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# EFFECT OF THE PRESENCE OF ALUMINUM IONS IN IRON SOLUTIONS ON THE FORMATION OF IRON OXYHYDROXIDES (FeOOH) AT ROOM TEMPERATURE UNDER ACIDIC ENVIRONMENT[1]

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**Abstract**—The hydrolytic behavior of Fe solutions at room temperature under acidic conditions was investigated. In the presence of Al ions, with Cl and $NO_3$ as associated anions, the Fe hydrolysis began almost instantaneously and a crystalline $\beta$-FeOOH (akaganeite) was formed in the $AlCl_3/FeCl_3$ system within a short period. Initially the particles were small with large surface area. However, with time the particles grew in size and the surface area decreased. After about 42 days of equilibration, the akaganeite particles grew to 60–300 nm long, 10–50 nm wide and with a surface area of 55 $m^2/g$, which is similar to other reports for akaganeite prepared at higher temperatures. In the $NO_3$ system [$Al(NO_3)_3/Fe(NO_3)_3$], lepidocrocite ($\gamma$-FeOOH) and goethite ($\alpha$-FeOOH) were formed. In a mixed anion system ($Cl/NO_3$) solid phases identified were akaganeite ($\beta$-FeOOH) and lepidocrocite ($\gamma$-FeOOH). The introduction of polynuclear hydroxy-Al along with monomer Al in Cl and $NO_3$ systems of Fe affected the quantity and quality of the solid phase. The crystallinity of $\beta$-FeOOH formed in the presence of polynuclear hydroxy-Al ions in a Cl-system was more disordered than when it formed in the presence of monomer Al-ions alone. In $NO_3$ systems, polynuclear hydroxy-Al hindered the formation of goethite ($\alpha$-FeOOH). Our experiments showed that Fe oxyhydroxides crystallize readily under acidic conditions in the presence of Al ions and the data also indicated that the Cl was essential for the crystallization of akaganeite, whereas goethite was formed in those systems when Cl was absent.

**Key Words**—Akaganeite, Aluminum, Hydroxy-aluminum ions, Iron hydrolysis, Transmission electron microscopy, X-ray diffraction.

## INTRODUCTION

The Fe oxyhydroxides and oxides (goethite $\alpha$-FeOOH; lepidocrocite $\gamma$-FeOOH; feroxyhyte $\delta$-FeOOH; hematite $\alpha$-$Fe_2O_3$; maghemite $\gamma$-$Fe_2O_3$ and ferrihydrite $5Fe_2O_3 \cdot 9H_2O$) are important minerals which occur in soils of different climatic regions (Schwertmann and Taylor, 1989). These minerals have distinct colors and many soils obtain their color from these minerals. Fe oxide and oxyhydroxide particles contribute to high specific surface area which influences many important soil properties—e.g., efficiency as sorbents and sinks for ionic and nonionic compounds, or stability of soil aggregates and porosity. In contact with the aqueous phase in soils, the surfaces of Fe oxide minerals are hydroxylated and develop pH dependent charge (variable charge). Soils containing amphoteric compounds as such require appropriate management techniques based on their particular nature and properties for growing plants.

There is a substantial amount of literature on the synthesis and properties of Fe oxide minerals (Schwertmann and Fischer, 1973; Taylor and Schwertmann, 1974, 1978; Cornell *et al.,* 1974, 1989; Schwertmann and Taylor, 1989; Taylor and McKenzie, 1980; Cornell and Giovanoli, 1988, 1989; Schwertmann, 1990). Many of these studies discuss the Fe oxide minerals which were synthesized in an alkaline environment and at temperatures much greater than those prevalent under ambient conditions.

However, in many acidic soil and aquatic environments the translocation and transformation of Fe oxide minerals takes place at ambient temperatures, <30°C, and invariably in the presence of other metal ions especially Al which is normally present. The concentration of Al in most normal acidic environments is $\leq 10^{-4}$ moles/liter, which proved to be too low to measure the reaction processes. There is lack of information on the effect of Al on the hydrolysis of Fe, which is very important in acidic environment. To obtain relevant information, experiments were carried out at somewhat higher concentration of Al ($8.33 \times 10^{-3}$ and $8.33 \times 10^{-4}$ moles/liter).

It was the objective of this study to: (1) investigate the hydrolytic behavior of Fe solutions in the presence of Al ions in association with Cl and $NO_3$ anions at room temperature under acidic environment; to (2) identify and characterize the solid phases formed; and to (3) compare these results with the solid phases formed at relatively elevated temperatures and in alkaline medium reported in literature.

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## EXPERIMENTAL

### *Fe solutions*

The Fe solutions were prepared in pyrex glass vessels by dissolving analytical grade $FeCl_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ salts in $CO_2$-free redistilled water. The concentration of Fe was 0.1 M and the solutions were freshly prepared for each experiment.

### *Al solutions*

A stock solution of 0.1 M $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was prepared in $CO_2$-free redistilled water. From this stock solution 0.01 M Al solutions were prepared for each experiment. For solutions which contained a mixture of monomer and polynuclear hydroxy-Al ions, 100 ml of each of 0.01 M $AlCl_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ solutions were titrated separately with 0.1 M NaOH under a $N_2$ atmosphere using a Metrohm titroprocessor. Increments of 0.05 ml of 0.1 M NaOH were added while vigorously stirring the Al solutions. The final OH/Al molar ratio of the titrated solutions was 1.5. After completing this titration, the concentrations of monomer and polynuclear Al species attain a stable state within one day and remain stable during at least 90 days (Singh and Kodama 1988). The concentration of monomer and polynuclear Al was $4.13 \times 10^{-3}$ and $4.60 \times 10^{-3}$ moles/liter, respectively.

To investigate the effect of concentration of Al ions on the hydrolysis of Fe, a further diluted solution of 0.001 M $AlCl_3 \cdot 6H_2O$ was used and similarly neutralized as above to OH/Al molar ratio of 1.5.

### *Hydrolysis of Fe solutions*

Eight preparations were made at ambient conditions to determine the effect of Al species (monomer Al and monomer + polynuclear Al) and anions (Cl and $NO_3$) on the hydrolytic products of Fe solutions. For each preparation, 250 ml of Al solution was transferred to a reaction vessel, while stirring vigorously with a magnetic stirrer, 50 ml of the 0.1 M Fe solution was added dropwise by an automatic buret. The total volume of each preparation was 300 ml, thus the concentration of Al and Fe was approximately 8.33 and 16.67 mmole/liter, respectively. The eight different systems were as follows:

1) monomer Al in $AlCl_3/FeCl_3$ system,
2) monomer Al in $AlCl_3/Fe(NO_3)_3$ system,
3) monomer Al in $Al(NO_3)_3/FeCl_3$ system,
4) monomer Al in $Al(NO_3)_3/Fe(NO_3)_3$ system,
5) monomer + polynuclear Al in $AlCl_3/FeCl_3$ system,
6) monomer + polynuclear Al in $AlCl_3/Fe(NO_3)_3$ system,
7) monomer + polynuclear Al in $Al(NO_3)_3/FeCl_3$ system,
8) monomer + polynuclear Al in $Al(NO_3)_3/Fe(NO_3)_3$ system.

There were also two more experimental systems: one with a dilute 0.001 M $AlCl_3 \cdot 6H_2O$ with $FeCl_3$ solution and another where 50 ml of 0.1 M $FeCl_3$ was added to 250 ml of distilled water in the absence of Al. During magnetic stirring, the preparations were protected from the heat from the electrical motor by circulating constant temperature water around the reaction vessels. The samples were aged for 3 h to 42 days. From time to time, a small volume of the sample suspension was withdrawn and examined for its solid content, the identification of the solid phase formed, and the composition of the supernatant solution.

### *Analytical techniques*

The colloidal precipitates of Fe which formed on hydrolysis were separated by centrifugation, or vacuum filtration using different pore size millipore filters. The pH of the supernatant was determined with an Orion ion analyzer. Analyses were done for Fe and Na by atomic absorption spectrophotometry, for monomer Al by an 8-quinolinate extraction method (Okura *et al.*, 1962) and for polynuclear Al by the reaction with 8-hydroxyquinoline for 0.5 h (Turner, 1969). For the elemental composition of akaganeite, the sample was ignited at 1000°C and digested in HCl. The resulting solution was analysed for Fe and Al by AA.

The Fe oxyhydroxide solid phases were examined by an X-ray powder diffraction method. The solid phases retained on the millipore filter were X-rayed directly by sticking the membranes on glass slides with a strip of double-coated Scotch® tape. This procedure was adapted because the colloidal particles were very small and could not be removed from the filter membrane surface. On aging, the particle size increased and solid materials were separated by centrifugation or easily removed from filter paper. After washing with $H_2O$, the solids were resuspended in water and one millilitre of the suspension containing about 10–30 mg of solid was pipetted onto a 25 × 30 mm glass slide and dried. XRD patterns were obtained on the oriented specimens by a fully automated SCINTAG PAD V X-ray diffractometer equipped with a graphite crystal monochromator and using CoK$\alpha$ radiation ($\gamma = 1.7902$ Å). In some cases XRD patterns were also obtained with randomly mounted samples after powdery samples were collected by freeze drying.

The morphology of the solid products obtained was examined by a Philips EM300 transmission electron microscope operated at 80 kV. A droplet of very dilute suspension (approx. 0.01%) was spotted onto a copper grid coated with a thin carbon film and dried in air for observation under the electron microscope.

Surface areas were measured by the BET method using a Quantasorb analyser. Thermogravimetric data were obtained with a Dupont instrument at the Institute for Research in Construction by the courtesy of National Research Council, Ottawa, Canada.

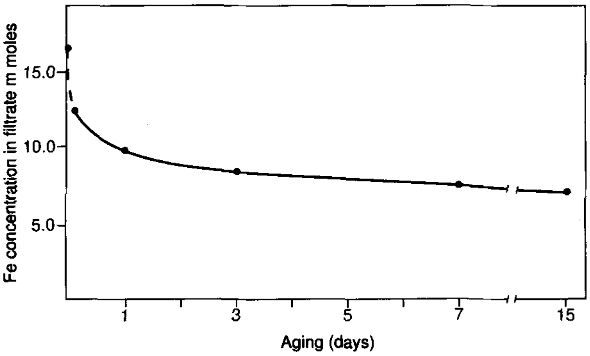

Figure 1. Decrease in the concentration of Fe in solution as a function of hydrolysis time.

Table 1. An estimate of the size of Fe oxyhydroxide colloidal particles from absorbance and different pore size filtrations.[1]

| Pore size of millipore filter (nm) | Absorbance | |
|---|---|---|
| | At 490 nm | At 520 nm |
| 450 | 0.939 | 0.434 |
| 200 | 0.672 | 0.315 |
| 50 | 0.075 | 0.043 |
| 25 | 0.066 | 0.038 |

[1] Hydrolytic reaction time = 48 h.

## RESULTS AND DISCUSSION

### *Hydrolytic processes and products*

Physical and chemical changes occurred very fast in the mixed solutions of Al and Fe. On the addition of the yellowish $FeCl_3$ solution to the clear solution of Al salts, the hydrolysis of Fe proceeded immediately, as the yellowish color turned into a deep burgundy wine color. Visual observations did not give an indication to the presence of colloidal particles. However, ultracentrifugation and micropore filtration confirmed that the deep burgundy coloration was due to the presence of colloidal particles. In the absence of Al ions this rapid hydrolysis of Fe did not occur. The initial concentration of 16.67 mmole Fe in $AlCl_3/FeCl_3$ system was reduced to 12.36, 9.85, 8.59 and 7.52 mmole after 3, 24, 72 and 168 h, respectively (Figure 1). The hydrolysis of Fe was completed in about 7 days in the present experiment. Of the total amount of Fe precipitated, about 47% was taken out of the solution in the first 3 h and $\approx$75% in 24 h of reaction time. In the system where the concentration of Al was one tenth that of the main experiments (0.001 M Al), the hydrolysis of Fe was slow and a smaller amount of akaganeite was formed.

The relative size of the colloidal particles was estimated by filtering the suspension through different pore size filters and then measuring the light absorbance on a Beckmann DU-7 spectrophotometer at two wavelengths of 490 and 520 nm. For $AlCl_3/FeCl_3$ system with 48 h aging, the majority of the colloidal particles of Fe oxyhydroxide compound were in the range of 50–200 nm (Table 1).

XRD data (Figure 2) of the Fe colloid obtained in the $AlCl_3/FeCl_3$ system at time intervals of 24 h, 3 days and 10 days indicated that the basic structural framework of akaganeite appeared to have formed after 24 h aging and its crystallinity was rapidly developed between 3 to 10 days of aging as indicated by the sharpness and intensity of the peaks. As will be discussed later, the final product of this system was a single crystalline phase of akaganeite. The synthesis and properties of akaganeite have been investigated by many scientists from various disciplines (Mackay, 1960, 1962; Soderquist and Jansson, 1966; Paterson and Tait, 1977; González-Calbet *et al.*, 1981; Borggaard, 1983), however, to our best knowledge this is the first report of the fast formation of akaganeite near the ambient temperature of acidic environment. Our research indicates that the presence of Al ions play an important role in the hydrolysis of Fe under acidic conditions. Although we are not able to offer any definite mechanism for this Fe hydrolysis but we do know that the concentration of Al ions in the system determined the rapidity of hydrolysis and the amount of precipitate formed.

### *Effect of anions (Cl, $NO_3$) and Al-species on hydrolysis of Fe solutions*

XRD patterns in Figures 3a–3f show that different anions and different species of Al significantly affected

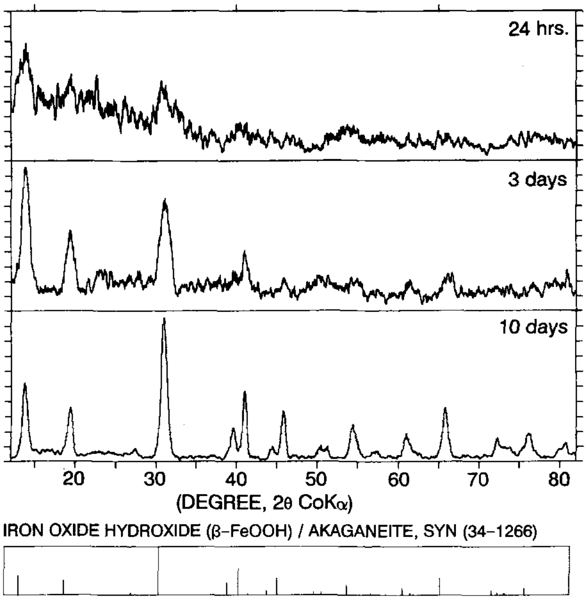

Figure 2. Typical XRD patterns showing the rapid crystallization of the FeOOH precipitate as a function of time of aging.

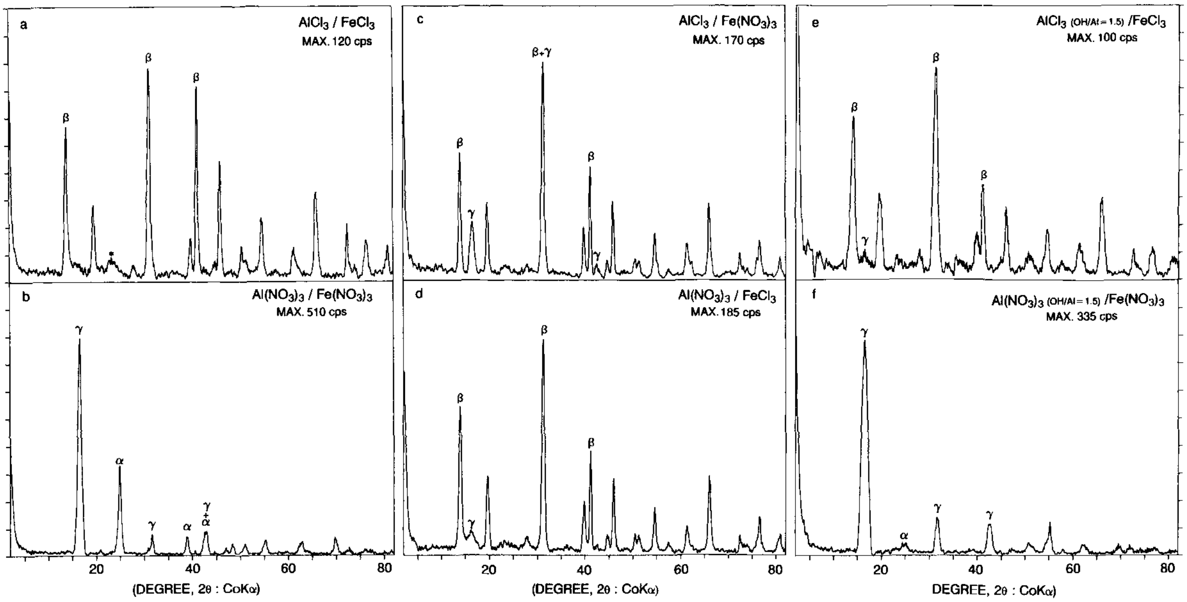

Figure 3. XRD patterns displaying the influence of different anions and of the Al ions on the phases of FeOOH crystallized on hydrolysis of Fe at ambient temperature (a) $AlCl_3/FeCl_3$; (b) $Al(NO_3)/Fe(NO_3)_3$; (c) $AlCl_3/Fe(NO_3)_3$; (d) $Al(NO_3)_3/FeCl_3$; (e) $AlCl_3(OH/Al = 1.5)/FeCl_3$; (f) $Al(NO_3)_3(OH/Al = 1.5)/Fe(NO_3)_3$. $\alpha$, $\beta$, $\gamma$ represent major diffraction lines of goethite, akaganeite and lepidocrocite, respectively.

the type of FeOOH phase being formed. In the $AlCl_3$/$FeCl_3$-monomer Al system (Figure 3a), akaganeite was the only crystalline phase of FeOOH. The peaks are quite sharp which indicated that the compound was represented by well ordered crystals. In the Al $(NO_3)_3$/$Fe(NO_3)_3$-monomer Al system (Figure 3b) there are two phases of FeOOH, lepidocrocite and goethite. In the mixed anion system ($Cl/NO_3$) and monomer Al (Figures 3c and 3d), the solid phases identified are akaganeite and lepidocrocite. The relative degree of crystal ordering of akaganeite was better than that of lepidocrocite.

The effect of the presence of polynuclear Al species is demonstrated in Figures 3e and 3f. In the Cl system, less ordered akaganeite was formed with a small amount of lepidocrocite (Figure 3e), whereas in the $NO_3$ system the lepidocrocite was the major phase of FeOOH (Figure 3f). The comparison of these results with their monomer Al counterparts indicated that polynuclear Al ions decreased the crystal ordering of akaganeite and aided the formation of lepidocrocite in the presence of Cl anions and hindered the formation of goethite in the presence of $NO_3$ anions. In the mixed Cl/$NO_3$ system the presence of polynuclear Al decreased the crystallinity of akaganeite as well as the lepidocrocite. However, the relative quantity of the lepidocrocite was increased (figure not shown).

The results of eight different experiments are summarized in Table 2. We found that akaganeite was only formed when Cl was present, as reported by many researchers. In the presence of another anion ($NO_3$) along with Cl ions, lepidocrocite appeared in the system and the formation of akaganeite was retarded. It is also noted that goethite appeared only in those systems when Cl was absent. This suggests that in pedoenvironments the coprecipitation of akaganeite and goethite may not occur. The $NO_3$ ions are favorable to the formation of lepidocrocite and goethite. However, the presence of polynuclear Al species along with monomer Al were beneficial to the formation of lepidocrocite over goethite. In general, polynuclear Al species appear to retard the crystallization of any form of FeOOH and this effect was greatest on goethite followed by lepidocrocite and akaganeite.

### *Characterization of the akaganeite formed*

*X-ray diffraction data.* As akaganeite was well crystallized within a relatively short period of time at room temperature under acidic conditions, we thought that such a formation of akaganeite was exceptional and it was worthy to characterize the mineral formed after 42 days aging. Table 3 shows the XRD data compared with the d-values, intensities and hkl indices given in JCPDS (card #34-1266). The agreement was very good except that the present material had two very weak unidentified diffraction lines at 4.49 and 1.824 Å and more than double the relative intensity for the diffraction line at 7.53 Å. Since this line is indexed as 110 (hkl), if the intensity anomaly were due to a specific crystal habit, the corresponding higher order lines such

Table 2. Summary of Fe oxyhydroxide phases identified in different systems as influenced by Al ions and anion species.

| System | | | | Product | |
|---|---|---|---|---|---|
| Al-component | | Fe-component | | Solid phasse | Relative crystallinity and yield |
| 1. Mono Al | Cl | Cl | Fe | $\beta$-FeOOH | |
| 2. Mono + Poly Al | Cl | Cl | Fe | $\beta$-FeOOH<br>$\gamma$-FeOOH | broader XRD peaks<br>broader XRD peaks |
| 3. Mono Al | $NO_3$ | $NO_3$ | Fe | $\gamma$-FeOOH<br>$\alpha$-FeOOH | |
| 4. Mono + Poly Al | $NO_3$ | $NO_3$ | Fe | $\gamma$-FeOOH<br>$\alpha$-FeOOH | broader XRD peaks<br>< quantity |
| 5. Mono Al | Cl | $NO_3$ | Fe | $\beta$-FeOOH<br>$\gamma$-FeOOH | |
| 6. Mono + Poly Al | Cl | $NO_3$ | Fe | $\gamma$-FeOOH<br>$\beta$-FeOOH | broader XRD peaks<br>broader XRD peaks |
| 7. Mono Al | $NO_3$ | Cl | Fe | $\beta$-FeOOH<br>$\gamma$-FeOOH | |
| 8. Mono + Poly Al | $NO_3$ | Cl | Fe | $\beta$-FeOOH<br>$\gamma$-FeOOH | broader XRD peaks<br>broader XRD peaks |

Mono Al = monomer Al, Poly Al = Polynuclear Al.

as the 220, 440 and 550 reflections at 3.744, 1.865 and 1.487 Å, respectively, should have similar increase. However, this was not the case. Crystal habit is not responsible for the anomaly. No apparent reason(s) for the anomaly was identified.

Table 3. Comparison of synthetic akaganeite XRD data (121-87) with the JCPDS data (card #34-1266).

| 121-87 | | | JCPDS (#34-1266) | |
|---|---|---|---|---|
| d (Å) | I/Io | hkl | d (Å) | I/Io |
| 7.53 | 97 | 110 | 7.467 | 40 |
| 5.30 | 48 | 200 | 5.276 | 30 |
| 4.49[1] | 3 | | | |
| 3.744 | 4 | 220 | 3.728 | 5 |
| 3.345 | 100 | 310 | 3.333 | 100 |
| 2.640 | 28 | 400 | 2.634 | 25 |
| 2.556 | 58 | 211 | 2.550 | 55 |
| 2.486 | 1 | | 2.483 | 2 |
| 2.361 | 9 | 420 | 2.356 | 9 |
| 2.300 | 37 | 301 | 2.295 | 35 |
| 2.107 | 9 | 321 | 2.103 | 7 |
| 2.070 | 7 | 510 | 2.066 | 7 |
| 1.957 | 21 | 411 | 1.954 | 20 |
| 1.865 | 4 | 440 | 1.862 | 4 |
| 1.824[1] | 3/8 | | 1.807 | 1 |
| 1.758 | 16 | 600 | 1.755 | 15 |
| 1.732 | 4 | 501, 431 | 1.730 | 3 |
| 1.659 | 1 | | 1.666 | 1 |
| 1.645 | 36 | 521 | 1.643 | 35 |
| 1.517 | 14 | 002 | 1.515 | 9 |
| 1.505 | 5 | 611 | 1.503 | 5 |
| 1.492 | 3 | | 1.489 | 3 |
| 1.487 | 3 | 112, 710, 500 | 1.485 | 3 |
| 1.458 | 3 | 640 | 1.457 | 1 |
| 1.447 | 16 | 541 | 1.445 | 15 |
| 1.384 | 7 | 730, 312 | | |
| 1.381 | 5 | | | |

[1] Unknown weak extra diffraction lines.

*Chemical data.* An air-dry sample of akaganeite was placed in an oven at 110°C overnight. The resulting weight loss was attributed to $H_2O(-)$. Subsequently the oven-dry sample was ignited at near 1000°C for 30 min. This ignition loss was allocated to $H_2O(+)$. The chemical composition of the ignited sample of akaganeite is given in Table 4. When corrected for insoluble residue and $H_2O(-)$, the reevaluated composition is 80.17% $F_2O_3$, 0.23% $Al_2O_3$ and 19.60% $H_2O(+)$. Since theoretical values of $F_2O_3$ and $H_2O$ for FeOOH are 89.87 and 10.13%, respectively, there is thus a discrepancy, which is largely due to overestimation of $H_2O(+)$. When 19.60% $H_2O(+)$ is normalized to the value of 10.13% $H_2O(+)$, the $F_2O_3$ and $Al_2O_3$ contents in our synthetic akaganeite would be 89.61 and 0.26%, respectively. The $Fe_2O_3$ content is very close to the theoretical value, 89.87%. In spite of the system containing Al, the amount of $Al_2O_3$ found in the mineral was minimal. This indicated that the structural incorporation of Al, if any, with akaganeite was negligibly small.

*Thermogravimetric data.* Figure 4 shows thermogravimetric (TG) and differential thermogravimetric (DTG)

Table 4. Chemical analysis of synthetic akaganeite.

| Component | Percent |
|---|---|
| $Fe_2O_3$ | 78.45 |
| $Al_2O_3$ | 0.23 |
| $H_2O$ (+) | 19.18 |
| $H_2O$ (−) | 2.23 |
| Insoluble residue | 0.37 |
| Total | 100.46 |

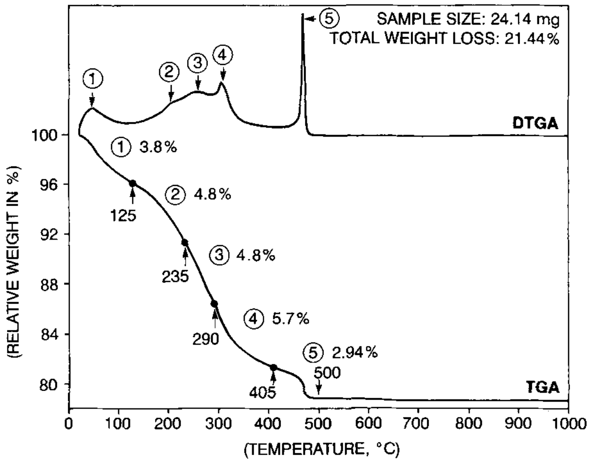

Figure 4. DTGA and TGA curves for a synthetic akaganeite from $AlCl_3/FeCl_3$ system; heating rate of 10°C/min and air flow of 5 ml/min.

curves of the synthetic akaganeite. Five different weight loss steps were: (1) up to 125°C (3.8% wt. loss); (2) 125°–235°C (4.8%); (3) 235°–290°C (4.8%); (4) 290°–405°C (5.1%); and (5) 405°–500°C (2.94%). The general shape of the weight loss curve is similar to the one reported by Paterson *et al.* (1982) for synthetic akaganeite prepared at 70°C. Total weight loss was 21.44% which was in good agreement with 21.41% obtained by oven-dry and ignition losses. Step 1 was evidently due to the hygroscopic moisture. Step 5 accompanying a sharp change in DTG curve was due to the dehydroxylation of akaganeite to transform to its oxide form, $\alpha$-$Fe_2O_3$ or $\gamma$-$Fe_2O_3$ or a mixture of both, which was compatible with the data from differential thermal analysis (Mackenzie, 1970). Steps 2, 3 and 4 were continuous and could not clearly be separated, indicating the presence of various types of bound water, water of crystallization, or hydroxyls. This appears to be reflected in the complexity of the akaganeite structure. Akaganeite has an open structure similar to hollandite ($\alpha$-$MnO_2$) (Burns and Burns, 1977). In akaganeite, four double chains of edge-shared $Fe(O,OH)_6$ octahedra are sharing corners of the double chains to form a tunnel structure. Actual crystals of akaganeite are spindle-shaped elongated along c-axis and built up of bundles of parallel rods. According to Gallagher (1970), each rod has a hollow (tube-like) structure with its shorter edge dimension (along a-axis) of about five akaganeite units. Thus crystals have channels which are large enough to trap water molecules, perhaps bound to some exposed broken bonds within channels. In addition to this, the structural features of akaganeite allow two types of hydroxyls, internal and external. Therefore, the continuous weight loss observed between 125° and 405°C should be considered as nearly simultaneous dehydration of those various waters or hydroxyls.

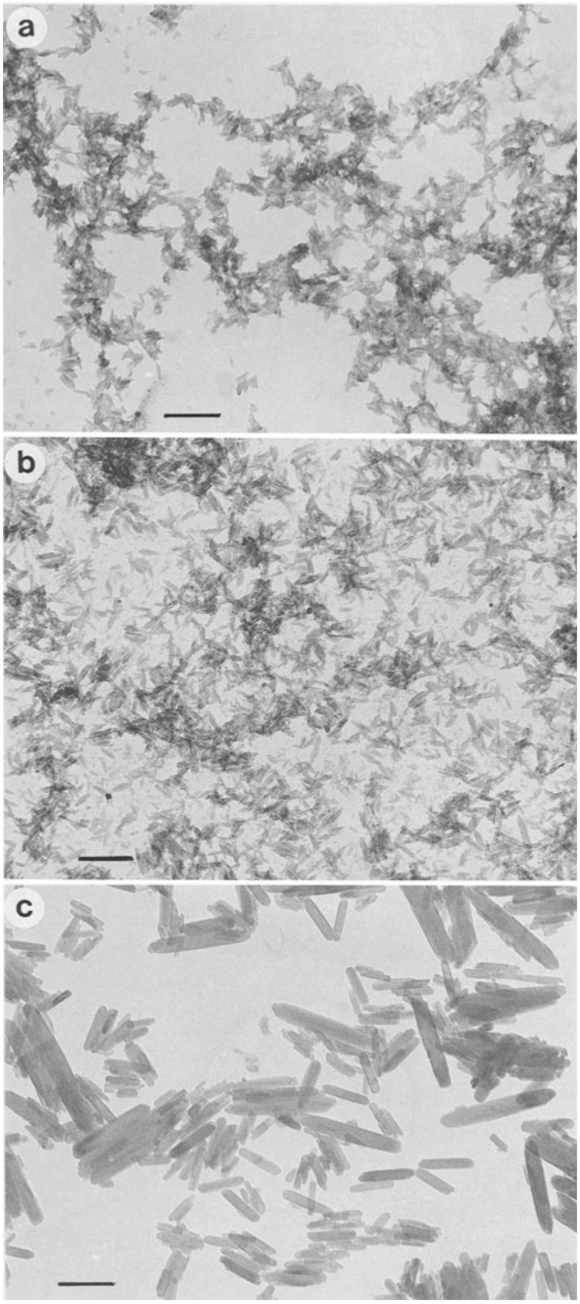

Figure 5. Transmission electron micrographs of synthetic akaganeite sample showing crystal formation and particle growth as function of time of hydrolytic reaction: (a) 3 h; (b) 14 days; (c) 42 days; bar scale is 10 nm in the micrographs.

*Electron microscopic observations.* Observations were made on the samples collected from three different stages (3 h, 2 weeks and 6 weeks) of aging (Figure 5). As seen from the electron micrographs given in Figure 5, crystals are lath-shaped elongated along the c-axis. Their size increases from 16 to 180 nm in average

Table 5. Particle size and surface area measurements of akaganeite.

| Reaction time | Particle size (nm) | Surface area ($m^2/g$) |
|---|---|---|
| 3 h | 12–20 long | — |
| | 2–5 wide | |
| 10 days | — | 116.5 |
| 14 days | 15–40 long | — |
| | 2–5 wide | |
| 42 days | 60–300 long | 55.0 |
| | 10–50 wide | |

length as aging proceeds (Table 5). The increase in size was associated with the decrease in surface area which was measured by a $N_2$ gas adsorption method. The surface area of 116.5 $m^2/g$ for 10 day-aged sample was decreased to 55.0 $m^2/g$ for 6 weeks aged sample (Table 5). It appears that during the hydrolysis of Fe solutions in the presence of Al, one could obtain different size crystals as function of aging time which will have an impact on the surface area.

## CONCLUSION

The results of our research show that Al ion species have a significant influence on the hydrolysis of Fe solutions in acidic condition and at ambient temperature environment. The nature of the Fe oxyhydroxide precipitate and the amount of the precipitate was affected by the amount and the type of Al ion present, as well as by the presence of different anions. The presence of Cl ions was a required condition for the formation of akaganeite. Goethite precipitated only in those systems where Cl was absent. Nitrate ions were favourable to the formation of lepidocrocite and goethite. The presence of polynuclear Al species generally retarded the crystallization of any form of FeOOH compound. The results suggest that under acidic pedoenvironment the coprecipitation of akaganeite and goethite may not occur.

Akaganeite ($\beta$-FeOOH), a relatively rare mineral in nature, precipitated easily in $AlCl_3/FeCl_3$ system at ambient temperature in the presence of Al ions. The growth in particle size and crystallinity of akaganeite increased rapidly on aging and this was associated with the change in surface area of akaganeite.

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