3+}$  is predominant only up to about pH 3.5.

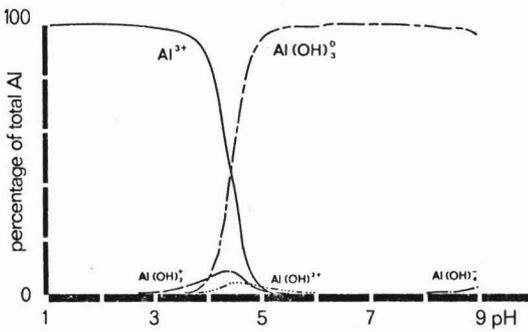
a p Al=3.



b p Al=4.5



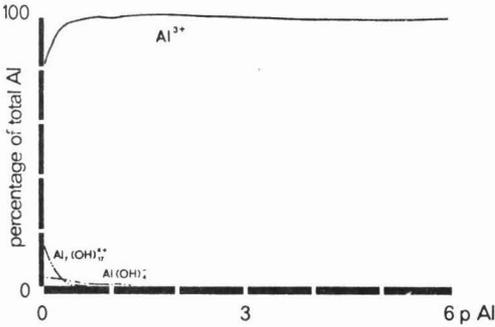
c p Al=6.



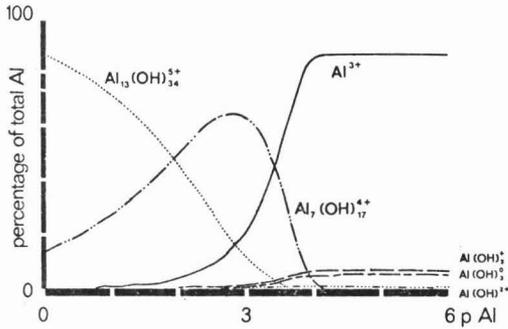
- $Al^{3+}$
- .....  $Al(OH)_2^{2+}$
- $Al(OH)_2^+$
- $Al(OH)_4^-$
- $Al(OH)_3^0$
- $Al_7(OH)_{17}^{4+}$
- .....  $Al_{13}(OH)_{34}^{5+}$

Fig. 1. Different aluminium species in solution as a function of pH at pAl 3.0, 4.5 and 6.0, calculated using the third set of  $pK_n$  values

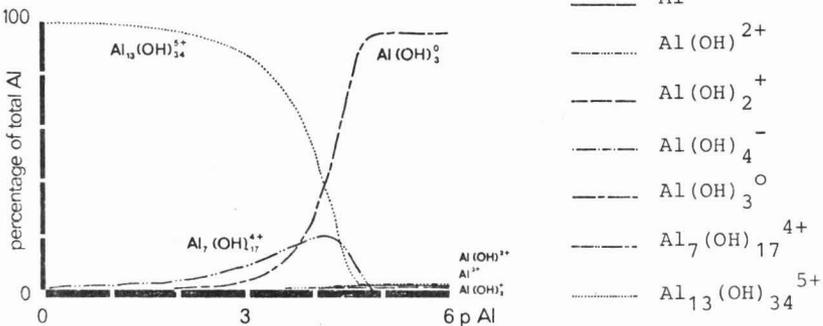
a pH=3.



b pH=4.



c pH=5.



- \_\_\_\_\_  $Al^{3+}$
- $Al(OH)_2^{2+}$
- $Al(OH)_2^+$
- $Al(OH)_4^-$
- $Al(OH)_3^0$
- $Al_7(OH)_{17}^{4+}$
- $Al_{13}(OH)_{34}^{5+}$

Fig. 2. Different aluminium species in solution as a function of pAl at pH 3, 4 and 5, calculated using the third set of  $pK_n$  values

The species  $\text{Al}(\text{OH})_3^0$  is present only at dilute Al concentrations ( $\text{pAl} \geq 4.5$ ) and at pH values  $> 3.5$ . As the Al concentration increases, this species becomes less predominant in acid pH ranges.

At dilute Al concentrations ( $\text{pAl} = 6$ ), only mononuclear species are predominant. At moderate concentrations of Al ( $\text{pAl} = 4.5$ ), the polynuclear species  $\text{Al}_7(\text{OH})_{17}^{4+}$  is also present in addition to  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})_3^0$  and at still higher Al concentration ( $\text{pAl} = 3$ ), the species  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  is also present in relatively large amounts.

The mononuclear species  $\text{Al}(\text{OH})_2^+$  appears to be present in all Al concentration ranges in the pH range 3 to 5, but only in relatively smaller amounts (always  $< 10\%$ ).  $\text{Al}(\text{OH})_2^{2+}$  is present at dilute Al concentrations in small amounts (always  $< 5\%$ ). In the high pH range of 8 to 9,  $\text{Al}(\text{OH})_4^-$  is present at all Al concentrations though in very small percentages; this species could be more prominent above pH 9, but it has not been studied. It may be noted that the species  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}_6(\text{OH})_{15}^{3+}$  and  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  do not seem to appear in the ranges of pH and Al concentration studied using the third set of  $\text{pK}_n$  values.

Taking  $\text{pAl}$  as the independent variable (Fig. 2a),  $\text{Al}^{3+}$  is the only species in solution at pH 3, except at very high Al concentrations not found in soil solutions when small amounts of  $\text{Al}_7(\text{OH})_{17}^{4+}$  (always  $< 15\%$ ) and  $\text{Al}(\text{OH})_4^-$  ( $< 5\%$ ) could exist. At pH 4 and 5 (Fig. 2b and 2c), polynuclear Al forms are found at the Al concentrations measurable in soil solutions;  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  being more

important at high Al concentrations.

Earlier models on Al species in solutions (e.g.: Sullivan and Singley, 1968; Marion et al., 1976) consisted of only mononuclear Al species. But, the results of this study indicates that the polynuclear hydroxy-aluminium species are also important in the acid pH range (pH 3 to 6), their relative amounts being dependent on the total Al concentration.

In these studies, an additional ionic strength factor,  $I_o$ , has been introduced in addition to the ionic strength contributed by H and Al ions. The ions contributing to  $I_o$  are supposed to have no reaction with the aluminium species.

#### 4. 4. pK<sub>sp</sub> values of gibbsites

##### 4. 4. 1. Laboratory gibbsite

The pK<sub>sp</sub> value of the laboratory-prepared gibbsite has been calculated as 34.14 on the assumption that the total Al is distributed between mononuclear and polynuclear Al forms. Though the temperature of the gibbsite solution was about 23° C. calculations were made on the assumption that the temperature was 25° C.

Singh (1974) reported a value of pK<sub>sp</sub> 33.96 ± 0.03 at 25° C for a sample of laboratory-prepared gibbsite; he had made corrections for only Al(OH)<sup>2+</sup> using the first stage hydrolysis of Al<sup>3+</sup>. For a sample of commercial gibbsite, Kittrick (1966) found a value of 34.03 ± 0.05 at 25° C on the assumption that all Al was 'monomeric' below pH 4. The sample used in the present experiment has

been prepared according to the method followed by Singh (1974) and about 15% of polynuclear hydroxy-Al has been experimentally determined in its equilibrium solution (section 4. 2). This shows that it is not correct to assume that all aluminium exists as mononuclear species even if the solution pH is less than 4 and therefore, corrections for mononuclear species alone are not sufficient to obtain accurate  $pK_{sp}$  values for gibbsite.

#### 4. 4. 2. Naturally occurring gibbsites

The  $pK_{sp}$  values of the Tunja samples as calculated for all the three assumptions on the distribution of Al species as mentioned in section 3. 3. 3. 5 are given in Table 3. Though the conditions were disturbed by the addition of NaOH,  $pK_{sp}$  values were the same at 90 days and 150 days, confirming that equilibrium has been attained within 90 days. The  $pK_{sp}$  value of the Tunja gibbsite is  $33.95 \pm 0.05$  (Tables 3 and 4) and that of the Minas Gerais sample is 34.01 (Table 3).

#### 4. 5. Al species in solution during the dissolution of naturally occurring gibbsites

$pAl^{3+} + 3 pOH^-$  values for the Tunja gibbsite under various conditions of particle size and initial pH, plotted against time are given in Fig. 3a, b and c. In these figures, two conditions are envisaged: firstly, that all Al exists as  $Al^{3+}$  and secondly, the total Al is distributed among all mono- and polynuclear hydroxy-aluminium species. Where total Al is considered to exist only as  $Al^{3+}$ , the  $pAl^{3+} + 3 pOH^-$  values could be easily calculated

TABLE 3  $pK_{sp}$  values of Tunja gibbsite sample at 150 days<sup>§</sup> (samples left undisturbed for 60 days)

| Description of sample     |               | Gibbsite:<br>water<br>ratio | Equilibrium<br>pH | +Equilibrium Al concentration (pAl <sup>3+</sup> ) |      |      | pK <sub>sp</sub> |       |       |
|---------------------------|---------------|-----------------------------|-------------------|--|------|------|------------------|-------|-------|
| Sample size<br>( $\mu$ m) | Initial<br>pH |                             |                   | (a)  | (b)  | (c)  | (a)              | (b)   | (c)   |
| <0.063                    | 3.7           | 1 : 250                     | 4.21              | 4.28   | 4.45 | 4.63 | 33.65            | 33.82 | 34.00 |
| <0.063                    | 4.0           | 1 : 250                     | 4.39              | 4.65   | 4.77 | 5.11 | 33.48            | 33.60 | 33.95 |
| 0.063-<br>0.200           | 3.7           | 1.250                       | 4.24              | 4.34   | 4.37 | 4.67 | 33.62            | 33.65 | 33.95 |

<sup>§</sup> The  $pK_{sp}$  values at 60 and 90 days are within the experimental error of the values at 150 days

<sup>+</sup> Activity coefficient corrections have been made for the pAl<sup>3+</sup>

(a), (b) and (c) are the three assumptions made for the calculations:

(a) All Al exists as Al<sup>3+</sup>, (b) Total Al is distributed between Al<sup>3+</sup>, Al(OH)<sup>2+</sup>, Al(OH)<sub>2</sub>, Al(OH)<sub>3</sub><sup>0</sup> and Al(OH)<sub>4</sub><sup>-</sup> and (c) Total Al is distributed among all species mentioned in Table 1; the

$pK_n$  values used are the third set values

TABLE 4  $pK_{sp}$  values<sup>+</sup> of the naturally occurring gibbsites used in the study of the nature of species during dissolution

| Sample                  | Description of the sample    |               | Gibbsite:<br>water<br>ratio | Equili-<br>brium<br>pH | Equilibrium<br>Al concn<br>(total Al)<br>pAl | $pK_{sp}$ (1) | Equilibrium<br>Al <sup>3+</sup> concn<br>pAl <sup>3+</sup> | $pK_{sp}$ (2) |
|-------------------------|------------------------------|---------------|-----------------------------|------------------------|--|---------------|--|---------------|
|                         | Particle size<br>( $\mu m$ ) | Initial<br>pH |                             |                        |  |               |  |               |
| <u>Tunja</u>            | <0.063                       | 3.7           | 1 : 100                     | 4.30                   | 4.43   | 33.53         | 4.83   | 33.93         |
| <u>Tunja</u>            | <0.063                       | 4.0           | 1 : 100                     | 4.36                   | 4.64   | 33.56         | 5.07   | 33.96         |
| <u>Tunja</u>            | 0.063-<br>0.200              | 3.7           | 1 : 100                     | 4.24                   | 4.25   | 33.53         | 4.64   | 33.92         |
| <u>Minas<br/>Gerais</u> | <0.063                       | 3.7           | "dialysis<br>bag" method    | 4.19                   | 4.34   | 33.77         | 4.58   | 34.01         |

<sup>+</sup> The values at 210 days are reported here; the values at 150 days are within the experimental error of these values

$pK_{sp}$  (1) denotes the value uncorrected for the hydroxy-Al species and  $pK_{sp}$  (2) denotes the values corrected for the hydroxy-Al species

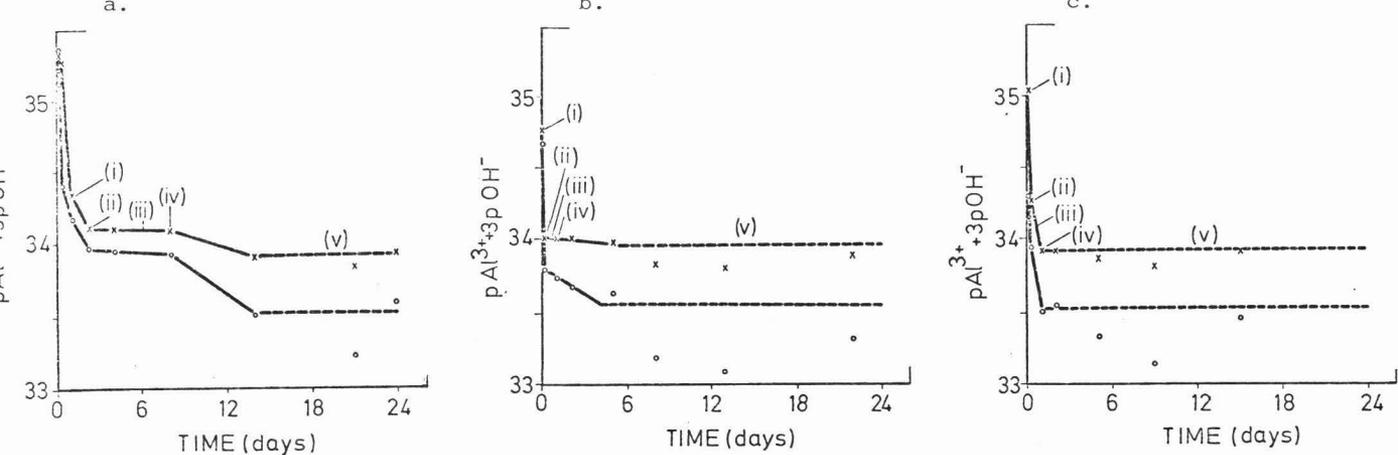


Fig. 3.  $pAl^{3+} + 3pOH^{-}$  values of Tunja gibbsite as a function of time

- a. Particle size  $< 0.063 \mu m$ , initial pH 3.7
- b. Particle size  $< 0.063 \mu m$ , initial pH 4.0
- c. Particle size  $0.063 - 0.200 \mu m$ , initial pH 3.7

The broken lines are drawn parallel to the x-axis corresponding to the  $pK_{sp}$  value of the gibbsite. The upper line refers to  $pK_{sp} \sim 33.95$  obtained when the total Al is considered to be distributed among all mono- and polynuclear species, and the lower line refers to  $pK_{sp} \sim 33.60$  when all the Al is considered to exist as  $Al^{3+}$ .

Only mononuclear Al species are present up to (i), the first traces of  $Al_7(OH)_{17}^{4+}$  appears at (i). Amount of  $Al_7(OH)_{17}^{4+}$  increases till (ii) and thereafter it remains almost constant till (iii). Traces of  $Al_{13}(OH)_{34}^{5+}$  appear at (iv) and at (v) both  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$  are present.

from measured aluminium and pH values after necessary activity coefficient corrections. In the case where total Al is expected to be distributed among all the mono- and polynuclear forms,  $\text{Al}^{3+}$  contribution was evaluated by introducing the measured Al concentration and pH values into the computer programme. The change of the mononuclear Al : polynuclear Al ratio with time is shown as Fig 4a, b and c.

In these presentations and discussions (i), (ii), (iii), (iv) and (v) refer to points indicated in the figures. Up to (i), it is theoretically shown that only mononuclear species are present, at (i), the first traces of  $\text{Al}_7(\text{OH})_{17}^{4+}$  appear and its amount increases till (ii), thereafter, the amount of  $\text{Al}_7(\text{OH})_{17}^{4+}$  remains approximately a constant (indicated by iii) till at (iv) when the species  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  appears. After that, the amounts of the polynuclear species ( $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ ) vary, their relative contribution changing with time, as indicated by (v), till equilibrium is reached after a few months.  $\text{pK}_{\text{sp}}$  values are found to be the same at 150 days and 210 days after the commencement of the dissolution experiments.

Contrary to expectations, the Tunja gibbsite with smaller particle size appears to move towards equilibrium much slower than those with the larger particle size and same initial pH (3.7). An "intermediate stationary state" noticed ( $\text{pAl}^{3+} + 3\text{pOH}^-$  remains constant for a few days; (iii) of Fig. 3a, 4a) corresponds to the time when an approximately constant amount of  $\text{Al}_7(\text{OH})_{17}^{4+}$  is predicted.

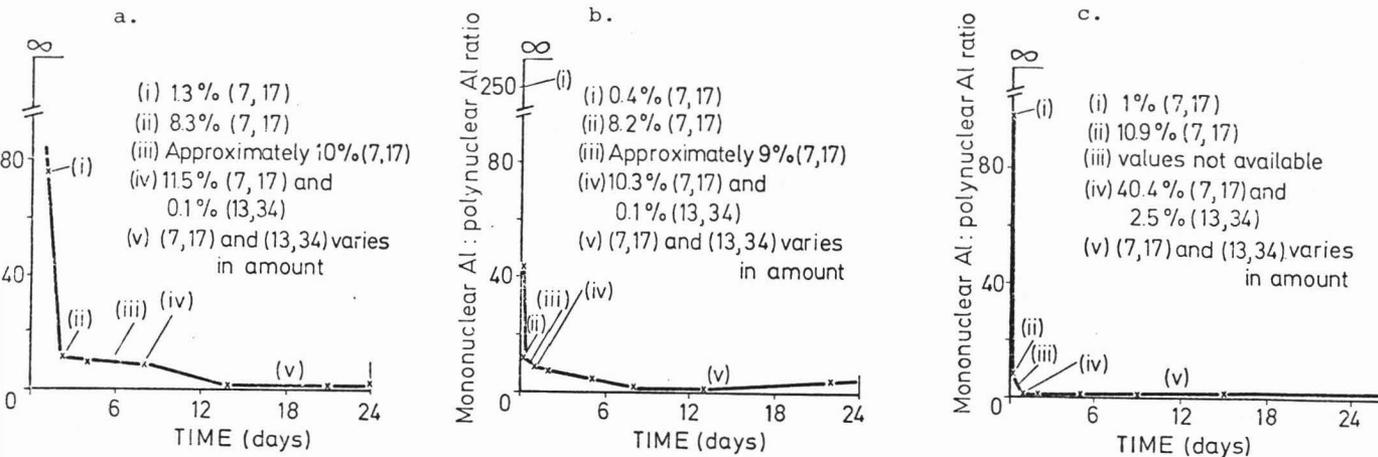


Fig. 4. Mononuclear Al : polynuclear Al in solution at different time intervals during the dissolution of the Tunja gibbsite

a. Particle size < 0.063  $\mu\text{m}$ , initial pH 3.7

b. Particle size < 0.063  $\mu\text{m}$ , initial pH 4.0

c. Particle size 0.063 - 0.200  $\mu\text{m}$ , initial pH 3.7

(7,17) and (13,34) refer to the Al species  $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$

It indicates the existence of two polynuclear species,  $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ , the "intermediate stationary state" ending when the second species,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ , comes into the picture. The presence of a least two polynuclear hydroxy-Al species in solution is again confirmed by obtaining a constant  $\text{pAl}^{3+} + 3\text{pOH}^-$  value only after a long time even though the mononuclear Al : polynuclear Al ratio attains an approximate constancy within a few days (Fig. 4a, b and c). Thus, the theoretical prediction can explain experimental observations; this is also an indirect proof for the validity of the new set of  $\text{pK}_n$  values. At equilibrium, the species  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  are present, their relative amounts being dependent on the conditions of experimentation such as the initial pH and particle size. The relative amounts of the various species in equilibrium gibbsite solutions are given in Table 5.

The species present in solution during the dissolution of the Minas Gerais gibbsite are of a more or less similar nature (Fig. 5a, b). Initially only mononuclear species are present in solution, then at (i) (after 10 days),  $\text{Al}_7(\text{OH})_{17}^{4+}$  comes into the picture and its amount increases. At 26 days, there was no trace of the second species,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ . However, at 150 days, this species was also found in solution and the  $\text{pAl}^{3+} + 3\text{pOH}^-$  value thereafter appears to remain constant. Though a  $\text{pK}_{\text{sp}}$  value of 34.01 is obtained (Table 4), it is doubtful whether equilibrium has been reached; the whole process appears to be much slower than in the case of Tunja gibbsite, probably because

TABLE 5 Percentages of the different hydroxy-Al species in equilibrium solutions of naturally occurring gibbsite samples

| Description of the sample |                                    |               | Gibbsite:<br>water<br>ratio | Percentage of total Al present as different species |                             |                            |                            |                                    |                                       |
|---------------------------|------------------------------------|---------------|-----------------------------|---|-----------------------------|----------------------------|----------------------------|------------------------------------|---------------------------------------|
| sample                    | Particle size<br>( $\mu\text{m}$ ) | Initial<br>pH |                             | $\text{Al}^{3+}$                                    | $\text{Al}(\text{OH})^{2+}$ | $\text{Al}(\text{OH})_2^+$ | $\text{Al}(\text{OH})_3^0$ | $\text{Al}_7(\text{OH})_{17}^{4+}$ | $\text{Al}_{13}(\text{OH})_{34}^{5+}$ |
| <u>Tunja</u>              | < 0.063                            | 3.7           | 1 : 250                     | 53.6  | 7.7                         | 2.5                        | 19.1                       | 16.6                               | 0.3                                   |
| <u>Tunja</u>              | < 0.063                            | 4.0           | 1 : 250                     | 32.8  | 7.3                         | 3.7                        | 43.5                       | 13.4                               | 0.3                                   |
| <u>Tunja</u>              | 0.063-<br>0.200                    | 3.7           | 1 : 250                     | 45.1  | 6.9                         | 2.4                        | 19.9                       | 24.9                               | 0.8                                   |
| <u>Tunja</u>              | < 0.063                            | 3.7           | 1 : 100                     | 38.3  | 6.7                         | 2.8                        | 26.0                       | 25.0                               | 0.9                                   |
| <u>Tunja</u>              | < 0.063                            | 4.0           | 1 : 100                     | 35.6  | 7.6                         | 3.6                        | 40.1                       | 12.7                               | 2.5                                   |
| <u>Tunja</u>              | 0.063-<br>0.200                    | 3.7           | 1 : 100                     | 38.6  | 5.9                         | 2.1                        | 16.8                       | 34.7                               | 1.7                                   |
| <u>Minas<br/>Gerais</u>   | < 0.063                            | 3.7           | "dialysis<br>bag" method    | 56.4  | 7.7                         | 2.4                        | 17.4                       | 15.8                               | 0.2                                   |

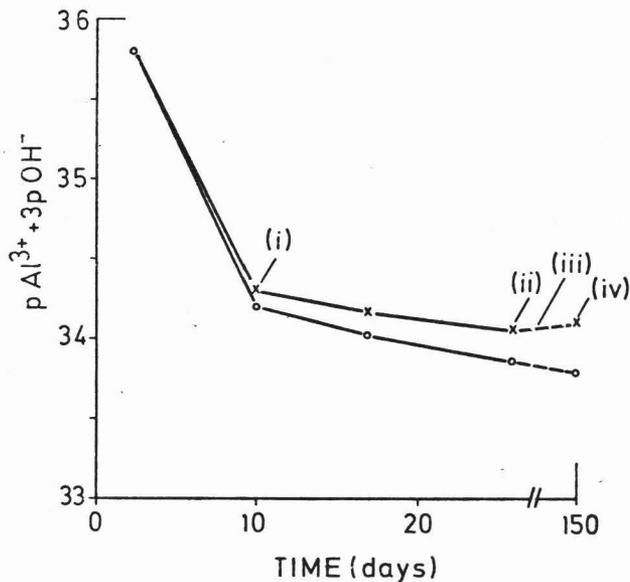


Fig. 5 a.  $pAl^{3+} + 3pOH^{-}$  values of Minas Gerais gibbsite (particle size  $< 0.063 \mu m$ , initial pH 3.7) as a function of time (For legend, see fig. 4)

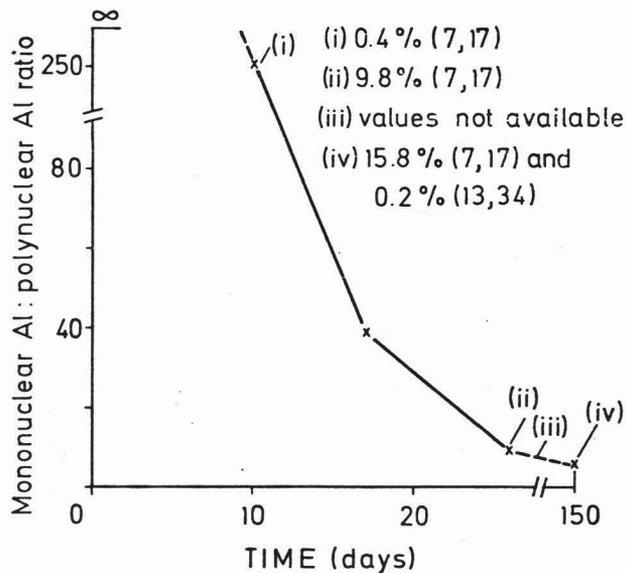


Fig. 5 b. Ratio of mononuclear Al : polynuclear Al in solution at different time intervals during the dissolution of Minas Gerais gibbsite (particle size  $< 0.063 \mu m$ , initial pH 3.7). (7,17) and (13,34) refer to the species  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$

of the presence of the dialysis bag and/or because of the inherent nature of the sample. In the equilibrium solution of the Minas Gerais gibbsite, the mononuclear species in solution are of similar nature as in the case of the Tunja gibbsite.

The polynuclear species in the solution in equilibrium with gibbsite appear to be  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$ . Brosset, Biedermann and Sillén (1954) suggested the formation of the species  $Al_6(OH)_{15}^{3+}$  in pure solution, but Biedermann (1964) later concluded that the solution could probably contain a mixture of  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$ . The polynuclear species,  $Al_6(OH)_{15}^{3+}$  does not come into the picture in any of these studies although Richburg and Adams (1970) had stressed its importance. This is probably because they did not consider the existence of  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$  and had taken  $pK_{6,15}$  as 36.0, the value of which is now found to be 44.17 (Table 1. 2). Though Aveston (1965) had predicted the existence of  $Al_2(OH)_2^{4+}$  and  $Al_{13}(OH)_{32}^{7+}$ , he had indicated several alternative possibilities.

Equilibrium between naturally occurring gibbsite and its constituent ions is reached only slowly; the time required depending on experimental conditions. This could be because many hydroxy-Al ions, both mono- and polynuclear, are present in solution and it takes some time for these ions to come into equilibrium with one another and with the solid phase. Calculations of  $pAl^{3+} + pOH^-$  values at various time intervals have indicated that equilibrium had not reached at the end of four weeks (Fig. 3a, b and c).

Equilibrium had been attained within 60 days under undisturbed conditions and within 150 days in most of the other cases. Nevertheless, the  $pAl^{3+} + 3 pOH^{-}$  values of the solution approach the solubility product of gibbsite relatively fast (within a few days of commencement of the dissolution of the sample).

4. 6. Polynuclear Al species in equilibrium solutions of montmorillonite and vermiculite clay minerals

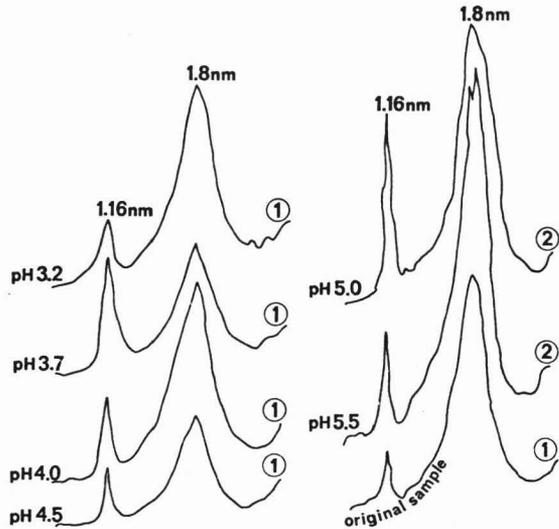
4. 6. 1. Characterisation of the clay minerals

The x-ray diagrams of the untreated and KCl-treated samples of montmorillonite and vermiculite are presented as Fig. 6 and 7. For montmorillonite, the basal distance (001) changed from 1.8 nm to 1.4 nm with KCl treatment. There was no further contraction. This shows that the montmorillonite is a lower charge member. The material also contains a minor contribution of mica/chlorite/interstratified mineral with an unchanged 1.16 nm peak.

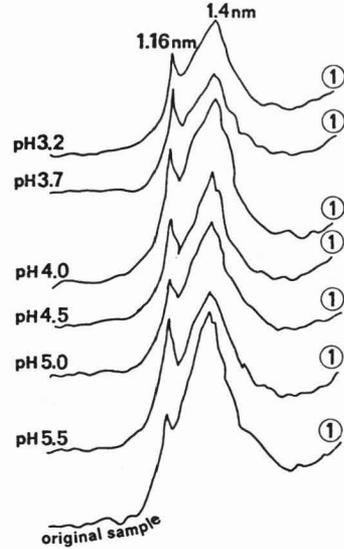
The vermiculite material contains the following: a low charge vermiculite not contracting with the applied KCl treatment from 1.4 nm to 1.0 nm, a montmorillonite contracting to 1.4 nm with the same treatment and a mineral with a low angle reflection, which may be a swelling chlorite not reacting to KCl treatment and finally a small amount of mica/chlorite/interstratified mineral. Further studies have not been made on the swelling chlorite in the montmorillonite and vermiculite samples.

The x-ray diagrams show that there is no apparent change in the structure of the minerals due to the

# UNTREATED



# KCL-TREATED



① recording scale 1000 I/s

② recording scale 400 I/s

Fig. 6. Smoothed tracings of x-ray diffraction diagrams of untreated and KCl-treated montmorillonite samples equilibrated to various pH values

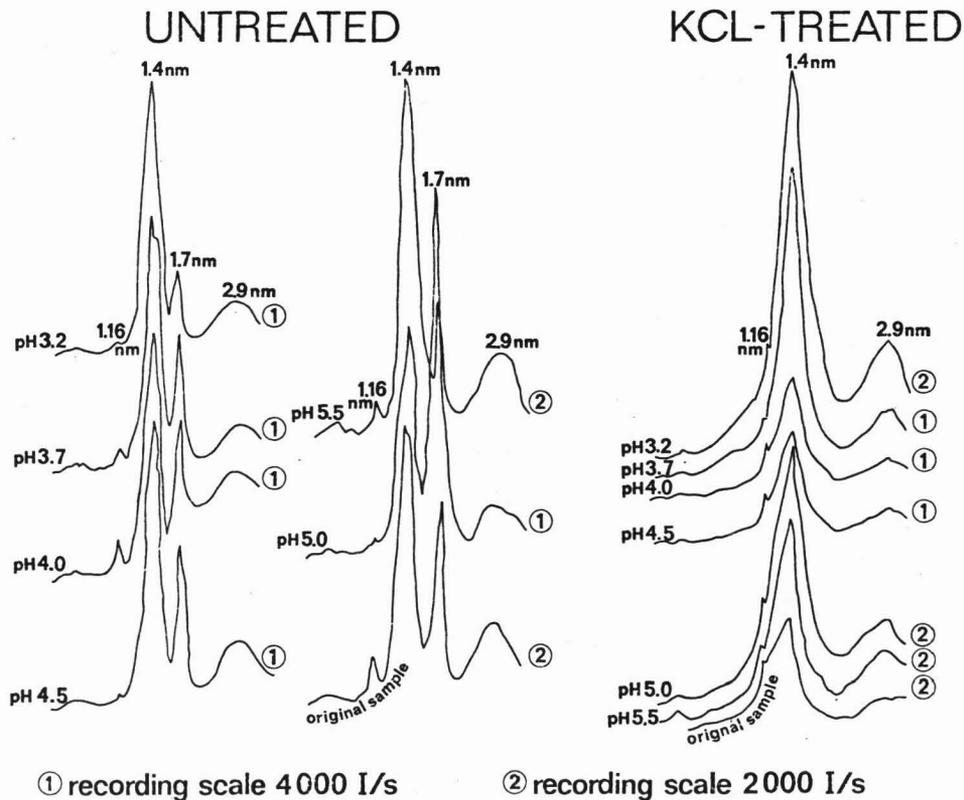


Fig. 7. Smoothed tracings of x-ray diffraction diagrams of untreated and KCl-treated vermiculite samples equilibrated to various pH values

pH treatments (Fig. 6 and 7).

4. 6. 2. Polynuclear Al species in the solutions with changes in pH and total Al

The amounts of polynuclear Al species expressed as percentages of the total Al present in the equilibrium solutions of montmorillonite and vermiculite adjusted to different pH values (3.2, 3.7, 4.0, 4.5, 5.0 and 5.5) are presented in Fig. 8 and 9. As mentioned earlier in section 3. 3. 4. 1, it was very difficult to maintain the pH of the suspensions at these desired values for all the samples. The final pH values of the suspensions, which are shown in Fig. 8a and 9a were different from the 'desired' values. In the case of all the montmorillonite samples, these final values had been constant for about two months prior to the analysis for polynuclear Al. But the values for vermiculite samples were not so much constant during this period.

For montmorillonite, the percentage of polynuclear Al increased with pH for both the first and the second set samples (see section 3. 3. 4. 1 for the description of the first and second set samples) with a maximum of about 75% at pH 5.0 to 5.5 (Fig. 8a). For the vermiculite samples also, the percentage of polynuclear Al in solution increased with pH and the maximum (almost 100% for the second set samples) was at pH 5 to 5.5 (Fig. 9a). At higher values of pH, the percentage of polynuclear Al seemed to be slightly less, but at this range, the total Al concentration itself was too low making it difficult to assess whether this decrease was real or not.

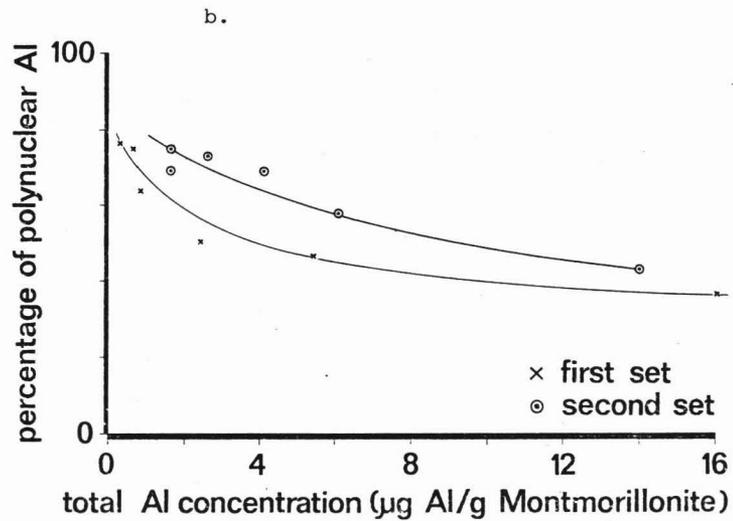
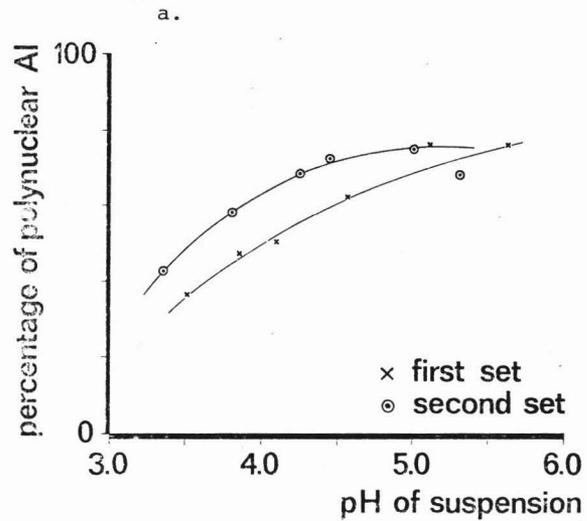


Fig. 8. Amount of polynuclear Al (percentage of total Al) in equilibrium montmorillonite solutions at:

- a. different pH of the suspensions
- b. different total Al concentration

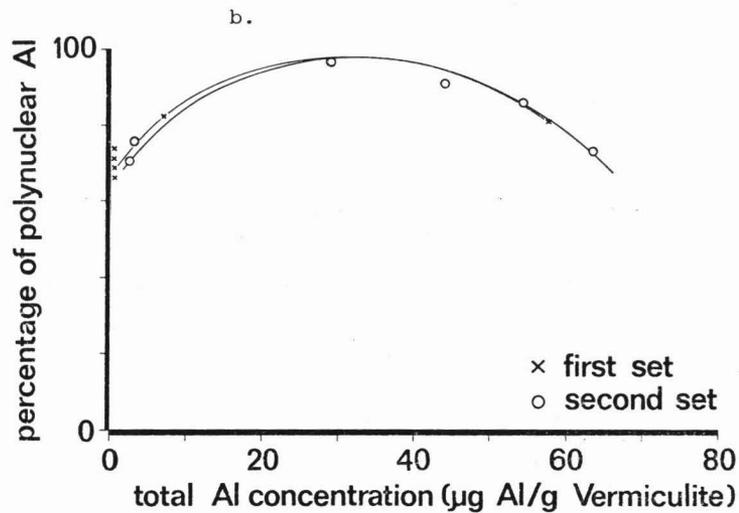
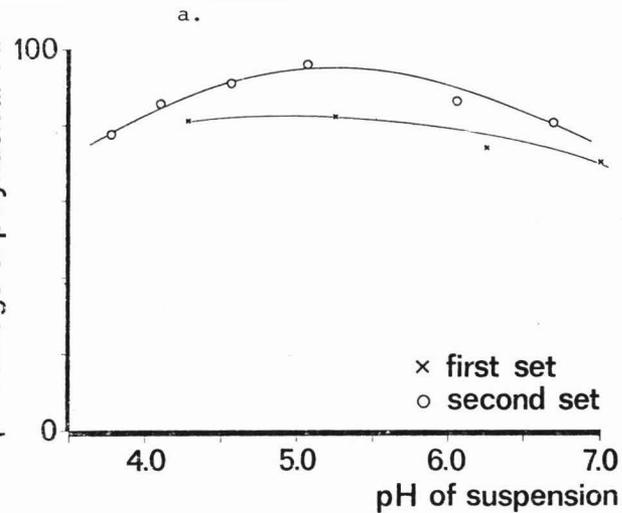


Fig. 9. Amount of polynuclear Al (percentage of total Al) in equilibrium vermiculite solutions at:

a. different pH of the suspensions

b. different total Al concentration

For montmorillonite, the percentage of polynuclear Al increased with decreasing concentration of total Al in solution (Fig. 8b). For vermiculite, the percentage of polynuclear Al was maximum at a total Al concentration of 30  $\mu\text{g}$  Al/g clay (which is equal to  $\text{pAl} = 3.04$ ), and at pH 5.0 to 5.5 as mentioned earlier. This is in agreement with the theoretical prediction presented in Fig. 1a. At total Al concentrations higher or lower than about 30  $\mu\text{g}$  Al/g clay, the amount of polynuclear Al was less.

The study indicates that more than 40% of the total Al in montmorillonite solution and more than 60% in vermiculite solution exist as polynuclear species in the pH ranges of the equilibrium solutions studied and that the amount of polynuclear Al depends on the solution pH (maximum for this set of experiments being at pH 5.0 to 5.5) and the total Al concentration of the solution.

#### 4. 7. Polynuclear Al species in solutions of soil samples equilibrated in the laboratory

The experimentally determined values of concentrations of polynuclear Al species of the 24 h-equilibrated samples of the Solling and Löss soils are given in Appendices II and III respectively. The theoretical values calculated using the third set of  $\text{pK}_n$  values are also given in the Appendices.

In the usual analytical procedure, the equilibrium soil solutions are obtained after equilibrating the soil samples with water for 24 h. The same procedure was adopted in these studies also. However, the effect of longer

duration of equilibration of the sample on the amount of polynuclear Al in the solution was also investigated and the results are presented in a later section (section 4. 7. 4).

The experimental values were determined by the method modified from Bache and Sharp (1976) as mentioned in section 3. 3. 2 . This method differentiates between slow and fast reacting species of Al. In addition to the polynuclear hydroxy-Al species, Al complexes involving sulphates, phosphates, organo-complexes etc. in soil solutions are also likely to be estimated as the slow reacting Al species.

It has already been shown earlier (section 4. 3) that the amount of polynuclear Al in the  $Al_2O_3/H_2O$  systems is dependent on the pH, total Al concentration and ionic strength of the system. In addition to these, there could be other factors also which influence the polynuclear Al concentration in soil solutions. The influence of some of such factors on the experimentally determined values of polynuclear Al concentration in soil solutions is examined.

#### 4. 7. 1. Effect of carbon content of soils

An overall perusal of the data on the C content of the soils and the experimental values of polynuclear Al species in solutions indicated some relations between the two parameters. However, in order to study the effect of C, the interference of other factors such as total Al concentration, pH and ionic strength has to be minimised. Therefore, the values of polynuclear Al vs C content were examined for soils of varying total Al concentration, pH

and ionic strength. This resulted in two arbitrary groups based on the total Al concentration: (i) soils of total Al  $< 1.2 \times 10^{-4}$  mol/l, and ii) soils of total Al  $> 1.2 \times 10^{-4}$  mol/l. Samples of very low total Al concentration were not considered because in such cases the error in the estimation of polynuclear Al is expected to be very high. In order to minimise the influence of pH and ionic strength, only such samples were selected whose pH and ionic strength varied within certain limits. For Solling soils, pH of the solutions of both the groups were between 3.4 and 4.0; the ionic strength of the first group varied from  $2.8 \times 10^{-3}$  mol/l and that of the second group from  $1.8-6 \times 10^{-3}$  mol/l. For the Löss soils, pH for both the groups varied from 3.3 to 4.5 (most of the samples had pH  $> 4$  - see Appendix III) and the ionic strength of the first and the second groups were  $1-6 \times 10^{-3}$  mol/l and  $2-8 \times 10^{-3}$  mol/l respectively.

The relationships between the C content of the soils and the experimental values of the percentage of polynuclear Al in solution of the two groups of Solling soil are given in Fig. 10a and 10b and of the Löss soil in Fig. 11a and 11b.

For the Solling soils, the experimental values of the percentage of polynuclear hydroxy-Al species in solution increases with the C content of soils and reaches a maximum value at about 9% C. This maximum value of the percentage of polynuclear Al was relatively higher (about 52%) in the first group of samples (Fig. 10a) which had lower concentration of total Al ( $0.35-1.2 \times 10^{-4}$  mol/l).

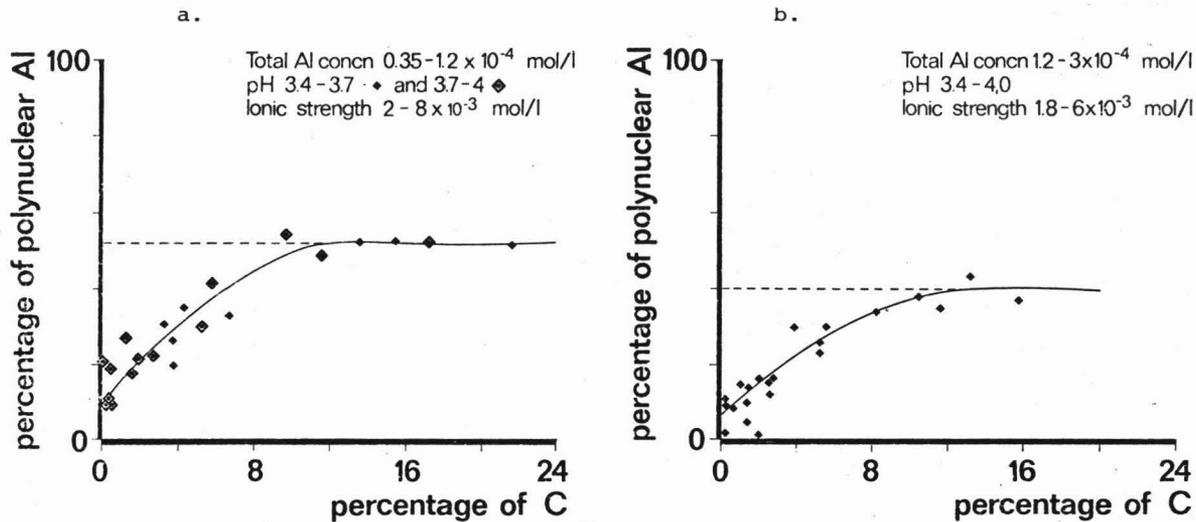


Fig. 10. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) solutions of Solling soils of varying carbon content:

- a. total Al concentration in the solution  
 $< 1.2 \times 10^{-4}$  mol/l
- b. total Al concentration in the solution  
 $> 1.2 \times 10^{-4}$  mol/l

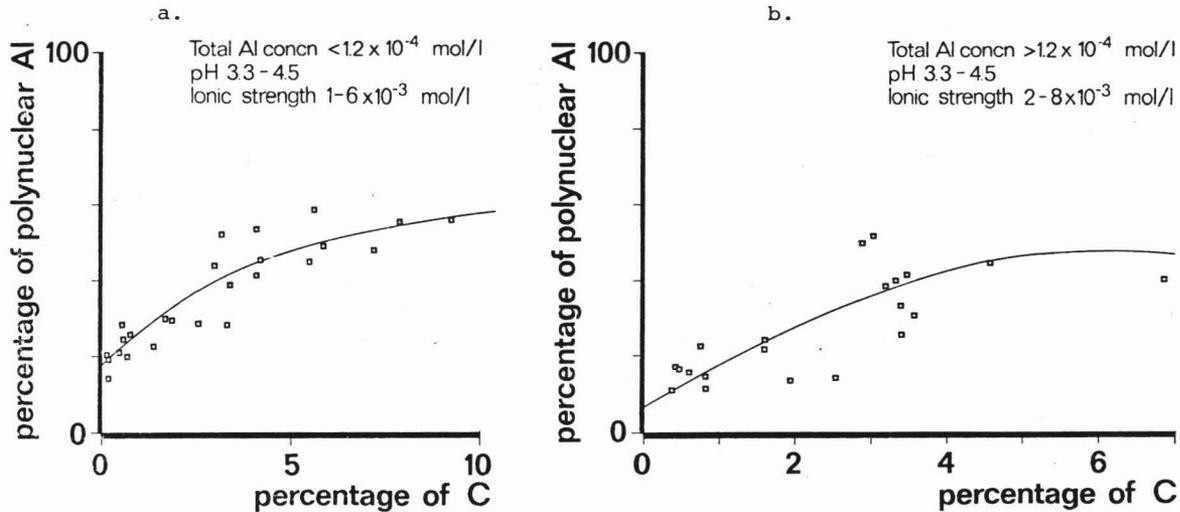


Fig. 11. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) solutions of Lüss soils of varying carbon content:

- a. total Al concentration in the solution  $< 1.2 \times 10^{-4}$  mol/l
- b. total Al concentration in the solution  $> 1.2 \times 10^{-4}$  mol/l

For the second group of samples with higher concentration of total Al ( $1.2-3.0 \times 10^{-4}$  mol/l), the maximum value of the percentage of polynuclear Al was about 40% (Fig. 10b).

For the Löss soils (which had relatively lower content of C than the Solling soils) also, the percentage of polynuclear hydroxy-Al in solution increases with the C content of the soil (Fig. 11a, 11b). However, unlike in the case of Solling soils, there was no definite maximum value of C content above which the percentage of polynuclear Al species was constant. This could be probably because the maximum C content in these samples was lower ( $< 10\%$ ) than that of the Solling soils.

The mean theoretical and experimental values of the concentration of polynuclear aluminium in the equilibrium (24 h) solutions of Solling and Löss soils of varying carbon contents are given in Tables 6 (Solling) and 7 (Löss). As in the case of the percentage of polynuclear Al species, the experimental values of polynuclear Al concentration also increased with increase in C content for both the soils at lower as well as higher total Al concentrations. On the other hand, the theoretical values of concentration were slightly decreasing with increase in C content. But the concentrations are too low and the standard deviations of means are relatively too high that it is not possible to say whether this is a real phenomenon or an apparent one due to the experimental error. Moreover, the experimental values of polynuclear Al are determined as the difference between the total Al and mononuclear Al (section 3. 3. 2),

Table 6 Mean experimental and theoretical values of polynuclear Al species in the equilibrium solutions of Solling soil samples of varying carbon contents

| C content (%)  | NO. of samples | Polynuclear Al in solution<br>( $10^{-4}$ mol/l) |                    | Corr. coeff. (r) between theor. and exptl values |
|--|----------------|--|--------------------|--|
|  |                | <u>Experimental</u>                              | <u>Theoretical</u> |  |
|  |                | Mean $\pm$ S.D.                                  | Mean $\pm$ S.D.    |  |
| 1. Total Al concentration $0.4-1.5 \times 10^{-4}$ mol/l |                |  |                    |  |
| < 1  | 21             | 0.199 $\pm$ 0.138                                | 0.097 $\pm$ 0.150  | - 0.055 NS                                       |
| 1-3  | 9              | 0.169 $\pm$ 0.044                                | 0.051 $\pm$ 0.068  | - 0.423 NS                                       |
| 3-5  | 8              | 0.312 $\pm$ 0.126                                | 0.057 $\pm$ 0.160  | 0.189 NS   |
| 5-9  | 6              | 0.543 $\pm$ 0.325                                | 0.050 $\pm$ 0.124  | 0.308 NS   |
| > 9  | 12             | 0.549 $\pm$ 0.283                                | 0.041 $\pm$ 0.141  | 0.400 NS   |
| 2. Total Al concentration $> 1.5 \times 10^{-4}$ mol/l   |                |  |                    |  |
| < 1  | 5              | 0.233 $\pm$ 0.094                                | 0.418 $\pm$ 0.300  | 0.053 NS   |
| 1-3  | 7              | 0.304 $\pm$ 0.140                                | 0.217 $\pm$ 0.260  | - 0.127 NS                                       |
| 5-9  | 1              | 0.474  | 0                  |  |
| > 9  | 1              | 0.534  | 0                  |  |

NS : not significant

Table 7 Mean experimental and theoretical values of polynuclear Al species in the equilibrium solutions of Lüss soil samples of varying C contents

| C content (%)  | No. of samples | Polynuclear Al in solution<br>( $10^{-4}$ mol/l) |                    | Corr. coeff. (r) between theor. and exptl values |
|--|----------------|--|--------------------|--|
|  |                | <u>Experimental</u>                              | <u>Theoretical</u> |  |
|  |                | Mean $\pm$ S.D.                                  | Mean $\pm$ S.D.    |  |
| 1. Total Al concentration $0.4-1.2 \times 10^{-4}$ mol/l |                |  |                    |  |
| <1   | 8              | 0.217 $\pm$ 0.044                                | 0.527 $\pm$ 0.126  | 0.524 +  |
| 1-3  | 4              | 0.260 $\pm$ 0.068                                | 0.509 $\pm$ 0.080  | 0.767 +  |
| 3-5  | 4              | 0.419 $\pm$ 0.069                                | 0.201 $\pm$ 0.229  | - 0.189 NS                                       |
| >5   | 4              | 0.412 $\pm$ 0.190                                | 0.079 $\pm$ 0.142  | 0.573 NS   |
| 2. Total Al concentration $> 1.2 \times 10^{-4}$ mol/l   |                |  |                    |  |
| <1   | 7              | 0.303 $\pm$ 0.037                                | 1.000 $\pm$ 0.301  | 0.626 +  |
| 1-3  | 5              | 0.518 $\pm$ 0.401                                | 1.050 $\pm$ 0.628  | 0.884 +++  |
| 3-5  | 8              | 0.795 $\pm$ 0.366                                | 0.651 $\pm$ 0.975  | 0.905 +++  |

NS : not significant

+ significant at 5% level

+++ significant at 0.1% level

which means that two determinations are involved and their analytical errors could be additive and consequently magnified.

For the sandy soils of the Löss area, the correlation between the experimental and theoretical values (Table 7) is much better than for the loamy soils of Solling district (Table 6), independent of C content. The latter contains more exchangeable  $Al^{3+}$  (Appendix IX), clay minerals and interlayer Al and these factors may have a direct bearing on the Al species in solution.

Carbon in soils is known to form complexes with Al through the involvement of organic acids like humic and fulvic acids (Kawaguchi and Kyuma, 1959; Schnitzer and Skinner, 1963; Schnitzer, 1969; Khan, 1969). When Al is determined by the 8-hydroxy quinoline method, Al existing as organo-aluminium complexes is estimated (Bache and Sharp, 1976), probably as the slowly reactable fraction. The close relationship between C content and slow reactable Al may, therefore, indicate the presence of organo-aluminium complexes. Since higher C content is found mostly in low pH values ( $\sim 3.5$ ), it seems that in the upper horizons (Ahe and Aeh horizons) of acid soils, up to 50% of the total Al in solution may exist as polynuclear forms (Appendix II), probably as organo-aluminium complexes.

#### 4. 7. 2. Effect of total Al concentration of the soil solutions

The influence of the total Al concentration on the amount of experimentally determined polynuclear hydroxy-Al

in solution was studied using soil samples with very low C content ( $< 1\%$ ) so that the effect of C was minimum, as well as the Solling samples with more than  $9\%$  C when the percentage of polynuclear Al species was little influenced by further increase in C content. Moreover, only such samples whose pH, sulphate concentration and ionic strength of the solution varied within narrower ranges were considered so as to minimise the influence of these factors on the percentage of polynuclear Al species. Fig. 12a shows the effect of total Al concentration on the percentage of polynuclear hydroxy-Al species in the solution of the Solling soils with pH 3.95 to 4.25, C content  $< 1\%$ , ionic strength  $1.3-3.0 \times 10^{-3}$  mol/l and  $\text{SO}_4^{2-}$  concentration  $< 10$  mg S/l. Similar results for the Solling soils with pH in the range of 3.35 - 3.85, C content  $> 9\%$ , ionic strength  $2.8-6.0 \times 10^{-3}$  mol/l and  $\text{SO}_4^{2-}$  concentration 5-20 mg S/l, are depicted in Fig. 12b. Fig. 13 refers to the Lüss soils (pH 4.1 - 4.4, C content  $< 1\%$ , ionic strength  $2-3.5 \times 10^{-3}$  mol/l and  $\text{SO}_4\text{-S}$  10-20 mg/l). These results indicate that the percentage of polynuclear Al increases with a decrease in the total Al concentration when other factors are almost constant. The studies with the montmorillonite and vermiculite clay minerals also had shown similar results (section 4. 6. 2).

#### 4. 7. 3. Effect of pH of the soil solutions

Because the C content of soils and total Al concentration of soil solutions have considerable influence on the experimental percentage of polynuclear Al species, soil

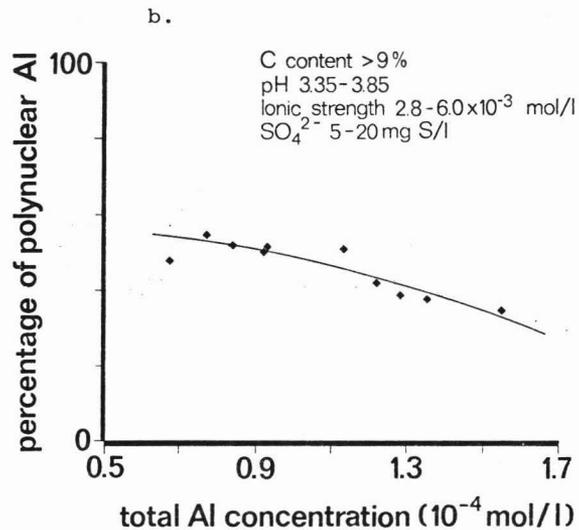
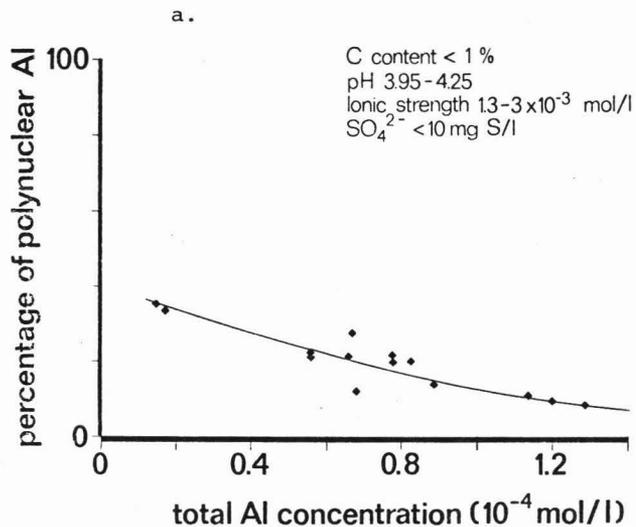


Fig. 12. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) Solling soil solutions of varying concentrations of total Al, when:

- a. carbon content of the soil < 1%
- b. carbon content of the soil > 9%

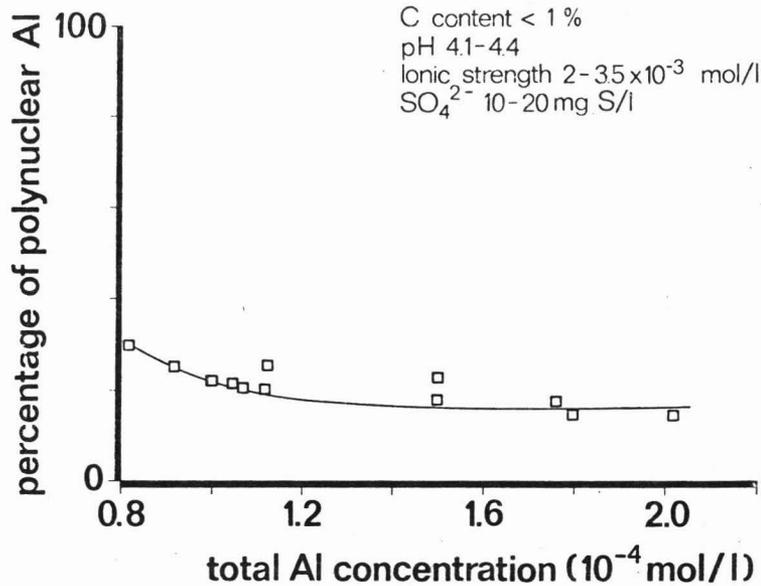


Fig. 13. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) Lüss soil solutions of varying concentration of total Al (soil with 1% C)

samples having a narrow range of variation of these factors were considered for the studies on the effect of pH on the percentage of polynuclear Al. The relationship between pH and percentage of polynuclear hydroxy-Al species for the Solling soil samples with carbon content less than 1%, total Al concentration  $0.1-1.5 \times 10^{-4}$  mol/l, ionic strength  $1.3-3.0 \times 10^{-3}$  mol/l and  $\text{SO}_4\text{-S} < 10$  mg/l is presented in Fig. 14 and for the Lüss soils with C content  $< 1\%$ , total Al concentration  $0.7-2.7 \times 10^{-4}$  mol/l, ionic strength  $1.6-4 \times 10^{-3}$  mol/l and  $\text{SO}_4\text{-S}$  10-20 mg/l in Fig. 15.

For Solling soil, the percentage of polynuclear Al is not dependent very much on solution pH (Fig. 14) as already noted earlier in Fig. 10. But, for the Lüss soil, the percentage of polynuclear Al increased slightly with the increase in pH under the conditions of this study (Fig. 15). This is in agreement with the theoretical predictions presented in Fig. 2.

#### 4. 7. 4. Effect of the duration of equilibration of soil samples

Table 7 shows that, for the Lüss soil, the mean values of theoretically predicted concentration of polynuclear Al in equilibrium (24 h) soil solutions were considerably higher than the experimental values at all levels of C content, when the concentration of total Al was relatively higher ( $> 1.2 \times 10^{-4}$  mol/l). When the total Al concentration was low ( $0.4-1.2 \times 10^{-4}$  mol/l), this phenomenon was observed only at C content  $< 3\%$ . This is also indicated by Fig. 16a and 16 b which depict

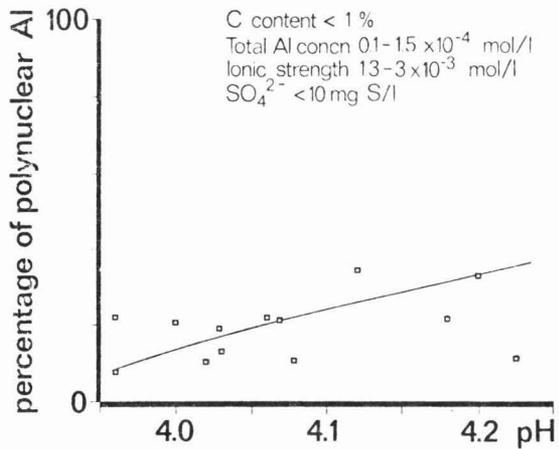


Fig. 14. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) Solling soil solutions at varying pH

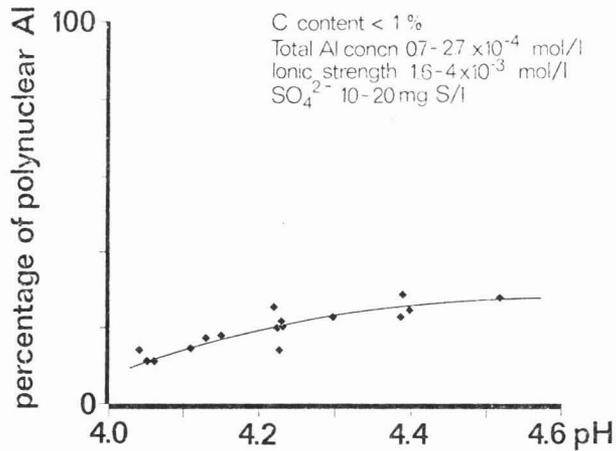


Fig. 15. Percentage of total Al existing as polynuclear Al in the equilibrium (24 h) Lüss soil solutions at varying pH

the percentage of polynuclear Al at different values of pH and total Al concentration for the Lüss soil from 30-40 cm and 40-50 cm depths where the C content is low. But, for the Solling soil, this trend of the theoretical values being higher than the experimental values was observed only for the samples with C content  $< 1\%$  and total Al concentration  $> 1.5 \times 10^{-4}$  mol/l (Table 6). The reason for this phenomenon could be that the time of equilibration (24 h) is not sufficient to bring all the polynuclear Al into solution and therefore the experimental values at 24 h equilibration could be underestimated.

In order to study the effect of the duration of equilibration on the percentage of polynuclear Al in solution, a few samples with low C content (14 samples from Solling and 16 from Lüss) were equilibrated with water for 20 days (section 3. 3. 5. 1). The mean values of the concentration of polynuclear Al in solutions of the same samples equilibrated for 24 h and 20 days are given in Table 8. The data for 20 days equilibration are given in Appendix IV (Solling) and Appendix V (Lüss).

Table 8 shows that prolonged equilibration for 20 days improved the correlation between the theoretical and experimental values in both the soils. The concentration of polynuclear Al in solutions also increased by longer equilibration in spite of the slight decrease in the concentration of total Al over this period. The increase in polynuclear Al was comparatively less in Solling soil which had also lower concentration of total Al in this study. For the Lüss soils, there was satisfying agreement between

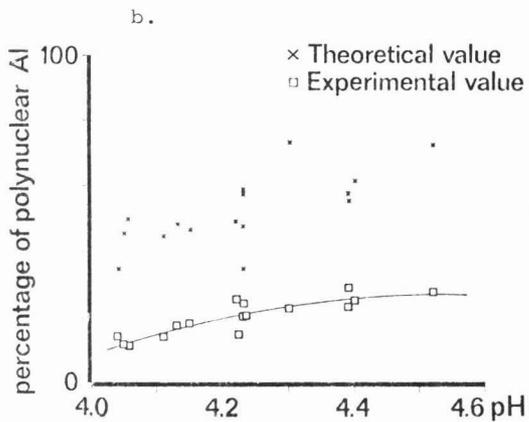
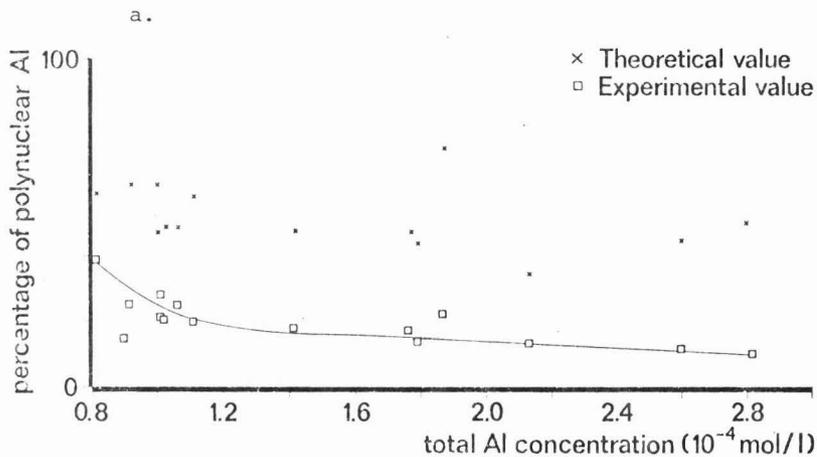


Fig. 16. Experimental and theoretical values of the percentage of total Al existing as polynuclear Al in the equilibrium (24 h) solutions of Löss soils of low C content (30-40 cm and 40-50 cm depths) at:

a. varying concentration of total Al in the solution

b. varying pH of the solution

Table 8 Mean values of concentration of polynuclear aluminium species in solutions of soils with low C content equilibrated for 24 h and 20 d

| Duration of equilibration | Concn of total Al in the equ. soil solution        | Concentration of polynuclear Al in equil. soil solutions<br>(10 <sup>-4</sup> mol/l) |                    | Corr. coeff. (r) between experimental and theor. values |
|---------------------------|--|--|--------------------|---|
|                           | Mean values $\pm$ S.D.<br>(10 <sup>-4</sup> mol/l) | <u>Experimental</u>  | <u>Theoretical</u> |   |
|                           |  | Mean $\pm$ S.D.  | Mean $\pm$ S.D.    |   |
| SOLLING SOIL (14 samples) |  |  |                    |   |
| 24 h                      | 0.809 $\pm$ 0.388                                  | 0.146 $\pm$ 0.102  | 0.104 $\pm$ 0.227  | 0.192 N.S.  |
| 20 d                      | 0.666 $\pm$ 0.423                                  | 0.204 $\pm$ 0.135  | 0.146 $\pm$ 0.219  | 0.863 +++   |
| LÜSS SOIL (16 samples)    |  |  |                    |   |
| 24 h                      | 1.431 $\pm$ 0.647                                  | 0.252 $\pm$ 0.061  | 0.727 $\pm$ 0.327  | 0.805 +++   |
| 20 d                      | 1.221 $\pm$ 0.549                                  | 0.419 $\pm$ 0.202  | 0.549 $\pm$ 0.438  | 0.937 +++   |

N.S. : not significant

+++ significant at 0.1% level

the theoretical and experimental values after 20 days equilibration.

This study suggests that the solutions obtained by equilibrating the soil samples with water for 24 h are not in equilibrium with respect to polynuclear Al and that the duration of equilibration has to be correspondingly longer depending upon the total Al concentration of the solutions. However, these are only broad indications; the results have to be confirmed by more detailed investigations.

#### 4. 8. Polynuclear Al species in soil solutions collected in the field (lysimeter solutions)

The theoretical and experimental values of the amounts of polynuclear Al species in the lysimeter solutions collected from the Beech and Spruce forest areas during April to September 1977 (section 3. 3. 5. 2) are given in Appendix VI and VII. Table 9 gives the mean values of  $I_0$  (additional ionic strength), total Al concentration and the experimental and theoretical values of concentration of polynuclear Al species as well as the correlation between them. The Table shows that there was no correlation between the experimental and theoretical values.

Since these solutions are not buffered, certain amount of error in pH measurements is to be expected. The extent of variation in the theoretical values caused by slight changes in pH within the pH range of the solutions was studied by altering the mean values of pH for the Beech and Spruce samples by 0.03, 0.05 and 0.10 units. Using these altered values of pH (3.99, 4.01 and 4.06 for Beech and 3.90, 3.92 and 3.97 for Spruce) in the computer

Table 9 Experimental and theoretical values of polynuclear aluminium species in lysimeter solutions

| Site   | Mean values of |                          |                          | Concentration of polynuclear aluminium  |               |   |               | Corr. coeff. (r) between exptl & theor. |
|--------|----------------|--------------------------|--------------------------|---|---------------|---|---------------|---|
|        | pH             | I <sub>o</sub>           | Total Al concn           | Experimental                            |               | Theoretical                             |               |   |
|        |                | (10 <sup>-3</sup> mol/l) | (10 <sup>-4</sup> mol/l) | Mean ± S.D.<br>(10 <sup>-4</sup> mol/l) | % of total Al | Mean ± S.D.<br>(10 <sup>-4</sup> mol/l) | % of total Al |   |
| Beech  | 3.96           | 0.937                    | 1.414                    | 0.189 ± 0.048                           | 13            | 0.079 ± 0.066                           | 6             | -0.198 NS                               |
| Spruce | 3.87           | 2.894                    | 6.164                    | 0.594 ± 0.237                           | 10            | 1.750 ± 0.689                           | 28            | 0.108 NS                                |

NS : not significant

programme and keeping the mean  $I_0$  and total Al concentration constant, the concentration of polynuclear Al was calculated. The differences between the theoretical and experimental values mentioned in Appendix VI and VII were plotted against pH and compared with the difference in polynuclear Al concentration corresponding to the modified pH values. Figure 17 shows the result for the Beech samples and Fig. 18 for the Spruce samples.

Fig. 17 shows that for the Beech samples, most of the values of the differences between the theoretical and experimental values of polynuclear Al species fall within the boundary marked by a change in the theoretical value caused by altering the pH by  $\pm 0.05$  unit from the mean value of pH. For the Spruce samples, majority of the values fall within the " $\pm 0.1$  pH boundary" with five samples lying outside. The analysis shows that errors in pH measurement may be an important factor contributing to the variation between the theoretical and experimental values of polynuclear Al species. This would also apply to the other soil solution data reported in section 4. 7. 4.

The difference between the experimental and theoretical values of polynuclear Al species was greater for the Spruce samples (which had relatively higher amounts of total Al) than for the Beech samples. This is probably because the lysimeter solutions are not in equilibrium with respect to polynuclear Al species. The experiment on the effect of duration of equilibration of soil samples on the amount of polynuclear Al in solution had also shown

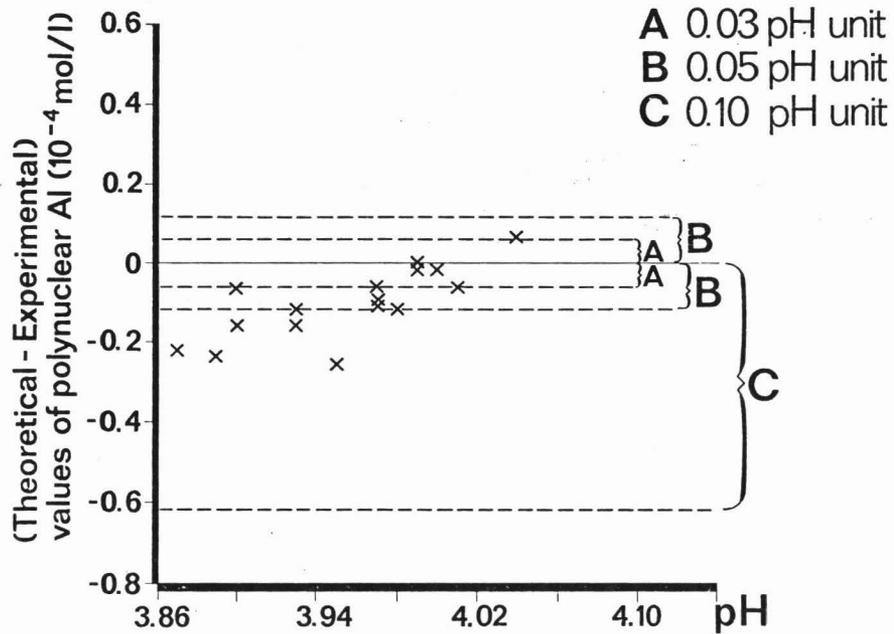


Fig. 17. Effect of slight changes in solution pH on the theoretical values of concentration of polynuclear Al in lysimeter solutions from the Beech site

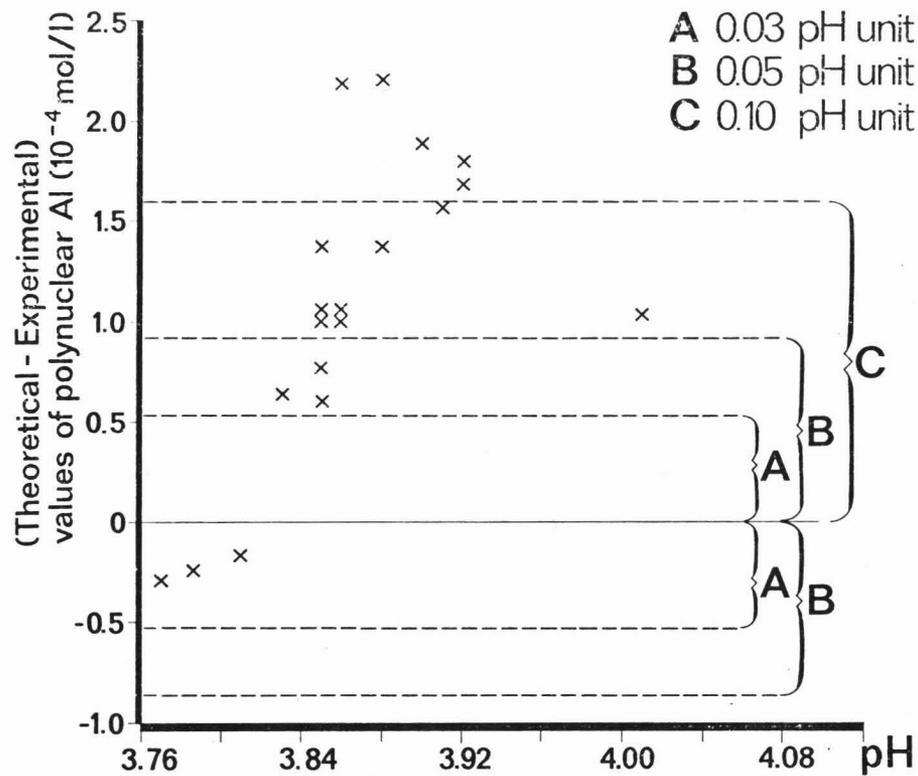


Fig. 18. Effect of slight changes in pH on the theoretical values of concentration of polynuclear Al in lysimeter solutions from the Spruce site

(section 4. 7. 4, Table 8) that the time of equilibration has to be correspondingly longer when the total Al concentration in the solution is higher. Moreover, it was found in the dissolution experiments with the gibbsite samples (section 4. 5) that it takes a long time for establishing equilibrium between the polynuclear Al species. This phenomenon of non-establishment of equilibrium with respect to polynuclear Al species may be true for the soil solutions collected in the field for all permeable soils with relatively rapid vertical water movement (0.5 to 1 m per year).

#### 4. 9. $pAl^{3+} + 3 pOH^-$ values of soil solutions

The values of  $pAl^{3+} + 3 pOH^-$  in the equilibrium (24 h) soil solutions were considered against pH for the Solling (Fig. 19) and the Lüss (Fig. 20) soils. In both soils, when the solution  $pH < 4$ , the  $pAl^{3+} + 3 pOH^-$  values are rather unsteady, whereas at pH higher than about 4, the values are almost constant and approximately equal to the  $pK_{sp}$  value of the naturally occurring Tunja gibbsite (section 4. 4. 2).

The variations in the  $pAl^{3+} + 3 pOH^-$  values with change in pH in the equilibrium (24 h) soil solutions were also studied for a large number (55) of soils collected from different parts of the Federal Republic of Germany. The results are depicted in Fig. 21 and the values are given in Appendix VIII. Similar to the results of the Solling and Lüss soils (Fig. 19, 20), below pH 4, the  $pAl^{3+} + 3 pOH^-$  values were changing, but above pH about 4,

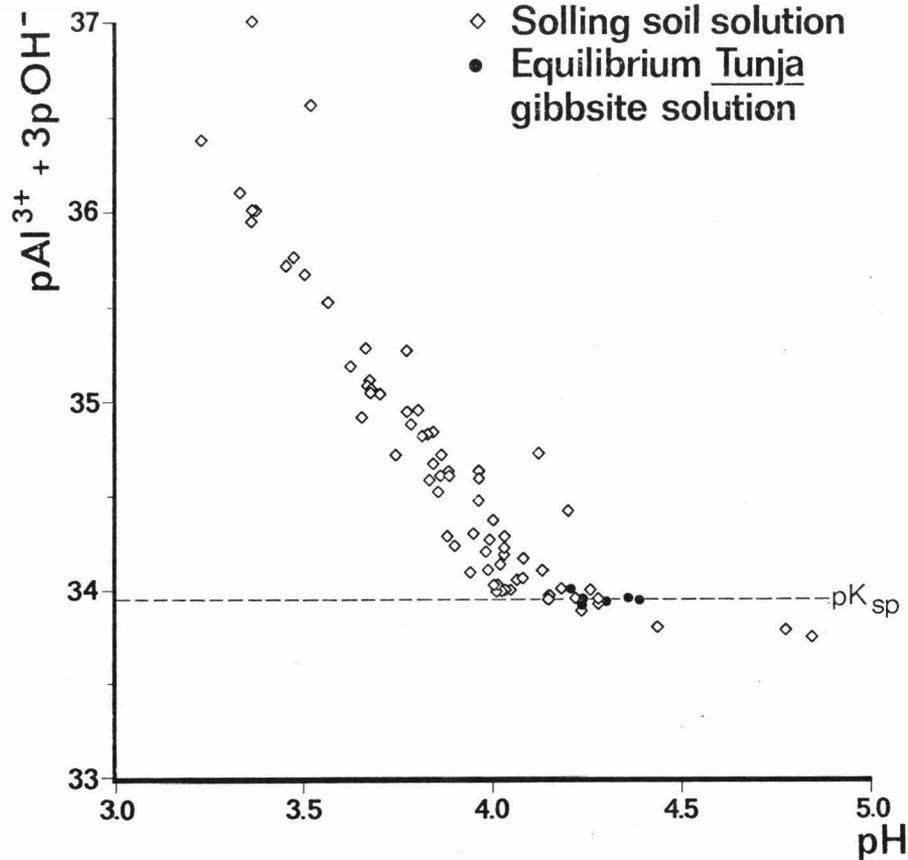


Fig. 19.  $pAl^{3+} + 3pOH^{-}$  values of equilibrium (24 h) solutions of Solling soils at varying solution pH

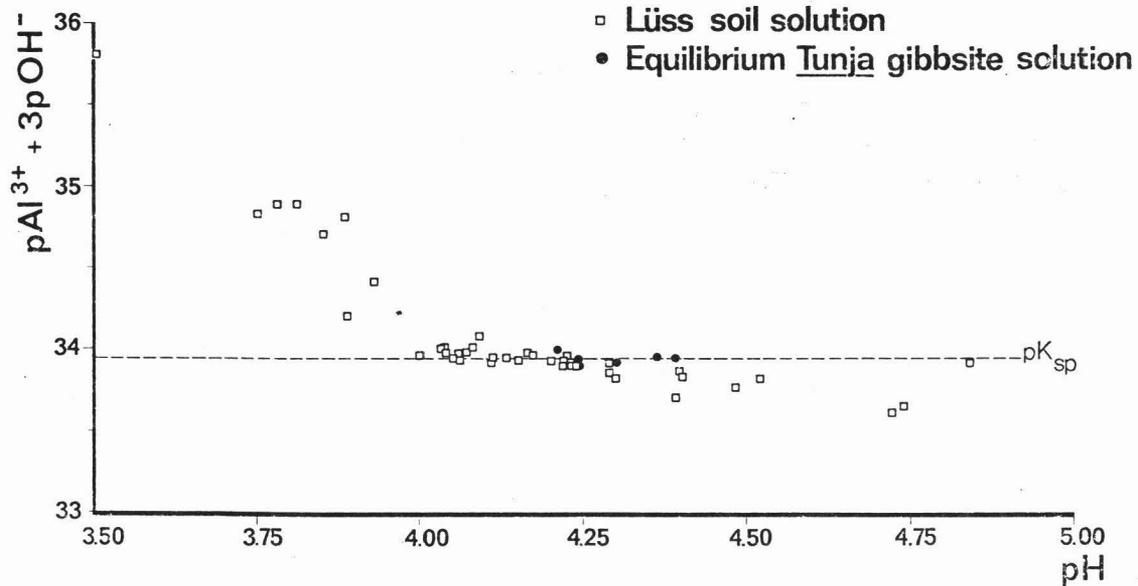


Fig. 20.  $pAl^{3+} + 3pOH^{-}$  values of equilibrium (24 h) solutions of Löss soils at varying solution pH



the values were almost constant and approached the  $pK_{sp}$  value of the naturally occurring gibbsite.

These results (Fig. 19, 20, 21) were obtained from soil solutions equilibrated for 24 h. But the previous results (section 4. 7. 4) had indicated that the equilibration for 24 h was not sufficient enough to bring all the polynuclear Al into solution. To study the possible effect of the length of time of equilibration on the ionic product values, the values were calculated for the Solling and the Lüss soil solutions after 20 days equilibration. Results are given in Fig. 22. The values are within the experimental limits of the values for the same samples of 24 h equilibration. The change in the amount of polynuclear Al species coming into solution after longer period of equilibration was not substantial enough to influence the  $pAl^{3+}$  values. Therefore, it seems that the longer period of equilibration which is shown to be necessary for attaining equilibrium with respect to polynuclear species (section 4. 7. 4) does not influence the concentration of  $Al^{3+}$  species. Fig. 22 also shows that at  $pH > 4$ , the  $pAl^{3+} + 3 pOH^{-}$  values are almost constant and approximately equal to the  $pK_{sp}$  value of the naturally occurring gibbsite.

The inconsistency of the ionic product values at pH less than 4 can be considered as an indication that some other compounds govern the solubility of Al at this range of pH. Blanchar and Scrivner (1972) attributed this phenomenon to the reactions occurring on the surface of aluminium oxides at low pH, resulting in an increase in the positive charge so that the conditions of congruent

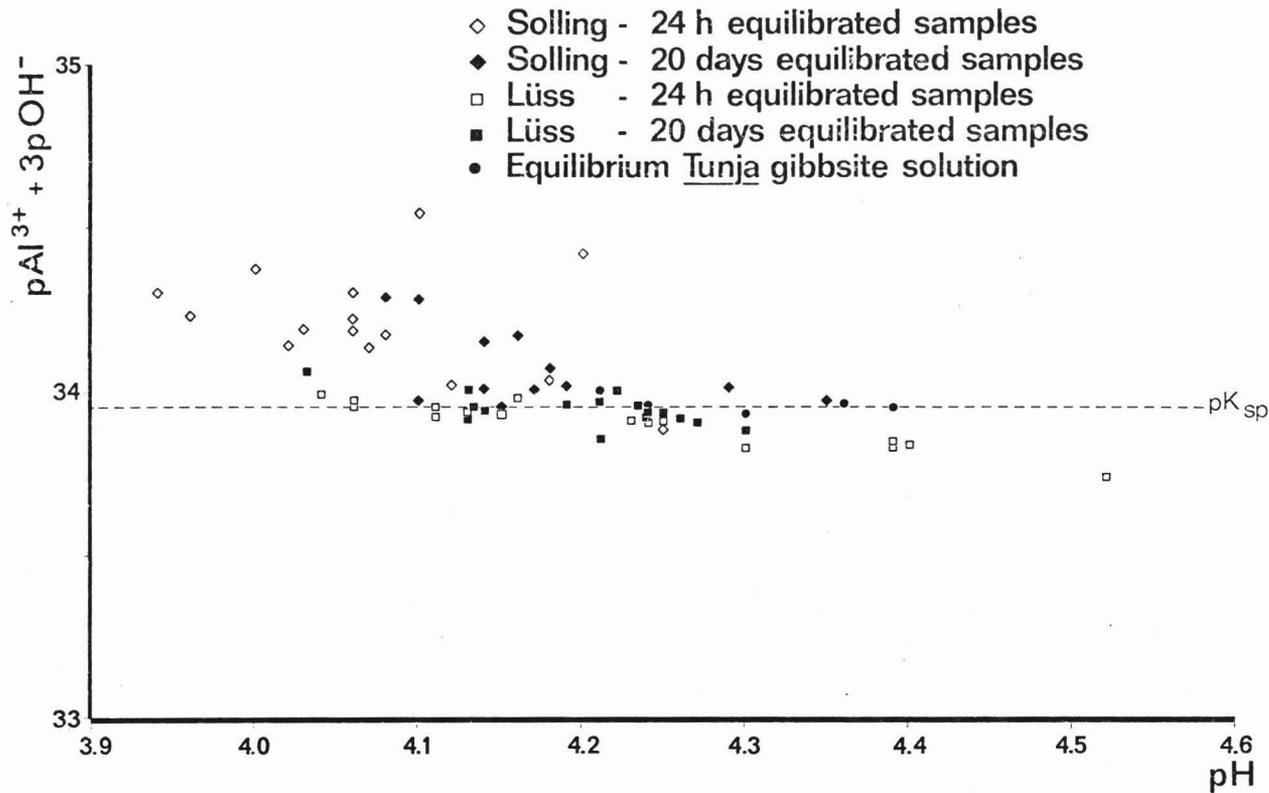


Fig. 22.  $pAl^{3+} + 3pOH^{-}$  values at varying pH of the solutions of selected Solling and Lüss soils with low C content, equilibrated for 24 h and 20 d

dissolution of Al would not be met with and constant values of  $pAl^{3+} + 3 pOH^-$  would not be expected. Accepting this explanation, Dalal (1975) assigned a uniform mean value for the  $pAl^{3+} + 3 pOH^-$  of the solution at  $pH < 4$ . But the results of the present study (Fig. 19-22) show that it is erroneous to give such a constant value. The nature of the compounds occurring in solution at this pH range could not be predicted from this study, but the involvement of organo-aluminium complexes could be postulated.

The constancy of the  $pAl^{3+} + 3 pOH^-$  values of the soil solution above pH 4 at a value near the  $pK_{sp}$  value of naturally occurring gibbsite indicates the formation of gibbsite-like (from the point of view of  $pK_{sp}$ ) substances. This view is strengthened by the fact that the equilibrium pH of the naturally occurring gibbsite is in the range of 4.2 to 4.5 (Tables 3 and 4), and the  $pAl^{3+} + 3 pOH^-$  values of the soil solutions are closest to the  $pK_{sp}$  values of naturally occurring gibbsite in the same pH range (Fig. 19 - 22).

Richburg and Adams (1974) obtained almost constant values of  $pAl^{3+} + 3 pOH^-$  when the ions  $Al_6(OH)_{15}^{3+}$  and  $Al(OH)^{2+}$  were considered together. But the pH of all their sample solutions were above 4 and the ion product value they reported was much above 34. Dalal (1975) who considered  $Al_5(OH)_{15}^{3+}$  and  $Al(OH)_3^0$  along with mononuclear ions obtained a constant value of almost 35. These values are much higher than the  $pK_{sp}$  value of gibbsite (33.95). In the present study, when  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$  are also considered, the  $pAl^{3+} + 3 pOH^-$  values of the soil

solutions above pH 4 are almost equal to the  $pK_{sp}$  value of gibbsite.

#### 4. 10. Conclusions

In the system  $Al_2O_3/H_2O$ , the equilibration between the polynuclear Al species  $Al_7(OH)_{17}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$  in solution needs a considerable amount of time, of the order of several months (section 4. 5). Before the equilibration between these species takes place, the  $pAl^{3+} + 3 pOH^-$  value of the system is already close to the solubility product of gibbsite.

The precipitation of new gibbsite crystals from an oversaturated solution is also a very slow process, taking several months (section 4. 2). It seems that in the acid pH range investigated, the formation of gibbsite crystals is associated with the existence of  $Al_{13}(OH)_{34}^{5+}$ . This species dominates at higher Al concentrations (Fig. 1) and pH values (Fig. 2) and is the last one appearing in solutions during the dissolution of naturally occurring gibbsite.

The buffering of H-ions by clay minerals results in the liberation of Al-ions from the clay lattice. In the pH range 3.3 to 5.6, 40 to 80% of the dissolved aluminium exist as polynuclear Al species in the solution. It is very likely that the interior surface of swelling clay minerals favours the "accumulation" of polynuclear Al species from the solution. Under conditions of non-equilibration with respect to polynuclear Al species, the rate of formation of interlayer Al may be much higher compared with the rate

of gibbsite formation. Since the solubility of both the binding forms is almost the same (section 4. 9), no gibbsite will be precipitated as long as interlayer Al can be formed. Gibbsite formation in soils seems to occur at pH values above 4 under conditions of impermeable soil layer, absence of swelling clay minerals and lack of evapotranspiration. The latter conditions are necessary to keep the soil solution for a time span of several months at the same place in the soil body in order to get equilibrated with respect to the polynuclear Al species.

In permeable soils, the solution percolating through soil is not in equilibrium with respect to the polynuclear Al species (section 4. 8).

In the surface horizon (Ahe, Aeh) of acid soils, there is strong evidence to indicate that organo-aluminium complexes play an important role (section 4. 7). It is likely that other complex ions, especially with sulphate as ligand, are important in soil solutions, particularly at lower pH values.

## 5. SUMMARY

This study was undertaken with the objectives of:

1. predicting the amounts of the various aluminium species in the  $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$  system as a function of pH, total Al concentration and ionic strength, and
2. investigating the nature of Al species in solution in equilibrium with:
  - a. naturally occurring and laboratory-prepared gibbsites,
  - b. clay minerals (montmorillonite and vermiculite) and
  - c. soil samples equilibrated in the laboratory, and studying the nature of Al species in soil solutions collected in the field.

As the first step, an equilibrium mononuclear - polynuclear Al species model was constructed using the literature values of the equilibrium constants ( $K_n$ ). The equilibria between  $\text{Al}^{3+}$  and any number of hydroxy-Al species with specified values of  $\text{p}K_n$  and ion size parameter (for the activity correction according to the Debye-Hückel equation) can be studied using this model, at a given pH, total Al concentration and an ionic strength factor,  $I_o$ , which results from the ions other than hydrogen and aluminium present in the solution.

For accurate predictions by the model, standard  $\text{p}K_n$  values of all the Al species at constant ( $25^\circ\text{C}$ ) temperature and low ionic strength are required. Such values are available for the species  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_4^-$ , but for the species  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,

$\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  and  $\text{Al}_{13}(\text{OH})_{32}^{7+}$ ,  $\text{pK}_n$  values only for 40° C and varying ionic strengths (1M, 2M or 3M  $\text{NaClO}_4$ ) are available. Therefore, for these four polynuclear hydroxy-Al species, the available  $\text{pK}_n$  values (first set) were corrected to low ionic strength, on theoretical basis, to get a second set of  $\text{pK}_n$  values. Both these sets of values were used in the computer model to predict the concentration of polynuclear hydroxy-Al species in the solution in equilibrium with a naturally occurring gibbsite. The concentration of polynuclear Al species was also determined experimentally by the 8-hydroxy quinoline method on the assumption that the solution contains only  $\text{H}^+$ ,  $\text{Al}^{3+}$  and hydroxy-Al species. By iterative comparison of the experimental and theoretical values, a new set (third set) of  $\text{pK}_n$  values was computed for the four species. These values are:  $\text{pK}_{(6,15)} = 44.17$ ,  $\text{pK}_{(7,17)} = 45.18$ ,  $\text{pK}_{(13,34)} = 91.05$  and  $\text{pK}_{(13,32)} = 98.65$ , where the first subscript denotes the number of Al ions and the second, the number of OH ions of the hydroxy-Al species. The validity of these values was tested by using them in the computer model for determining the percentage of polynuclear Al species in an equilibrium system of a laboratory-prepared sample of gibbsite; there was good agreement between the theoretical and experimental values. This set (third set) of  $\text{pK}_n$  values was used in further studies.

The solubility product ( $\text{pK}_{\text{sp}}$ ) values of a naturally occurring sample of gibbsite was determined as 33.95 at 25° C, and that of the laboratory-prepared sample as 34.14.

For these calculations, the contribution of  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}_2(\text{OH})_2^{4+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{Al}(\text{OH})_4^-$  and of the polynuclear hydroxy-Al species  $\text{Al}_6(\text{OH})_{15}^{3+}$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$ ,  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  and  $\text{Al}_{13}(\text{OH})_{32}^{7+}$  to the total Al concentration was considered.

In the equilibrium solution of the naturally occurring gibbsite,  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})^{2+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$ ,  $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  were predicted to be present, their relative concentrations being dependent on the experimental conditions of initial pH of the suspension and size of the particles.

It was observed that during the dissolution of the naturally occurring gibbsite, a considerable time (of the order of a few weeks) was necessary for establishing equilibrium between gibbsite and its constituent ions. However, during the equilibration process between the polynuclear species ( $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$ ) which starts after a few days of the initiation of dissolution of the sample, the  $\text{pAl}^{3+} + 3 \text{pOH}^-$  values of the solution are close to the solubility product of gibbsite.

Using the computer model, the nature of Al species likely to occur in soil solutions at the range of values of pH, total Al concentration and  $I_0$  expected in the soil solutions was predicted. It showed that when other conditions are identical, the relative amounts of Al species are dependent on the total Al concentration also in addition to pH. The species  $\text{Al}_7(\text{OH})_{17}^{4+}$  and  $\text{Al}_{13}(\text{OH})_{34}^{5+}$  are found to be the only polynuclear species in solution in the pH range 3-6, particularly at relatively higher

concentrations of total Al ( $pAl < 4.5$ ). The species  $Al_6(OH)_{15}^{3+}$  and  $Al_{13}(OH)_{32}^{7+}$  do not seem to be present under the situations studied. In dilute concentrations of total Al ( $pAl > 4.5$ ), the neutral species  $Al(OH)_3^0$  is present in relatively large amounts. At  $pH < 3$ , all the Al at the total Al concentration range found in soil solutions is predicted to exist as  $Al^{3+}$ .

More than 40% of the total Al in the equilibrium solutions of montmorillonite was experimentally determined to be in the polynuclear forms, the amount of which increased with pH and decreased with increase in the total Al concentration. For the vermiculite samples, the polynuclear Al species accounted for more than 60% of the total Al concentration; at pH 5 to 5.5 and a total Al concentration of  $11 \times 10^{-4}$  mol/l, almost all aluminium existing in the polynuclear forms.

The studies were then extended to soil solutions. The soil samples representing various depths from the Solling and Lüss areas were equilibrated with water for 24 h and the equilibrium soil solutions were analysed for H and Al, as well as for the ions that are expected to contribute to the ionic strength (Na, K, Ca,  $NH_4$ , Mg, Fe, Mn, Cl,  $NO_3$ ,  $PO_4$  and  $SO_4$ ). The concentration of polynuclear Al species was determined experimentally and predicted using the computer model. The theoretically predicted values of polynuclear hydroxy-Al in 24 h-equilibrated soil solutions did not agree with the experimental values, especially when the C content of the soil was high. As the experimental method used to determine polynuclear Al is a measure

of all slow reacting Al species, the alumino-complexes (involving sulphates, phosphates, organo complexes etc.) in soil solutions are likely to be estimated as 'polynuclear' Al species by this method.

The influence of C, total Al and the pH on the amount of polynuclear Al (experimental values) was analysed using such of the soil samples where the influence of other factors except the one under study was expected to be a minimum. When a few samples of low C content were equilibrated for 20 days, there was better agreement between the theoretical and experimental values suggesting that 24 h equilibration was not sufficient to bring all the polynuclear Al into solution.

The percentage of polynuclear Al in soil solutions increased with C content of soils for both the soils. For the Solling soils, the percentage was maximum at about 9% C, this maximum value being dependent on the total Al concentration. For the Lüss soils, which had relatively lower content of C, there was no such maximum value of C beyond which the amount of polynuclear Al was independent of C content. For both the soils, the percentage of polynuclear Al decreased with increase in the concentration of total Al. The pH did not seem to have much effect on the percentage of polynuclear Al for the Solling soils, but for the Lüss soils, polynuclear Al was found to increase with increase in pH.

The concentration of polynuclear Al was determined theoretically and experimentally from the lysimeter solutions collected for 6 months (April-September 1977)

from the Beech and Spruce forest research sites of the IBP in Solling. There was lack of agreement between the theoretical and experimental values. One of the reasons for this difference could be the errors in pH measurements of these unbuffered solutions because a small change in the pH of the solution has been found to have considerable influence on the theoretically predicted value of polynuclear Al concentration. Moreover, the lysimeter solutions may not be in equilibrium with respect to polynuclear Al species particularly in these permeable soils with relatively rapid vertical movement of water.

The  $\text{pAl}^{3+} + 3 \text{pOH}^-$  values of the equilibrium solutions for Solling and Lüss soils and for a population (55) of soils from different parts of Germany were calculated. The values were dependent on pH up to about pH 4. Above pH 4, the values were almost constant and equal to the  $\text{pK}_{\text{sp}}$  value (33.95) of naturally occurring gibbsite. In spite of this, gibbsite is not formed in these soils probably as a consequence of the non-equilibration with respect to polynuclear Al species.

## 6. LITERATURE

- Aveston, J. 1965. Hydrolysis of the aluminium ion: Ultracentrifugation and acidity measurements. J. Chem. Soc. 4438-4443.
- Bache, B. W. 1974. Soluble aluminium and calcium-aluminium exchange in relation to the pH of dilute calcium chloride suspensions of acid soils. J. Soil Sci. 25: 320-332.
- Bache, B. W. and Sharp, G. S. 1976. Soluble polymeric hydroxy-aluminium in acid soils. J. Soil Sci. 27: 167-174.
- Biedermann, G. 1964. Studies of the hydrolysis equilibria of cations by EMF methods. Svensk Kemisk Tidskrift 76: 362-384.
- Blanchar, R. W. and Scrivner, C. L. 1972. Aluminium and iron ion products in acid extracts of samples from various depths in a Menfro soil. Soil Sci. Soc. Am. Proc. 36: 897-901.
- Bohn, H. L. and Peech, M. 1969. Phosphatoiron III and phosphatoaluminium complexes in dilute solutions. Soil Sci. Soc. Am. Proc. 33: 873-876.
- Bolt, G. H. and Bruggenwert, M. G. M. 1976. Soil Chemistry - A. Basic Elements. Developments in Soil Science, Vol. 5A. Elsevier, Amsterdam.
- Breemen, N. van. 1973. Soil forming processes in acid sulphate soils. In Acid Sulphate Soils (ed. H. Dost). pp. 66-130 . Wageningen.
- Brosset, C., Biedermann, G. and Sillén, L.G. 1954. Studies on the hydrolysis of metal ions. XI. The aluminium ion,  $Al^{3+}$ . Acta Chem. Scand. 8: 1917-1926.

- Dalal, R. C. 1975. Hydrolysis products of solution and exchangeable aluminium in acidic soils. *Soil Sci.* 119: 127-131.
- Dezelic, N., Bilinski, H. and Wolf, R. H. H. 1971. Precipitation and hydrolysis of metallic ions. IV. Studies on the solubility of aluminium hydroxide in aqueous solutions. *J. Inorg. Nuclear Chem.* 33: 791-798.
- Fassbender, H. W. and Ahrens, E. 1977. *Laborvorschriften und Praktikumsanleitung. Göttinger Bodenkundliche Berichte* 47: 1-88.
- Ferreiro, E. A. and Helmy, A. K. 1976. The point of zero charge of hydrous aluminium oxide. *Z. Pflanzenernaehr. Bodenk.* 1976: 757-766.
- Frink, C. R. and Peech, M. 1962a. The solubility of gibbsite in aqueous solutions and soil extracts. *Soil Sci. Soc. Am. Proc.* 26: 346-347.
- Frink, C. R. and Peech, M. 1962b. Determination of aluminium in soil extracts. *Soil Sci.* 93: 317-324.
- Frink, C. R. and Peech, M. 1963a. Hydrolysis of the aluminium ion in dilute aqueous solutions. *Inorganic Chemistry* 2: 473-478.
- Frink, C. R. and Peech, M. 1963b. Hydrolysis and exchange reactions of the aluminium ion in hectorite and montmorillonite suspensions. *Soil Sci. Soc. Am Proc.* 27: 527-530.
- Fripiat, J. J. Caubelaert, F. van and Bosmans, H. 1965. Structure of aluminium cations in aqueous solutions. *J. Phys. Chem.* 69: 2458-2461.

- Hem, J. D. and Roberson, C. E. 1967. Form and Stability of Aluminium Hydroxide Complexes in Dilute Solution - Chemistry of Aluminium in Natural Water - Geological Survey Water Supply Paper 1827 A. United States Government Printing Office, Washington, D.C.
- Hsu, P. H. 1963. Effect of initial pH, phosphate and aluminium silicate on the determination of aluminium with aluminon. *Soil Sci.* 96: 230-238.
- Hsu, P. H. 1973. Effect of sulphate on crystallization of  $Al(OH)_3$  from aging hydroxy-aluminium solutions. I.C.S.O.B.A. 3. Congrès Int., Nice, France IV (Alumine): 613-619.
- Hsu, P. H. 1977. Aluminium hydroxides and oxyhydroxides. In Minerals in Soil Environments pp. 99-143. *Soil Sci. Soc. Am., Madison, Wisconsin.*
- Hsu, P. H. and Bates, T. F. 1964a. Formation of x-ray amorphous and crystalline aluminium hydroxides. *Mineral Mag.* 33: 749-768.
- Hsu, P. H. and Bates, T. F. 1964b. Fixation of hydroxy-aluminium polymers by vermiculite. *Soil Sci. Soc. Am. Proc.* 28: 763-769.
- Hsu, P. H. and Rich, C. I. 1960. Aluminium fixation in a synthetic cation exchanger. *Soil Sci. Soc. Am. Proc.* 24: 21-25.
- Jameson, R. F. and Salmon, J. E. 1954. Aluminium phosphates: Phase-diagram and ion-exchange studies of the system aluminium oxide-phosphoric acid-water at 25° C. *J. Chem. Soc.* 4013-4017.
- Kaddah, M. T. and Coleman, N. T. 1967a. Salt displacement and titration of  $AlCl_3$ -treated trioctahedral vermiculites. *Soil Sci. Soc. Am. Proc.* 31: 328-332.
- Kaddah, M. T. and Coleman, N. T. 1967b. Salt displacement of acid-treated trioctahedral vermiculites. *Soil Sci. Soc. Am. Proc.* 31: 333-336.

- Kawaguchi, K. and Kyuma, K. 1959. On the complex formation between soil humus and polyvalent cations. Soil Plant Food 5: 54-63.
- Kettämaa, J. 1955. The hydrolysis of aluminium chloride. Acad. Sci. Fenn. Ann. Ser. A., Sec. II., No. 67.
- Khan, S. V. 1969. Interaction between the humic acid fraction of soils and certain metallic cations. Soil Sci. Soc. Am. Proc. 33: 851-854.
- Kissel, D. E., Gentsch, E. P. and Thomas, G. W. 1971. Hydrolysis of non-exchangeable acidity in soils during salt extractions of exchangeable acidity. Soil Sci. 111: 293-297.
- Kittrick, J. A. 1966. The free energy of formation of gibbsite and  $\text{Al}(\text{OH})_4^-$  from solubility measurements. Soil Sci. Soc. Am. Proc. 30: 595-598.
- Kwong, N. F., Kg Kee and Huang, P. M. 1975. Influence of citric acid on the crystallization of aluminium hydroxides. Clays Clay Minerals 23: 164-165.
- Kwong, N. F., Ng Kee and Huang, P. M. 1977. Influence of citric acid on the hydrolytic reactions of aluminium. J. Soil Sci. Soc. Am. 41: 692-697.
- Lindsay, W. L., Peech, M. and Clark, J. S. 1959. Solubility criteria for the existence of variscite in soils. Soil Sci. Soc. Am. Proc. 23: 357-360.
- Marion, G. M., Hendricks, D. M., Dutt, G. R. and Fuller, W. H. 1976. Aluminium and silica solubility in soils. Soil Sci. 121: 76-85.
- Matijevic, E., Mathai, K. G., Otterwill, R. H. and Kerker, M. 1961. Detection of metal ions hydrolysis by coagulation. III. Aluminium. J. Phys. Chem. 65: 826-830.
- McLean, E. O. 1976. Chemistry of soil aluminium. Commun. Soil Sci. Plant Analysis 7: 619-636.

- Nair, V. D. and Prenzel, J. 1978. Calculations of equilibrium concentrations of mono- and polynuclear hydroxy-aluminium species at different pH and total aluminium concentrations. *Z. Pflanzenernaehr. Bodenk.* (In Press).
- Okura, T., Goto, K. and Yotuyanagi, T. 1962. Forms of aluminium determined by an 8-hydroxy quinolinolate extraction method. *Anal. Chem.* 34: 581-582.
- Ragland, J. L. and Coleman, N. T. 1960. The hydrolysis of aluminium salts in clay and soil systems. *Soil Sci. Soc. Am Proc.* 24: 457-460.
- Raupach, M. 1957. Investigations into the nature of soil pH. *CSIRO Soil Pub. No. 9.*
- Raupach, M. 1963. Solubility of simple aluminium compounds expected in soils. IV. Reactions of aluminium hydroxide under acid conditions. *Aust. J. Soil Res.* 1: 55-62.
- Rawajfih, Z. 1975. The Solubilities of Aluminium-Hydroxy Sulphate Compounds as a Possible Mechanism of Sulphate Retention by Soils. Ph. D. Dissertation, Auburn Univ.
- Rich, C. I. 1970. Conductometric and potentiometric titration of exchangeable aluminium. *Soil Sci. Soc. Am. Proc.* 34: 31-38.
- Richburg, J. S. and Adams, F. 1970. Solubility and hydrolysis of Al in soil solutions. *Soil Sci. Soc. Am. Proc.* 34: 728-734.
- Robertson, G. 1950. The colorimetric determination of aluminium in silicate minerals. *J. Sci. Food Agri.* 1: 59-63.
- Rooksby, H. P. 1961. Oxides and hydroxides of aluminium and iron. In *The X-ray Identification and Crystal Structures of Clay Minerals* (ed. G. Brown). pp. 354-392. Mineralogical Society, London.

- Salmon, J. E. and Wall, J. G. L. 1958. Aluminium phosphates: II. J. Chem. Soc. 1128-1134.
- Sawhney, B. L. 1968. Aluminium interlayers in layer silicates. Effect of OH/Al ratio of Al solution, time of reaction and type of structure. Clays Clay Minerals 16: 157-163.
- Schnitzer, M. 1969. Reactions between fulvic acid, a soil humic compound and inorganic soil constituents. Soil Sci. Soc. Am. Proc. 33: 75-81.
- Schnitzer, M. and Skinner, S. I. M. 1963. Organo-metallic interactions in soil : 1. Reactions between a number of metal ions and the organic matter of a podzol Bh horizon. Soil Sci. 96: 86-93.
- Sillén, L. G. 1959. Quantitative studies of hydrolytic equilibria. Quart. Rev. (London) 13: 146-148.
- Sillén, L. G. 1962. Hydrolytic aqueous species. Lecture, Houston, Texas. (Cited by Aveston, J. 1965. J. Chem. Soc. 4438-4443).
- Sillén, L. G. and Martell, A. E. 1964. Stability Constants of Metal-Ion Complexes. Spec. Pub. No. 17. Chem. Soc., London.
- Sillén, L. G. and Martell, A. E. 1971. Stability Constants of Metal-Ion Complexes. Spec. Pub. No. 25. Chem. Soc., London.
- Singh, S. S. 1974. The solubility product of gibbsite at 15<sup>o</sup>, 25<sup>o</sup> and 35<sup>o</sup> C. Soil Sci. Soc. Am. Proc. 38: 415-417.
- Singh, S. S., and Brydon, J. E. 1967. Precipitation of aluminium by calcium hydroxide in the presence of wyoming bentonite and sulphate ions. Soil Sci. 103: 162-167.

- Singh, S. S. and Brydon, J. E. 1969. Solubility of basic aluminium sulphates at equilibrium in solution and in the presence of montmorillonite. *Soil Sci.* 107: 12-16.
- Singh, S. S. and Brydon, J. E. 1970. Activity of aluminium hydroxy sulphate and the stability of hydroxy aluminium interlayers in montmorillonite. *Can. J. Soil Sci.* 50: 219-225.
- Sullivan, J. H. Jr. and Singley, J. E. 1968. Reactions of metal ions in dilute aqueous solution : Hydrolysis of aluminium. *J. Am. Water Works Assoc.* 60: 1280-1287.
- Tanabe, H. 1954. Aluminium compounds. II. Composition of basic aluminium solution. *J. Pharm. Soc. Japan* 74: 866-872.
- Turner, R. C. 1968a. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: I. Theoretical treatment of the effect of the formation of mono- and polynuclear hydroxyaluminium ions, precipitations and crystallization on curves representing the titration of  $AlCl_3$  with a base. *Soil Sci.* 106: 291-296.
- Turner, R. C. 1968b. Conditions in solution during the formation of gibbsite in dilute Al salt solutions: II. Effect of length of time of reaction on the formation of polynuclear hydroxyaluminium cations, the substitution of other anions for  $OH^-$  in amorphous  $Al(OH)_3$  and the crystallization of gibbsite. *Soil Sci.* 106: 338-344.
- Turner, R. C. 1969. Three forms of aluminium in aqueous systems determined by 8-quinolate extraction methods. *Can. J. Chem.* 47: 2521-2527.

- Turner, R. C. and Ross, G. J. 1970. Conditions in solution during the formation of gibbsite in dilute Al salt solutions. IV. Effect of Cl concentration and temperature and a proposed mechanism for gibbsite formation. *Can. J. Chem.* 48: 723-729.
- Turner, R. C. and Singh, S. S. 1971. The role of sparingly soluble solids and cation exchange reactions in controlling conditions in soil solutions. *Soil. Sci. Soc. Am. Proc.* 35: 445-449.
- White, R. E., Tiffin, L. O. and Taylor, A. W. 1976. The existence of polymeric complexes in dilute solutions of aluminium and orthophosphate. *Plant and Soil* 45: 521-529.

7. APPENDICES

APPENDIX I

The mononuclear - polynuclear aluminium species model

Let  $A_n$  denote a hydroxy-aluminium species in solution:  $Al_{i_n}(OH)_{j_n}^{z_n}$ . Consider as a physico-chemical system, an aqueous solution of N different such species ( $H_2O$ ,  $H^+$ ,  $OH^-$ ,  $A_1$ , ...,  $A_N$ ).

Let  $A_1$  be the aluminium ion  $Al^{3+}$  ( $i_1 = 1$ ,  $j_1 = 0$ ).

The charge of the aluminium species is given by  $z_n = 3i_n - j_n$ . The charge can be zero, i.e.  $Al(OH)_3^0$ . All concentrations are given in moles/litre:

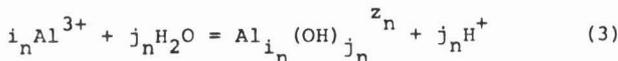
$c_n = [A_n]$ . The total analytical aluminium concentration is denoted by  $c$ .

$$c = \sum_{n=1}^N i_n \cdot c_n \quad (1)$$

Let  $a_n$  be the activity and  $f_n$  the activity coefficient of the aluminium species  $A_n$ :

$$(A_n) = a_n = c_n \cdot f_n \quad (2)$$

Let  $K_n$  be the equilibrium constant for the formation of  $A_n$  from  $Al^{3+}$  and water



$$K_n = \left( \frac{a_n \cdot a_H^{j_n}}{a_1 i_n} \right) \quad \text{equilibrium} \quad (4)$$

The problem may be stated as follows:

Given a pH and a total aluminium concentration  $c$ , what are the equilibrium concentrations  $c_n$  of  $N$  aluminium species for which  $N - 1$  equilibrium constants  $K_n$  are specified? The values of pH and  $c$  may be analytically determined. If they are set arbitrarily, they may refer to a non-equilibrium state with respect to the formation of precipitates. In this calculation, a precipitate (i.e. a solid phase) is not considered. The system is assumed to be at standard temperature and pressure throughout (25° C, 1 atm).

As a first approximation, we disregard the activity coefficients so that  $a_n = c_n$  for values of  $n = 1, \dots, N$ . We have to search for  $N$  unknown concentrations for which  $N - 1$  equilibrium equations are available (4).

$$K_n = \frac{c_n \cdot a_H^{j_n}}{c_1^{i_n}}, \quad n = 2, \dots, N,$$

$$c_1 = [Al^{3+}] \quad \text{and} \quad a_H = 10^{-pH} \quad (5)$$

The specification of  $c$  with equation (1) yields a further equation, and we have a system of  $N$  equations with  $N$  unknown parameters. Introduction of (5) in (1) gives:

$$c - c_1 - \sum_{n=2}^N (i_n \cdot K_n \cdot c_1^{i_n} / a_H^{j_n}) = 0 \quad (6)$$

Writing  $x$  instead of  $c_1$  in (6), we get a polynomial in  $x$ ,  $f(x)$ , with  $f(c_1) = 0$ . We have  $f(0) = c$  and  $f(c) < 0$ . Therefore  $f$  assumes the value zero in  $[0, c]$ , which is the only physically meaningful range for  $c_1$ . We have  $f'(x) < 0$  for  $x > 0$  and therefore in  $[0, c]$ ,  $f$  is monotonically decreasing and the root is unique. This root was approximated by Newton's technique.

Given  $c_1$ , all  $c_n$ -values can be calculated from (5).

In the next step, the activity coefficients were introduced. Substituting equation (2) in equation (4) gives:

$$c - c_1 - \sum_{n=2}^N i_n \cdot K_n (c_1 \cdot f_1)^{i_n} / (a_H^{j_n} \cdot f_n) = 0 \quad (7)$$

instead of (6).

The activity coefficients  $f_n$  were calculated using the extended Debye-Hückel equation (Bolt and Bruggerwert, 1976 p. 17)

$$-\log f_n = \frac{0.51 z_n^2 \sqrt{I}}{1 + 0.33 \frac{a_n}{z_n} \sqrt{I}} \quad (8)$$

where  $a_n$  is an ion-size parameter of the aluminium species,  $A_n$ , and  $I$  is the ionic strength.

$$I = I_0 + \frac{1}{2} (a_H/f_H + \sum_{n=1}^N c_n \cdot z_n^2) \quad (9)$$

where  $I_0$  is the basic ionic strength of ions present in the system but not involved in reactions under study. For any

given  $I$ , equation (7) can be solved as easily as (6). But  $I$ , in turn, depends on the Al concentration  $c_n$  to be calculated from equation (7). We have to solve, therefore, another implicit function  $I = f_I(I)$ . In this case, the existence and uniqueness of the solution were not studied. The usual iteration procedure (Bolt and Bruggenwert, 1976, p. 28) was used:

The  $m$ -th value of  $I$ ,  $I_m$ , was used to calculate  $c_n$ -values using equations (7) and (8). The  $c_n$  values were used to calculate  $I_{m+1}$  by using equation (9). The results were accepted, if  $I_{m+1}$  differed from  $I_m$  by less than 0.2%.

Using these equations, a computer programme was prepared, which, at a given pH and total aluminium concentration,  $c$ , calculates the equilibrium concentrations  $c_n$  for as many hydroxy-aluminium species as required, provided their equilibrium constants  $K_n$  are specified. If the Debye-Hückel activity corrections are to be used, the programme requires the ionic diameters  $\delta_n$  and an ionic strength,  $I_o$ , in addition.

APPENDIX II

Experimental and theoretical values of the concentration of polynuclear aluminium and the  $pAl^{3+} + 3 pOH^{-}$  values of the equilibrium (24 h) solutions of Solling soils

| Description of soil  |         | Depth (cm) | C%    | SO <sub>4</sub> <sup>2-</sup> (mg S/l) | pH   | I   | I <sub>o</sub>   | Total Al conc. (10 <sup>-4</sup> mol/l) | Polynuclear Al concentration (10 <sup>-4</sup> mol/l) |             | pAl <sup>3+</sup> + 3 pOH <sup>-</sup> |
|----------------------|---------|------------|-------|--|------|---|------------------|---|---|-------------|--|
| Profile & Sample No. | Horizon |            |       |  |      | (ionic strength) (10 <sup>-3</sup> mol/l) | (addl I) (mol/l) |   | Exptl   | Theoretical |  |
| 1                    | 2       | 3          | 4     | 5                                      | 6    | 7   | 8                | 9                                       | 10  | 11          | 12                                     |
| Solling 1            |         |            |       |  |      |   |                  |   |   |             |  |
| 2228                 | Ah Sw   | 0-6        | 4.00  | 6.41                                   | 3.77 | 1.279                                     | 1.007            | 0.541                                   | 0.156   | 0           | 35.28                                  |
| 2229                 | Sw      | 6-23       | 0.79  | 7.85                                   | 3.80 | 1.670                                     | 1.304            | 0.830                                   | 0.300   | 0           | 34.88                                  |
| 2230                 | Sw Sd   | 23-30      | 0.43  | 7.48                                   | 3.86 | 1.490                                     | 1.151            | 1.038                                   | 0.445   | 0           | 34.61                                  |
| 2231                 | Sd      | 30-40      | 0.18  | 6.41                                   | 4.12 | 1.256                                     | 1.192            | 0.148                                   | 0.052   | 0           | 34.02                                  |
| Solling 2            |         |            |       |  |      |   |                  |   |   |             |  |
| 2232                 | Ah      | 0-2        | 17.28 | 5.44                                   | 3.81 | 1.554                                     | 1.138            | 0.830                                   | 0.430   | 0           | 34.84                                  |
| 2233                 | Aeh     | 2-4        | 5.89  | 4.49                                   | 3.86 | 1.314                                     | 1.000            | 0.717                                   | 0.296   | 0           | 34.75                                  |
| 2234                 | Bv      | 4-40       | 1.63  | 8.99                                   | 4.08 | 1.354                                     | 0.993            | 1.008                                   | 0.119   | 0.143       | 34.06                                  |
| 2235                 | Cv      | 40-70      | 0.46  | 5.68                                   | 4.03 | 1.160                                     | 0.786            | 0.889                                   | 0.474   | 0.158       | 34.19                                  |
| Solling 3            |         |            |       |  |      |   |                  |   |   |             |  |
| 2236                 | Ah      | 0-1        | 21.76 | 6.38                                   | 3.57 | 2.359                                     | 1.805            | 0.919                                   | 0.474   | 0           | 35.53                                  |
| 2237                 | Ah      | 1-2        | 6.84  | 5.49                                   | 3.53 | 2.520                                     | 2.011            | 1.097                                   | 0.371   | 0           | 36.59                                  |
| 2238                 | Aeh Bv  | 2-18       | 2.87  | 5.34                                   | 3.96 | 0.967                                     | 0.708            | 0.519                                   | 0.119   | 0           | 34.59                                  |

| 1         | 2       | 3     | 4     | 5     | 6    | 7     | 8     | 9     | 10    | 11    | 12    |
|-----------|---------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|
| 2239      | Bv      | 18-54 | 1.31  | 4.81  | 4.06 | 0.760 | 0.636 | 0.556 | 0.141 | 0.066 | 34.29 |
| 2240      | II Cv   | 54-75 | 0.35  | 4.26  | 4.00 | 0.727 | 0.529 | 0.660 | 0.141 | 0.024 | 34.39 |
| 2241      | III Cv  | 75-90 | 0.10  | 4.10  | 3.96 | 0.718 | 0.548 | 0.563 | 0.126 | 0     | 34.54 |
| Solling 4 |         |       |       |       |      |       |       |       |       |       |       |
| 2242      | Aeh     | 0-2   | 13.45 | 9.62  | 3.38 | 2.644 | 1.929 | 1.119 | 0.593 | 0     | 36.02 |
| 2243      | Aeh Bv  | 2-7   | 4.14  | 11.22 | 3.23 | 3.028 | 2.238 | 1.423 | 0.054 | 0     | 36.38 |
| 2244      | Bv 1    | 7-30  | 1.99  | 17.79 | 3.84 | 3.139 | 2.067 | 2.758 | 0.445 | 0.083 | 34.65 |
| 2245      | II Bv 2 | 30-59 | 0.34  | 10.44 | 4.28 | 1.591 | 1.492 | 0.711 | 0.148 | 0.288 | 33.92 |
| 2246      | II S Bv | 59-78 | 0.09  | 9.26  | 4.02 | 1.678 | 1.236 | 1.138 | 0.122 | 0.069 | 34.14 |
| 2247      | II Cv   | 78-90 | 0.19  | 8.02  | 4.06 | 1.556 | 1.211 | 0.778 | 0.170 | 0.025 | 34.19 |
| Solling 5 |         |       |       |       |      |       |       |       |       |       |       |
| 2248      | Ah Sw   | 0-10  | 9.72  | 7.12  | 3.83 | 1.431 | 1.042 | 0.756 | 0.415 | 0     | 34.82 |
| 2249      | Sw 1    | 10-22 | 1.93  | 5.93  | 3.88 | 1.234 | 0.685 | 0.845 | 0.237 | 0     | 34.61 |
| 2250      | Sw 2    | 22-50 | 0.47  | 5.77  | 4.03 | 1.002 | 0.599 | 0.786 | 0.156 | 0.015 | 34.22 |
| Solling 6 |         |       |       |       |      |       |       |       |       |       |       |
| 2251      | Ah Sw   | 22-32 | 11.62 | 5.13  | 3.84 | 1.080 | 0.742 | 0.668 | 0.319 | 0     | 34.83 |
| 2252      | Sw      | 32-46 | 1.19  | 4.81  | 3.96 | 0.821 | 0.505 | 0.667 | 0.185 | 0     | 34.47 |
| 2253      | II Sd 1 | 46-65 | 0.80  | 6.73  | 4.18 | 0.983 | 0.727 | 0.563 | 0.119 | 0.072 | 34.04 |
| 2254      | II Sd 2 | 65-80 | 0.34  | 4.65  | 4.20 | 0.743 | 0.523 | 0.178 | 0.059 | 0     | 34.42 |

| 1         | 2      | 3      | 4    | 5     | 6    | 7     | 8     | 9     | 10    | 11    | 12    |
|-----------|--------|--------|------|-------|------|-------|-------|-------|-------|-------|-------|
| Solling 7 |        |        |      |       |      |       |       |       |       |       |       |
| 2255      | Ah Sw  | 0-4    | 8.27 | 6.09  | 3.36 | 2.134 | 1.309 | 1.119 | 0.378 | 0     | 37.06 |
| 2257      | Sw     | 10-80  | 3.83 | 5.19  | 3.50 | 1.472 | 0.877 | 0.986 | 0.256 | 0     | 35.67 |
| 2258      | Sd     | 80-100 | 0.71 | 7.82  | 3.96 | 1.399 | 0.851 | 1.290 | 0.104 | 0.031 | 34.23 |
| Solling 8 |        |        |      |       |      |       |       |       |       |       |       |
| 2256      | Sw Bsv | 34-45  | 0.50 | 7.44  | 3.94 | 1.393 | 0.842 | 1.216 | 0.111 | 0.112 | 34.30 |
| 2259      | Ahe    | 0-5    | 5.37 | 6.96  | 3.77 | 1.533 | 1.108 | 1.008 | 0.304 | 0     | 34.87 |
| 2260      | Ae Bv  | 5-8    | 3.37 | 8.22  | 3.68 | 1.535 | 1.037 | 1.052 | 0.326 | 0     | 35.12 |
| 2261      | Bvs    | 8-34   | 2.64 | 8.98  | 3.85 | 1.802 | 1.074 | 1.394 | 0.163 | 0     | 34.51 |
| 2262      | Sw Bsv | 45-57  | 1.59 | 9.84  | 4.00 | 1.943 | 1.089 | 1.809 | 0.089 | 0.331 | 34.06 |
| 2263      | Sw Sd  | 57-70  | 0.41 | 6.32  | 4.01 | 1.363 | 0.816 | 1.245 | 0.148 | 0.097 | 34.12 |
| 2264      | Sd     | 70-90  | 0.25 | 5.29  | 3.98 | 1.337 | 0.757 | 1.230 | 0.133 | 0.044 | 34.20 |
| Solling 9 |        |        |      |       |      |       |       |       |       |       |       |
| 2265      | Ah     | 0-1    | 5.26 | 10.58 | 3.77 | 1.763 | 1.567 | 0.889 | 0.267 | 0     | 34.95 |
| 2266      | Aeh    | 1-5    | 3.57 | 9.46  | 3.68 | 2.126 | 1.365 | 1.245 | 0.208 | 0     | 35.06 |
| 2267      | Ah Bv  | 5-8    | 1.90 | 7.69  | 3.87 | 2.186 | 1.143 | 1.239 | 0.371 | 0.040 | 34.27 |
| 2268      | Bv     | 8-47   | 1.41 | 7.92  | 4.04 | 1.725 | 0.957 | 1.586 | 0.133 | 0.373 | 34.03 |
| 2269      | Sw Bv  | 47-60  | 0.30 | 5.45  | 4.15 | 1.093 | 0.651 | 0.904 | 0.534 | 0.244 | 33.98 |
| 2270      | C      | 60-80  | 0.15 | 4.49  | 4.84 | 0.917 | 0.832 | 0.222 | 0.133 | 0.029 | 33.73 |

| 1          | 2     | 3     | 4     | 5     | 6    | 7     | 8     | 9     | 10    | 11    | 12    |
|------------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|
| Solling 10 |       |       |       |       |      |       |       |       |       |       |       |
| 2271       | Ah    | 0-2   | 11.38 | 17.31 | 3.36 | 3.315 | 2.197 | 1.542 | 0.534 | 0     | 33.95 |
| 2272       | Ahe   | 2-9   | 5.20  | 13.63 | 3.45 | 2.770 | 1.949 | 1.423 | 0.326 | 0     | 35.71 |
| 2273       | Bsv   | 9-17  | 2.80  | 8.81  | 3.74 | 2.422 | 1.540 | 1.912 | 0.311 | 0     | 34.72 |
| 2274       | Bv    | 17-47 | 0.92  | 10.42 | 3.99 | 1.841 | 1.165 | 1.586 | 0.230 | 0.165 | 34.11 |
| 2275       | Sw Bv | 47-56 | 0.38  | 11.06 | 4.15 | 1.764 | 1.244 | 1.394 | 0.208 | 0.609 | 33.94 |
| 2276       | Sd    | 56-70 | 0.15  | 9.30  | 4.04 | 1.409 | 0.936 | 1.053 | 0.341 | 0     | 34.05 |
| Solling 11 |       |       |       |       |      |       |       |       |       |       |       |
| 2277       | Ah    | 0-2   | 13.08 | 16.67 | 3.37 | 3.262 | 2.525 | 1.216 | 0.534 | 0     | 36.03 |
| 2278       | Ahe   | 2-8   | 5.22  | 16.73 | 3.33 | 2.738 | 2.149 | 1.351 | 0.348 | 0     | 36.10 |
| 2279       | Ae    | 8-10  | 3.80  | 17.31 | 3.47 | 2.704 | 2.123 | 1.091 | 0.215 | 0     | 35.76 |
| 2280       | Bs    | 10-13 | 2.54  | 18.50 | 3.66 | 3.229 | 2.180 | 2.224 | 0.341 | 0     | 34.91 |
| 2281       | Bv    | 13-41 | 1.31  | 18.11 | 3.94 | 3.252 | 1.861 | 3.076 | 0.435 | 0.692 | 34.07 |
| 2282       | Bv Sw | 41-59 | 0.44  | 14.33 | 4.23 | 2.446 | 1.779 | 1.483 | 0.163 | 0.878 | 33.88 |
| 2283       | Sw Sd | 59-80 | 0.25  | 15.39 | 3.90 | 2.680 | 1.629 | 2.068 | 0.237 | 0.236 | 34.23 |
| Solling 12 |       |       |       |       |      |       |       |       |       |       |       |
| 2284       | Ah    | 0-4   | 15.47 | 14.43 | 3.66 | 2.504 | 1.843 | 0.919 | 0.489 | 0     | 35.26 |
| 2285       | Ae    | 4-17  | 3.83  | 9.07  | 3.70 | 1.838 | 1.215 | 0.934 | 0.460 | 0     | 35.12 |
| 2286       | Sw Bs | 17-26 | 2.87  | 4.58  | 4.21 | 1.021 | 0.793 | 0.519 | 0.156 | 0.078 | 34.02 |
| 2287       | Sd Sw | 26-40 | 1.37  | 3.93  | 4.77 | 0.753 | 0.707 | 0.208 | 0.119 | 0.026 | 33.78 |
| 2288       | Sd    | 40-60 | 0.35  | 5.05  | 4.26 | 0.673 | 0.608 | 0.296 | 0.044 | 0.014 | 34.09 |

| 1          | 2     | 3     | 4     | 5     | 6    | 7     | 8     | 9     | 10    | 11    | 12    |
|------------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|
| Solling 13 |       |       |       |       |      |       |       |       |       |       |       |
| 2289       | Ah    | 0-4   | 15.76 | 19.56 | 3.67 | 3.161 | 2.552 | 1.371 | 0.511 | 0     | 35.09 |
| 2290       | Aeh   | 4-6   | 10.35 | 18.27 | 3.68 | 2.852 | 2.292 | 1.275 | 0.489 | 0     | 35.08 |
| 2291       | Bvs   | 6-11  | 4.68  | 6.61  | 4.43 | 1.323 | 1.005 | 0.756 | 0.371 | 0.454 | 33.80 |
| 2292       | Sw 1  | 11-30 | 1.94  | 5.93  | 4.28 | 1.121 | 0.887 | 0.556 | 0.170 | 0.171 | 33.93 |
| 2293       | Sw 2  | 30-52 | 2.53  | 4.42  | 4.13 | 0.917 | 0.640 | 0.571 | 0.170 | 0.032 | 34.12 |
| 2294       | Sw Sd | 52-65 | 0.83  | 6.03  | 4.22 | 1.047 | 0.760 | 0.830 | 0.030 | 0.314 | 33.93 |
| 2295       | Sd    | 65-90 | 0.25  | 7.12  | 4.08 | 1.067 | 0.755 | 0.682 | 0.074 | 0.025 | 34.17 |
| Solling 14 |       |       |       |       |      |       |       |       |       |       |       |
| 2296       | Ah    | 0-2   | 5.58  | 14.75 | 3.61 | 2.480 | 1.882 | 1.572 | 0.474 | 0     | 35.19 |
| 2298       | Aeh   | 2-16  | 2.34  | 9.78  | 3.83 | 1.805 | 1.206 | 1.334 | 0.237 | 0     | 34.59 |
| 2299       | Bsv   | 16-35 | 0.80  | 14.11 | 4.05 | 2.149 | 1.279 | 1.824 | 0.385 | 0.569 | 34.00 |
| 2300       | Bv Sw | 40-55 | 0.31  | 14.17 | 4.01 | 2.192 | 1.357 | 1.601 | 0.148 | 0.240 | 34.08 |
| 2301       | Sd    | 55-70 | 0.11  | 8.94  | 4.07 | 1.429 | 1.053 | 0.838 | 0.178 | 0.051 | 34.13 |

APPENDIX III

Experimental and theoretical values of the concentration of polynuclear aluminium and  $pAl^{3+} + 3 pOH^{-}$  values of the equilibrium (24 h) solutions of Lüss soils

| Description of soil |            | C%   | SO <sub>4</sub> <sup>2-</sup><br>(mg S/l) | pH   | I<br>(ionic strength)<br>(10 <sup>-3</sup> mol/l) | I <sub>o</sub><br>(Addl I)<br>(mol/l) | Total Al concn<br>(10 <sup>-4</sup> mol/l) | Polynuclear Al concentration<br>(10 <sup>-4</sup> mol/l) |          | pAl <sup>3+</sup> +<br>3 pOH <sup>-</sup> |
|---------------------|------------|------|---|------|---|---------------------------------------|--|--|----------|---|
| Sample No.          | Depth (cm) |      |   |      |   |                                       |  | Exptl  | Theoret. |   |
| 1                   | 2          | 3    | 4   | 5    | 6   | 7                                     | 8  | 9  | 10       | 11  |
| 2721                | 0-4        | 3.21 | 10.7                                      | 4.84 | 1.688   | 1.510                                 | 0.126                                      | 0.067  | 0.001    | 33.92                                     |
| 2722                | 4-10       | 3.48 | 58.9                                      | 3.75 | 7.985   | 7.213                                 | 1.838                                      | 0.764  | 0        | 34.83                                     |
| 2723                | 10-20      | 3.02 | 15.9                                      | 4.39 | 4.414   | 3.297                                 | 2.981                                      | 1.534  | 2.506    | 33.75                                     |
| 2724                | 20-30      | 1.92 | 10.8                                      | 4.29 | 1.704   | 1.189                                 | 1.049                                      | 0.308  | 0.600    | 33.86                                     |
| 2725                | 30-40      | 0.80 | 10.8                                      | 4.22 | 1.660   | 1.092                                 | 1.131                                      | 0.285  | 0.558    | 33.90                                     |
| 2726                | 40-50      | 0.48 | 12.0                                      | 4.23 | 1.822   | 1.291                                 | 1.049                                      | 0.219  | 0.501    | 33.90                                     |
| 2727                | 0-4        | 9.26 | 7.4                                       | 3.93 | 1.718   | 1.223                                 | 1.038                                      | 0.593  | 0.023    | 34.41                                     |
| 2728                | 4-10       | 4.14 | 10.6                                      | 8.78 | 1.918   | 1.399                                 | 0.927                                      | 0.496  | 0        | 34.89                                     |
| 2729                | 10-20      | 4.15 | 9.8                                       | 4.09 | 1.759   | 1.209                                 | 1.049                                      | 0.441  | 0.181    | 34.04                                     |
| 2730                | 20-30      | 2.60 | 10.5                                      | 4.20 | 1.706   | 1.159                                 | 1.112                                      | 0.319  | 0.449    | 33.92                                     |
| 2731                | 30-40      | 0.75 | 11.7                                      | 4.30 | 1.809   | 1.094                                 | 1.872                                      | 0.337  | 1.112    | 33.81                                     |
| 2732                | 40-50      | 0.38 | 13.3                                      | 4.15 | 1.995   | 1.224                                 | 1.505                                      | 0.259  | 0.704    | 33.93                                     |

| 1    | 2     | 3    | 4    | 5    | 6     | 7     | 8     | 9     | 10    | 11    |
|------|-------|------|------|------|-------|-------|-------|-------|-------|-------|
| 2733 | 0-4   | 5.79 | 13.5 | 6.45 | 2.074 | 2.049 | 0.178 | 0.089 | 0     | --    |
| 2734 | 4-10  | 3.37 | 39.8 | 3.85 | 5.783 | 5.278 | 1.112 | 0.429 | 0     | 34.71 |
| 2735 | 10-20 | 3.36 | 30.5 | 4.22 | 5.099 | 4.558 | 1.205 | 0.478 | 0.555 | 33.93 |
| 2736 | 20-30 | 1.67 | 30.7 | 4.16 | 5.153 | 4.545 | 1.208 | 0.245 | 0.401 | 33.98 |
| 2737 | 30-40 | 0.61 | 30.1 | 4.40 | 4.537 | 4.109 | 0.908 | 0.226 | 0.561 | 33.83 |
| 2738 | 40-50 | 0.18 | 28.1 | 4.23 | 4.154 | 3.728 | 0.853 | 0.126 | 0.295 | 33.96 |
| 2739 | 0-4   | 7.18 | 5.0  | 4.54 | 1.223 | 0.981 | 0.341 | 0.163 | 0.122 | 33.81 |
| 2740 | 4-10  | 5.76 | 5.6  | 4.17 | 1.925 | 1.468 | 0.945 | 0.559 | 0.291 | 33.97 |
| 2741 | 10-20 | 3.55 | 19.2 | 3.99 | 2.801 | 2.220 | 1.538 | 0.471 | 0.012 | 33.93 |
| 2742 | 20-30 | 2.55 | 21.4 | 4.06 | 3.084 | 1.944 | 2.280 | 0.322 | 0.946 | 33.97 |
| 2743 | 30-40 | 0.64 | 16.9 | 4.11 | 2.434 | 1.562 | 1.798 | 0.256 | 0.799 | 33.95 |
| 2744 | 40-50 | 0.27 | 10.7 | 4.23 | 1.626 | 1.449 | 1.075 | 0.215 | 0.520 | 33.90 |
| 2745 | 0-4   | 0.85 | 38.4 | 3.82 | 4.784 | 4.370 | 0.927 | 0.300 | 0     | 34.89 |
| 2746 | 4-10  | 3.50 | 40.8 | 3.39 | 5.432 | 4.635 | 1.501 | 0.612 | 0     | 35.94 |
| 2747 | 10-20 | 3.27 | 9.8  | 4.04 | 2.102 | 1.333 | 1.501 | 0.611 | 0.299 | 34.05 |
| 2748 | 20-30 | 1.63 | 11.2 | 4.07 | 2.138 | 1.283 | 1.761 | 0.426 | 0.613 | 33.98 |
| 2749 | 30-40 | 0.82 | 14.3 | 4.04 | 2.508 | 1.445 | 2.131 | 0.308 | 0.744 | 33.99 |
| 2750 | 40-50 | 0.46 | 14.0 | 4.13 | 2.209 | 1.365 | 1.761 | 0.308 | 0.852 | 33.93 |

| 1    | 2     | 3    | 4    | 5    | 6     | 7     | 8     | 9     | 10    | 11    |
|------|-------|------|------|------|-------|-------|-------|-------|-------|-------|
| 2751 | 0-4   | 7.87 | 4.0  | 3.99 | 1.017 | 0.750 | 0.519 | 0.289 | 0     | 34.51 |
| 2752 | 4-10  | 5.51 | 4.5  | 3.88 | 0.955 | 0.667 | 0.482 | 0.215 | 0     | 34.51 |
| 2753 | 10-20 | 3.39 | 15.4 | 4.03 | 2.444 | 1.620 | 1.761 | 0.456 | 0.410 | 34.03 |
| 2754 | 20-30 | 1.91 | 18.2 | 4.11 | 2.885 | 1.733 | 2.372 | 0.415 | 1.293 | 33.92 |
| 2755 | 30-40 | 0.84 | 18.9 | 4.06 | 3.097 | 1.763 | 2.817 | 0.297 | 1.414 | 33.95 |
| 2756 | 40-50 | 0.35 | 19.6 | 4.05 | 3.260 | 1.852 | 2.669 | 0.356 | 1.382 | 33.96 |
| 2757 | 0-4   | 4.24 | 17.6 | 3.89 | 3.309 | 2.141 | 2.539 | 0.789 | 0.114 | 34.20 |
| 2758 | 4-10  | 3.35 | 20.3 | 4.06 | 3.773 | 2.309 | 3.372 | 1.119 | 1.872 | 33.93 |
| 2759 | 10-20 | 2.86 | 14.3 | 4.74 | 3.692 | 3.188 | 2.279 | 1.182 | 1.997 | 33.60 |
| 2760 | 20-30 | 3.25 | 16.9 | 4.4  | 2.645 | 2.116 | 1.160 | 0.329 | 0.095 | 33.04 |
| 2761 | 30-40 | 0.75 | 20.3 | 4.23 | 2.809 | 2.277 | 1.112 | 0.222 | 0.535 | 33.91 |
| 2762 | 40-50 | 1.41 | 16.7 | 4.39 | 2.313 | 1.974 | 0.734 | 0.659 | 0.406 | 33.84 |
| 2763 | 0-4   | 4.54 | 14.7 | 4.08 | 2.586 | 2.035 | 1.371 | 0.274 | 0.331 | 34.02 |
| 2764 | 4-10  | 4.14 | 10.9 | 4.76 | 1.674 | 1.380 | 0.686 | 0.315 | 0.437 | 33.64 |
| 2765 | 10-20 | 3.00 | 11.1 | 4.24 | 1.720 | 1.219 | 1.056 | 0.411 | 0.527 | 33.90 |
| 2766 | 20-30 | 1.17 | 16.9 | 4.48 | 2.278 | 1.903 | 0.815 | 0.245 | 0.531 | 33.77 |
| 2767 | 30-40 | 0.46 | 18.9 | 4.39 | 2.579 | 2.183 | 0.815 | 0.237 | 0.479 | 33.83 |
| 2768 | 40-50 | 0.23 | 16.7 | 4.52 | 2.619 | 2.175 | 1.038 | 0.208 | 0.575 | 33.74 |

## APPENDIX IV

Experimental and theoretical values of the concentration of polynuclear aluminium and the  $pAl^{3+} + 3 pOH^{-}$  values of the equilibrium (20 days) solutions of Solling soils

| Sample No. | pH   | Ionic strength (I)<br>( $10^{-3}$ mol/l) | Addl ionic strength ( $I_0$ ) | Total Al concn ( $10^{-4}$ mol/l) | Polynuclear Al concentration ( $10^{-4}$ mol/l) |          | $pAl^{3+} + 3 pOH^{-}$ |
|------------|------|--|-------------------------------|-----------------------------------|---|----------|------------------------|
|            |      |  |                               |                                   | Exptl   | Theoret. |                        |
| 2231       | 4.29 | 1.186                                    | 1.127                         | 0.085                             | 0.044   | 0        | 34.58                  |
| 2235       | 4.35 | 1.642                                    | 1.429                         | 0.330                             | 0.182   | 0.057    | 33.97                  |
| 2240       | 4.16 | 1.383                                    | 1.159                         | 0.434                             | 0.185   | 0.012    | 34.17                  |
| 2241       | 4.14 | 1.040                                    | 0.880                         | 0.512                             | 0.297   | 0.021    | 34.15                  |
| 2246       | 4.10 | 1.627                                    | 1.392                         | 0.489                             | 0.119   | 0.004    | 34.28                  |
| 2247       | 4.06 | 1.829                                    | 1.527                         | 0.600                             | 0.104   | 0.004    | 34.30                  |
| 2250       | 4.15 | 1.380                                    | 0.978                         | 1.342                             | 0.441   | 0.576    | 33.94                  |
| 2253       | 4.17 | 1.141                                    | 0.993                         | 0.760                             | 0.289   | 0.170    | 34.00                  |
| 2254       | 4.29 | 1.351                                    | 1.239                         | 0.356                             | 0.026   | 0.044    | 34.02                  |
| 2256       | 4.19 | 1.552                                    | 1.206                         | 0.626                             | 0.159   | 0.110    | 34.02                  |
| 2258       | 4.10 | 1.647                                    | 1.224                         | 1.701                             | 0.482   | 0.695    | 33.96                  |
| 2282       | 4.14 | 2.609                                    | 2.067                         | 0.986                             | 0.215   | 0.238    | 34.01                  |
| 2295       | 4.18 | 1.468                                    | 1.194                         | 0.549                             | 0.156   | 0.058    | 34.07                  |
| 2301       | 4.08 | 1.425                                    | 1.153                         | 0.552                             | 0.159   | 0.056    | 34.27                  |

APPENDIX V

Experimental and theoretical values of the concentration of polynuclear aluminium and the  $pAl^{3+} + 3 pOH^{-}$  values of the equilibrium (20 days) solutions of Lüss soils

| Sample No. | pH   | Ionic strength (I)<br>( $10^{-3}$ mol/l) | Addl ionic (I <sub>o</sub> )<br>(mol/l) | Total Al concn<br>( $10^{-4}$ mol/l) | Polynuclear Al concentration<br>( $10^{-4}$ mol/l) |          | $pAl^{3+} + 3 pOH^{-}$ |
|------------|------|--|---|--------------------------------------|--|----------|------------------------|
|            |      |  |   |                                      | Exptl  | Theoret. |                        |
| 2725       | 4.24 | 1.332                                    | 0.859                                   | 0.901                                | 0.348  | 0.402    | 33.91                  |
| 2726       | 4.19 | 1.442                                    | 0.996                                   | 0.871                                | 0.345  | 0.287    | 33.96                  |
| 2731       | 4.21 | 1.835                                    | 1.239                                   | 1.212                                | 0.411  | 0.606    | 33.91                  |
| 2732       | 4.15 | 1.634                                    | 1.039                                   | 1.089                                | 0.374  | 0.369    | 33.97                  |
| 2737       | 4.23 | 3.756                                    | 3.296                                   | 0.989                                | 0.463  | 0.413    | 33.93                  |
| 2738       | 4.24 | 3.172                                    | 1.804                                   | 0.741                                | 0.252  | 0.252    | 33.95                  |
| 2743       | 4.14 | 2.174                                    | 1.583                                   | 1.612                                | 0.534  | 0.751    | 33.94                  |
| 2744       | 4.13 | 1.250                                    | 0.783                                   | 0.960                                | 0.337  | 0.235    | 34.00                  |
| 2749       | 4.21 | 2.287                                    | 1.505                                   | 2.613                                | 1.067  | 1.893    | 33.85                  |
| 2750       | 4.13 | 2.006                                    | 1.313                                   | 1.649                                | 0.589  | 0.759    | 33.94                  |
| 2755       | 4.13 | 2.492                                    | 1.674                                   | 2.090                                | 0.423  | 1.128    | 33.92                  |
| 2756       | 4.03 | 2.359                                    | 1.551                                   | 1.572                                | 0.319  | 0.293    | 34.06                  |
| 2761       | 4.26 | 2.104                                    | 1.642                                   | 0.856                                | 0.241  | 0.378    | 33.91                  |
| 2762       | 4.30 | 2.340                                    | 1.855                                   | 0.960                                | 0.389  | 0.522    | 33.87                  |
| 2767       | 4.27 | 1.968                                    | 1.546                                   | 0.856                                | 0.315  | 0.394    | 33.90                  |
| 2768       | 4.22 | 1.460                                    | 1.101                                   | 0.558                                | 0.222  | 0.107    | 34.00                  |

## APPENDIX VI

Experimental and theoretical values of the concentration of polynuclear aluminium in the lysimeter solutions from the Beech forest sites

| Sample  | pH   | Ionic strength (I) | Addl ionic strength ( $I_o$ ) | Total Al concn ( $10^{-4}$ mol/l) | Polynuclear Al concentration ( $10^{-4}$ mol/l) |             |       |
|---------|------|--------------------|-------------------------------|-----------------------------------|---|-------------|-------|
|         |      |                    |                               |                                   | Exptl   | Theoretical |       |
| Apr. 77 | 1515 | 3.93               | 1.672                         | 0.927                             | 1.423   | 0.137       | 0.021 |
|         | 1516 | 3.89               | 1.491                         | 0.805                             | 1.287   | 0.271       | 0.028 |
|         | 1517 | 3.99               | 1.209                         | 0.503                             | 1.460   | 0.166       | 0.144 |
| May 77  | 1901 | 3.99               | 1.549                         | 0.856                             | 1.382   | 0.182       | 0.181 |
|         | 1902 | 3.97               | 1.704                         | 0.944                             | 1.516   | 0.152       | 0.094 |
|         | 1903 | 3.95               | 1.620                         | 0.897                             | 1.360   | 0.285       | 0.030 |
| June 77 | 2523 | 3.98               | 1.511                         | 0.848                             | 1.364   | 0.164       | 0.042 |
|         | 2524 | 3.93               | 1.631                         | 0.911                             | 1.537   | 0.192       | 0.033 |
|         | 2525 | 3.95               | 1.581                         | 0.895                             | 1.434   | 0.259       | 0.062 |
| July 77 | 3983 | 3.97               | 1.524                         | 0.867                             | 1.382   | 0.159       | 0.060 |
|         | 3984 | 4.04               | 1.645                         | 1.009                             | 1.305   | 0.134       | 0.197 |
|         | 3985 | 4.00               | 1.42                          | 0.789                             | 1.305   | 0.114       | 0.098 |
| Aug. 77 | 5318 | 3.97               | 1.621                         | 0.936                             | 1.409   | 0.175       | 0.065 |
|         | 5319 | 3.99               | 1.794                         | 1.017                             | 1.651   | 0.239       | 0.206 |
|         | 5320 | 4.01               | 1.095                         | 1.162                             | 1.361   | 0.190       | 0.130 |
| Sep. 77 | 5732 | 3.90               | 1.872                         | 1.111                             | 1.598   | 0.171       | 0.014 |
|         | 5733 | 3.90               | 2.142                         | 1.279                             | 1.675   | 0.183       | 0.018 |
|         | 5734 | 3.87               | 1.704                         | 1.105                             | 1.166   | 0.221       | 0     |

## APPENDIX VII

Experimental and theoretical values of the concentration of polynuclear aluminium in the lysimeter solutions from the Spruce forest site

| Sample  | pH   | Ionic strength<br>(I)<br>( $10^{-3}$ mol/l) | Addl ionic strength<br>(I <sub>o</sub> )<br>( $10^{-3}$ mol/l) | Total Al concn<br>( $10^{-4}$ mol/l) | Polynuclear Al concentration<br>( $10^{-4}$ mol/l) |             |       |
|---------|------|---|--|--------------------------------------|--|-------------|-------|
|         |      |   |  |                                      | Exptl  | Theoretical |       |
| Apr. 77 | 1545 | 3.86  | 5.619  | 2.491                                | 7.461  | 0.504       | 2.697 |
|         | 1546 | 3.85  | 6.114  | 3.064                                | 7.234  | 0.845       | 2.230 |
|         | 1547 | 3.92  | 4.875  | 2.799                                | 5.129  | 0.122       | 1.922 |
| May 77  | 1931 | 3.88  | 6.691  | 3.411                                | 7.080  | 0.483       | 2.689 |
|         | 1932 | 3.90  | 5.965  | 3.027                                | 6.530  | 0.314       | 2.206 |
|         | 1933 | 4.01  | 5.192  | 2.669                                | 5.388  | 0.518       | 1.551 |
| June 77 | 2553 | 3.85  | 5.565  | 2.815                                | 6.702  | 0.798       | 1.877 |
|         | 2554 | 3.88  | 4.929  | 2.278                                | 5.07   | 0.536       | 1.922 |
|         | 2555 | 3.91  | 5.612  | 2.914                                | 5.838  | 0.727       | 2.291 |
| July 77 | 4013 | 3.86  | 6.195  | 3.118                                | 6.546  | 0.875       | 1.924 |
|         | 4014 | 3.85  | 5.666  | 2.939                                | 6.252  | 0.766       | 1.549 |
|         | 4015 | 3.92  | 5.651  | 2.932                                | 5.233  | 0.267       | 1.958 |
| Aug. 77 | 5348 | 3.86  | 6.437  | 3.221                                | 6.719  | 1.048       | 2.037 |
|         | 5349 | 3.77  | 6.010  | 3.139                                | 5.872  | 0.535       | 0.235 |
|         | 5350 | 3.81  | 4.609  | 2.418                                | 4.335  | 0.376       | 0.181 |
| Sep. 77 | 5762 | 3.85  | 6.944  | 3.216                                | 6.563  | 0.707       | 1.730 |
|         | 5763 | 3.83  | 6.293  | 3.166                                | 6.304  | 0.559       | 1.195 |
|         | 5764 | 3.85  | 5.656  | 2.789                                | 5.855  | 0.703       | 1.306 |

## APPENDIX VIII

pAl<sup>3+</sup> + 3 pOH<sup>-</sup> values of various equilibrium soil solutions

| Description of soil    |               | pH   | Al conc.<br>(10 <sup>-4</sup><br>mol/l) | I<br>(ionic<br>strength)<br>(10 <sup>-2</sup> mol/l) | I <sub>o</sub><br>(Addl I) | pAl <sup>3+</sup> +<br>3 pOH <sup>-</sup> |
|------------------------|---------------|------|---|--|----------------------------|---|
| Place &<br>Number      | Depth<br>(cm) |      |   |  |                            |   |
| Eschrode (1966)        |               |      |   |  |                            |   |
| 972                    | 20-30         | 3.85 | 1.2075                                  | 0.9632   | 0.9018                     | 34.74                                     |
| 977                    | 20-30         | 3.85 | 2.3282                                  | 1.1136   | 1.0017                     | 35.47                                     |
| 1022                   | 20-30         | 3.90 | 1.4572                                  | 0.2933   | 0.2214                     | 35.39                                     |
| Sprakensehl (1966)     |               |      |   |  |                            |   |
| 1191                   | 10-20         | 4.08 | 1.6068                                  | 0.6689   | 0.5924                     | 34.04                                     |
| 1192                   | 20-30         | 3.72 | 1.4946                                  | 0.6016   | 0.5248                     | 34.97                                     |
| 1193                   | 30-40         | 3.93 | 1.3178                                  | 0.5778   | 0.4630                     | 34.43                                     |
| 1227                   | 10-20         | 4.00 | 0.5091                                  | 0.1823   | 0.1543                     | 34.53                                     |
| 1228                   | 20-30         | 3.84 | 0.6613                                  | 0.1367   | 0.0977                     | 34.85                                     |
| 1229                   | 30-40         | 4.21 | 0.2753                                  | 0.0822   | 0.0667                     | 34.63                                     |
| Syke/Westermark (1966) |               |      |   |  |                            |   |
| 1389                   | 0-10          | 5.05 | 0.2229                                  | 0.4795   | 0.4690                     | 33.68                                     |
| 1391                   | 0-10          | 3.85 | 1.1487                                  | 0.3107   | 0.2519                     | 34.64                                     |
| 1392                   | 0-10          | 4.18 | 0.6827                                  | 0.3487   | 0.3147                     | 34.05                                     |
| 1393                   | 0-10          | 5.05 | 0.1286                                  | 0.7443   | 0.7380                     | 33.89                                     |

|      |       |      |        |        |        |       |
|------|-------|------|--------|--------|--------|-------|
| 1466 | 10-20 | 4.18 | 0.3240 | 0.6852 | 0.6673 | 34.37 |
| 1467 | 20-30 | 4.48 | 0.2250 | 1.4798 | 1.4680 | 34.02 |
| 1468 | 30-40 | 4.12 | 0.3181 | 0.2708 | 0.2526 | 34.44 |
| 1469 | 40-50 | 4.18 | 0.6714 | 0.4487 | 0.4151 | 34.07 |

Walsrode (1967)

|      |       |      |        |        |        |       |
|------|-------|------|--------|--------|--------|-------|
| 1157 | 0-10  | 4.27 | 0.5260 | 0.5034 | 0.4770 | 34.01 |
| 1158 | 10-20 | 4.17 | 0.9060 | 1.0627 | 1.0185 | 34.06 |
| 1159 | 20-30 | 4.31 | 0.2566 | 0.4755 | 0.4615 | 34.15 |
| 1160 | 30-40 | 4.21 | 0.2291 | 0.6480 | 0.6346 | 34.43 |
| 1163 | 0-10  | 4.00 | 1.2545 | 0.7148 | 0.6578 | 34.27 |
| 1164 | 10-20 | 4.33 | 1.3841 | 1.0127 | 0.9481 | 33.87 |
| 1165 | 20-30 | 4.50 | 1.2688 | 0.7635 | 0.7048 | 33.77 |
| 1166 | 30-40 | 4.35 | 1.1766 | 0.9512 | 0.8960 | 33.87 |

Lüb (1967)

|      |       |      |         |        |        |       |
|------|-------|------|---------|--------|--------|-------|
| 1683 | 10-20 | 3.62 | 4.9343  | 0.6467 | 0.4126 | 34.76 |
| 1684 | 20-30 | 3.92 | 1.9849  | 0.8149 | 0.7196 | 34.31 |
| 1685 | 30-40 | 4.08 | 1.5265  | 0.5670 | 0.4941 | 34.04 |
| 1686 | 40-60 | 4.00 | 2.1091  | 0.5273 | 0.4274 | 34.08 |
| 1691 | 10-20 | 3.68 | 11.8336 | 1.9530 | 1.4100 | 34.65 |
| 1692 | 20-30 | 3.98 | 3.3501  | 1.5105 | 1.3545 | 34.09 |
| 1693 | 30-40 | 3.98 | 4.4820  | 1.4564 | 1.0080 | 34.03 |
| 1694 | 40-60 | 3.75 | 9.8463  | 2.0309 | 1.5789 | 35.25 |

## Radolfhausen (1971)

|     |       |      |        |        |        |       |
|-----|-------|------|--------|--------|--------|-------|
| 907 | 0-10  | 3.50 | 1.2221 | 0.5318 | 0.4609 | 35.69 |
| 908 | 10-20 | 3.62 | 1.7263 | 0.5064 | 0.4167 | 35.19 |
| 909 | 20-30 | 3.70 | 3.0542 | 0.6940 | 0.5466 | 34.74 |
| 910 | 30-40 | 3.65 | 4.2748 | 0.9971 | 0.7935 | 35.79 |
| 911 | 40-50 | 3.77 | 2.8013 | 1.2605 | 1.1259 | 35.65 |

## Radolfhausen (1972)

|     |       |      |        |        |        |       |
|-----|-------|------|--------|--------|--------|-------|
| 618 | 0-10  | 3.87 | 1.2601 | 0.4576 | 0.3941 | 34.58 |
| 619 | 10-20 | 3.64 | 1.2231 | 0.7486 | 0.6821 | 35.32 |
| 620 | 20-30 | 3.79 | 4.1509 | 1.5879 | 1.3930 | 34.45 |
| 621 | 30-40 | 3.69 | 8.5242 | 2.0816 | 1.6878 | 34.49 |
| 622 | 40-50 | 3.72 | 2.9920 | 1.0935 | 0.9493 | 34.75 |

## Jembke (1974)

|      |       |      |        |        |        |       |
|------|-------|------|--------|--------|--------|-------|
| 2033 | 0-10  | 4.40 | 2.6536 | 0.6482 | 0.5268 | 33.77 |
| 2034 | 10-20 | 4.05 | 1.8271 | 0.6188 | 0.5321 | 34.05 |
| 2035 | 20-40 | 3.95 | 2.2793 | 0.4935 | 0.3853 | 34.14 |
| 2036 | 40-60 | 3.98 | 2.6054 | 0.5469 | 0.4244 | 34.07 |
| 2037 | 60-80 | 4.00 | 1.8271 | 0.4089 | 0.3217 | 34.10 |

## Eschwege (1974)

|      |       |      |        |        |        |       |
|------|-------|------|--------|--------|--------|-------|
| 3746 | 0-05  | 3.85 | 0.9340 | 0.3330 | 0.2839 | 34.74 |
| 3747 | 05-10 | 3.95 | 0.9636 | 0.4133 | 0.3639 | 34.54 |

|      |        |      |        |        |        |       |
|------|--------|------|--------|--------|--------|-------|
| 3748 | 10-20  | 4.08 | 0.7931 | 0.5334 | 0.4917 | 34.22 |
| 3749 | 20-30  | 4.10 | 0.9340 | 0.5386 | 0.4936 | 34.12 |
| 3750 | 30-50  | 4.58 | 0.0815 | 0.3582 | 0.3532 | 34.24 |
| 3751 | 50-70  | 4.00 | 1.5937 | 0.5072 | 0.4355 | 34.15 |
| 3752 | 70-100 | 4.02 | 0.3113 | 0.4219 | 0.4031 | 34.07 |

