

THE INFLUENCE OF ALUMINUM ON THE FORMATION OF IRON OXIDES. IV. THE INFLUENCE OF [Al], [OH], AND TEMPERATURE

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Abstract—Ferrihydrite was transformed to goethite and/or hematite at various temperatures, [OH], and [Al]. Increasing temperature and [Al] favored hematite, increasing [OH] favored goethite. A given [Al] induces hematite more effectively at lower [OH]. Al substitution in goethites increased linearly with log[Al], but was independent of temperature. At a given [Al], substitution increased with decreasing [OH]. In a plot of Al/Fe in the goethite against $[Al]/[Fe(OH)_4^-]$ in solution a straight line was obtained for all preparations independent of [OH].

Key Words—Aluminum, Ferrihydrite, Goethite, Hematite, Iron oxides.

INTRODUCTION

When pure ferrihydrite is kept under water, variation of pH, temperature, salt content, or suspension concentration can influence the nature of the product, i.e., whether goethite (FeOOH) or hematite (Fe₂O₃) or both are produced. Consequently, numerous procedures have been used to produce a required product. However, when Al is also added to the system in an attempt to form Al-substituted iron oxides, the formation of hematite seems to be favored (Gastuche *et al.*, 1964; Wolska, 1976; Schwertmann *et al.*, 1977, 1979). In a previous paper (Lewis and Schwertmann, 1979), it was shown that preparation of a pure goethite is possible by storing ferrihydrite in 1 M KOH containing Al both in the presence or absence of the original nitrate anions. In addition, goethites with equally high Al substitution formed from pure Fe-ferrihydrite stored in KOH containing dissolved Al as well as from Al-ferrihydrites stored in KOH. Consequently, it was decided to study the influence of Al concentration, pH, and temperature on the relative proportion of goethite and hematite in the final mixture and on the degree of Al substitution in these oxides.

MATERIALS AND METHODS

Merck Analytical Grade reagents were used and all preparations were aged in polyethylene containers.

X-ray diffraction (XRD) data were obtained on gently pressed powder samples using CoK α radiation analyzed by a Philips diffractometer with a graphite diffracted beam monochromator. The extent of Al substitution in any goethite formed was assessed by measuring the position of the 111 peak after running all

diffraction traces on two separate pressings under standardized conditions without an internal standard. The accuracy and reproducibility of the same pressing were within 0.02°2 θ . The change in position resulting from Al substitution was assumed to be linearly related to the mole composition (Vegard, 1921). When both goethite and hematite were produced, approximate values for the composition were obtained by comparing the areas of the goethite 110 and the hematite 012 peaks with those of standard mixtures of the pure oxides. The amount of unchanged ferrihydrite remaining at the end of the storage periods was estimated by the acid-ammonium oxalate extraction technique of Schwertmann (1964). Fe and Al in both oxalate and concentrated HCl extracts were determined using a Perkin Elmer 420 Atomic Absorption Spectrophotometer (AA) with an acetylene/air flame for Fe and an acetylene/nitrous oxide flame for Al. No mutual interference of Al and Fe was noticed.

Preparation of precipitates for storage in KOH

Preliminary experiments. Fifteen mmole of KOH solution (0.6 M) were added slowly with shaking to 5 mmole of Fe(III)-nitrate solution (0.1 M) and the resultant precipitate (total volume 75 ml) allowed to stand for 15 min. A calculated amount of extra KOH (2 M) was then added to ensure that when all additions had been made the final KOH concentration was 1 M. After 0-3 hr the required amount of Al was added as a solution of aluminum nitrate dissolved in a slight known excess of KOH (0.7 M KAlO₂ in 1.5 M KOH) to give a total volume of 250 ml).

Recommended technique. A standard solution of potassium aluminate in KOH (0.25 M Al) was prepared by dissolving a weighed amount of aluminum nitrate in distilled water and pouring the resultant solution slowly with stirring into sufficient standardized KOH solution

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Table 1. Effect of preliminary treatment on the nature of products following storage at 70°C in 1 M KOH.

Sample	Storage period			Products ²				W.H.H. ³ (°2θ)		
	Pre-liminary ¹ (hours)	At 70°C (days)	Al conc. (M)	G	H	F	Al	G ₁₁₀	G ₁₁₁	H ₀₁₂
1	3	15	0	99	0	1	—	.75	.59	—
2	3	15	0.1	99	0	1	—	.91	.73	—
3	3	15	0.2	99	0	1	—	.80	.66	—
4	0	15	0.5	0	50	50	—	—	—	.23
5	0	14	0.1	32	33	35	—	.28	.28	.20
6	0	14	0.2	0	34	66	—	—	—	.22
7	0	14	0.3	0	28	72	b,gi	—	—	.20
8	0	14	0.4	0	13	87	b,gi	—	—	.20
9	0	14	0.5	0	8	92	b	—	—	.21
10	1	13	0.3	99	0	1	gi	.60	.65	—
11	3	13	0.3	99	0	1	gi	.75	.70	—

¹ Preliminary period in Al-free alkali.

² Final products: G = goethite, H = hematite, F = ferrihydrite, all as percentage of the added iron. Al = aluminum hydroxides, b = bayerite, gi = gibbsite.

³ Width at half peak height (uncorrected). Instrumental broadening is $0.20 \pm 0.02^\circ 2\theta$ as determined with $\text{Pb}(\text{NO}_3)_2$.

to supply 4 moles of KOH per mole of Al, and also sufficient extra KOH to keep the KOH concentration at 0.5 M when finally made to volume. The required volume of this aluminate solution was dispensed into polyethylene bottles and calculated volumes of water and further standardized KOH added to supply sufficient alkali to precipitate the Fe subsequently added and also to adjust the whole suspension to the desired final KOH level. Finally, a measured volume of a freshly prepared solution of Fe(III)-nitrate (1 M) was added rapidly to the swirled alkaline Al solution. The bottle was then sealed and the suspension shaken vigorously by hand for a few seconds before placing into air ovens maintained at the desired temperatures.

In most cases the total amount of Al in the system was at least equal to that of the Fe. Therefore changes in Al concentration during crystal growth would be slight, and the products that crystallized would have formed under essentially constant conditions. At lower Al concentrations it was necessary to increase the volume of solution to supply the appropriate amount of Al. This resulted in a wide range of suspension concentrations from 20 mmole Fe/liter in the majority of cases down to a minimum of 1 mmole Fe/liter. However, since it had been shown (Lewis and Schwertmann, 1979) that at 1 M KOH the concentration of suspension (particularly for low levels) was not important except insofar as it controlled the Al concentration, it was expected that the same principle would apply to other levels of KOH.

After the required period, during which the suspensions were periodically shaken briefly by hand, the products were washed by centrifugation, adjusting the second and subsequent washes to a pH of about 8 to allow maximum flocculation and efficient removal of soluble material with negligible loss of solids. After

thorough washing the solids were dried, usually by heating overnight in an air oven at 70°C followed by gentle crushing and thorough mixing before storing in glass vials for later analyses.

RESULTS AND DISCUSSION

Effect of pretreatment

Preliminary experiments were aimed at testing the influence of elevated temperature on the rate of conversion of the ferrihydrite to crystalline oxides since earlier work at 20°C (Lewis and Schwertmann, 1979) showed that in the presence of 1 M KOH the rate of crystallization decreased markedly with increasing levels of Al. Data given in Table 1 for three batches of preparations stored at 70°C for 13–15 days indicate the problems of reproducibility which can be encountered in mixed Fe/Al systems unless all variables are recognized and carefully controlled. In samples 1–3 the freshly precipitated ferrihydrites were unintentionally allowed to stand for 3 hr in 0.6–0.7 M KOH before the Al was added; whereas sample 4 had been kept at pH 7. At the time of addition of the aluminate, suspensions 1, 2, and 3 were slightly lighter in color than sample 4, the pure ferrihydrite. After storage at 70°C for 15 days, samples 1–3 had been almost entirely converted to crystalline material as shown by the amount of iron extracted by acid-oxalate. The products were purely goethite with some Al substitution, inferred from the shift of the 111 peak, increasing with Al addition. However, sample 4 showed no goethite, being a mixture of well-crystallized hematite and unchanged ferrihydrite. The slight yellowing in color of suspensions 1–3 before addition of the aluminate solution suggested that conversion of ferrihydrite to goethite had probably begun and that on addition of aluminate, the goethite seeds were

Table 2. Nature of crystalline products after storage for 16 days at 70°C at various [OH] and [Al].

KOH (M)	Al (mM)	Products ¹		Al in goethite (mole %)		KOH (M)	Al (mM)	Products ¹		Al in goethite (mole %) XRD ²
		G	H	XRD ²	AA ³			G	H	
1.0	0	100	—	0	0	0.03	0	100	—	0
	20	100	—	4	6.0		1	100	—	6
	40	100	—	8	9.1		2	90	10	7
	60	100	—	11	12.4		3	75	25	9
	80	100	—	14	14.5		4	65	35	11
	100	100	—	14	15.5		6	40	60	15
	110	85	15	14			10	20	80	19
	120	70	30	14						
	130	65	35	15						
	150	15	85	17						
0.3	0	100	—	0	0	0.01	0	100	—	0
	10	100	—	4	7.3		0.5	50	50	8
	20	100	—	8	11.7		0.7	45	55	11
	30	100	—	12	14.4		1	42	58	14
	40	85	15	15			1.4	40	60	15
	50	50	50				2	35	65	16
	60	25	75				4	15	85	20
							6	10	90	~25
					8	3	97			
					10	<2	>98			
0.1	0	100	—	0	0	0.001	0	100	—	
	5	100	—	7	10.0		1	3	97	
	6	100	—	9	10.5		2	<1	>99	
	7	100	—	9	11.3		3	—	100	
	8	100	—	10	12.8		4	—	100	
	9	95	5	11			5	—	100	
	10	92	8	11						
	15	80	20	13						
	20	50	50	15						
	25	40	60	19						

¹ G = goethite, H = hematite, as percentage of the crystalline material produced.

² X-ray powder diffraction estimate.

³ Determined after dissolution in conc. HCl.

able to grow rapidly, subsequently incorporating Al into the structure.

In samples 5–9 of Table 1, the possibility of forming pure goethite seeds was eliminated (see recommended technique). The influence of Al on the products was quite different from that observed in samples 1–3 (Table 1). Only at the lowest level of Al addition (sample 5 at 0.1 M Al) was any goethite formed (together with similar quantities of hematite) but due to lack of prenucleation a considerable fraction of the initial precipitate was still oxalate-extractable. However, the goethite which formed was much better crystalline than in samples 1–3 as indicated by the much smaller widths of the 110 and 111 peaks. In addition, the content of Al in the goethite estimated by X-ray diffraction was much greater for sample 5 (15 mole %) than in sample 2 (4 mole %), the comparable preparation of the initial batch.

At an aluminate concentration of ≥ 0.2 M no goethite was formed. Mixtures of hematite and residual ferrihydrite were found with the amount of hematite decreasing as the Al level increased. At levels of alumi-

nate ≥ 0.3 M, considerable amounts of gibbsite and/or bayerite were also detected.

Samples 10 and 11 were prepared to check whether storage of a pure Fe ferrihydrite in 0.75 M KOH at 20°C for short periods (1 or 3 hr) could influence the nature of the product or its composition. The data in the table confirm that preliminary storage allowed purely goethite to be produced at an Al concentration at which, without such preliminary storage, hematite would be produced as the only crystalline product. In addition, at 3 hr of preliminary storage, the apparent Al content of the goethite (as indicated by the position of the 111 peak) was lower (8 mole %) than at 1 hr (11 mole %).

The conclusion from the above experiments must be that without preliminary storage the addition of Al seems to enhance considerably the formation of hematite (or deter goethite nucleation). By contrast, any period of contact with strong KOH in the absence of aluminate tends to predispose the system towards goethite formation, thereby suppressing the tendency to form hematite. This is presumably due to the relatively high solubility of ferrihydrite in strongly alkaline solu-

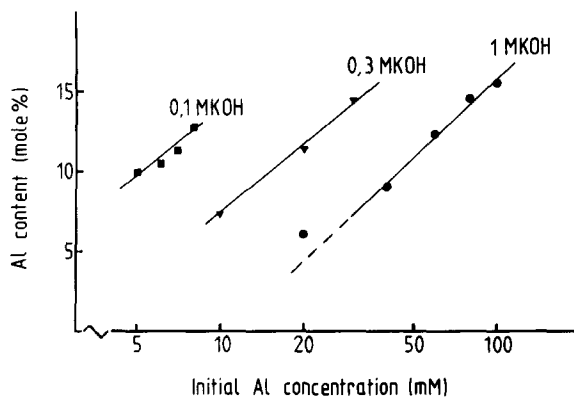


Figure 1. Relationship between Al content of goethite as determined chemically and initial Al concentration in solution at various KOH concentrations.

tion leading to a very high rate of goethite nucleation. Because of this preliminary nucleation, the goethites from samples 10 and 11 are unlikely to be entirely uniform within each crystal since the initial seed would be Al-free, whereas any subsequent growth would contain Al. No evidence for this could, however, be obtained from XRD line profiles (no asymmetric or double peaks). Also, chemical confirmation was difficult due to the presence of crystalline aluminum oxides which also formed at the high level of Al addition used in this series.

Effect of KOH and Al concentration

A constant storage period of 16 days at 70°C was used to determine the influence of KOH and Al concentration on the nature and balance of the crystalline oxides without any prenucleation. The results of this series are given in Table 2. Over the whole range of KOH used (0.001 to 1.0 M) a pure Fe system rapidly produced goethite as the only product. However, as the concentration of Al increased there was an increasing amount of hematite produced, which occurred together with goethite at low levels of Al, or as the only product at 0.001 M KOH and $[Al] > 0.002$ M. The data in Table 2 indicate that as the concentration of KOH decreased, decreasing levels of Al could be tolerated before any hematite was formed.

At any given KOH concentration and wherever goethite was produced, the extent of Al incorporation into the structure increased with Al concentration in the original solution. On the other hand, data are presented in Table 3 which show that for a constant concentration of Al in the initial mixture, the degree of Al substitution in the goethite increased as the KOH concentration decreased. Thus the level of Al incorporation into the goethite structure is dependent on the concentration of both KOH and Al.

This is illustrated further in Figure 1 which shows the

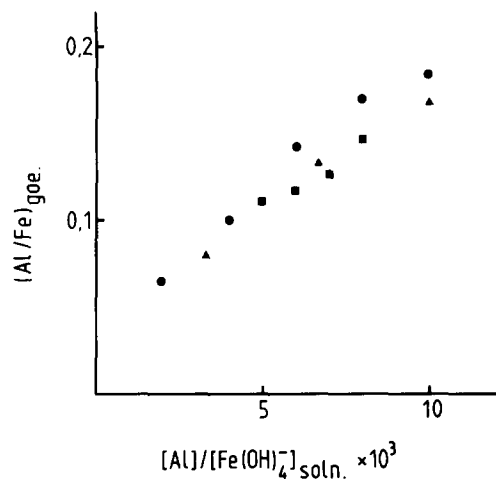


Figure 2. Relationship between Al/Fe mole ratio of goethite and $[Al]/[Fe(OH)_4^-]$ mole ratio in solution at 1 M (●), 0.3 M (▲), and 0.1 M (■) KOH.

composition of the goethite as a function of the aluminum concentration in solution for the three levels of KOH for which Al substituted goethites were produced as the only crystalline phase. (No gibbsite or bayerite was detected.) The linear relationship between the Al content of the goethite and the logarithm of the concentration of Al in the solution which was shown for goethites produced at 20°C (Lewis and Schwertmann, 1979) also holds for the 70°C series. Figure 1 also shows that if the KOH concentration of the suspension is decreased, the Al concentration needed to achieve a given level of incorporation into the goethite also decreases. This is due to the fact that the concentration of $Fe(OH)_4^-$, the soluble Fe species which feeds the growing goethite crystal, is also dependent on the KOH concentration. If $pK_{s4}[pFe(OH)_4^- - pOH^-]$ is taken as 5 (as given for ferrihydrite by Lengweiler *et al.*, 1961), $[Fe(OH)_4^-]$ of the supernatant solutions can be calculated. A plot of the Al/Fe mole ratio of the goethite against the ratio "initial Al concentration/ $[Fe(OH)_4^-]$ in solution" (Figure 2) indicates that the ratio of ions

Table 3. Effect of KOH concentration in goethite production at 70°C in 0.01 M aluminate after 16 days.

KOH (M)	Product ¹		Al in goethite (mole %) ²
	G	H	
1.0	100	0	1
0.3	100	0	3
0.1	97	3	11
0.03	20	80	19
0.01	<2	>98	n.d.

¹ G = goethite, H = hematite, as percentage of the crystalline material produced.

² Estimated from position of the 111 reflection. n.d. = not detected.

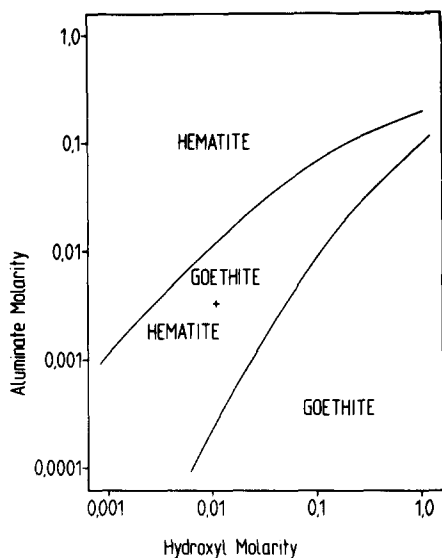


Figure 3. Fields of formation of goethite and hematite at 70°C and various Al and KOH concentrations after more than 16 days of storage.

in the crystalline product is directly related to the ratio in the solution phase and that this relation is the same for all three KOH levels. Since the curve must go through the origin the relationship in its lower part is most probably curvilinear. The slope of the linear part is very low, indicating the low competing power of Al for incorporation into the goethite crystal within this concentration range.

In Figure 3 the crystalline form of the iron oxides produced at 70°C is shown as a function of the initial concentrations of Al and KOH. For all Al concentrations below the lower line, storage at 70°C produced goethite only; therefore this line indicates approximately the conditions of KOH and Al which are critical if pure goethites are to be obtained. As the Al concentration was increased above this critical level the amount of hematite gradually increased until finally a concentration of Al was reached at which hematite was the only crystalline product. In view of the excess of Al added, the upper limit of Al substitution, i.e., ~15 mole %, was reached in all of these hematites. They were relatively well crystalline and showed little or no differential line broadening in contrast to those prepared at much lower pH (5–7) (for details, see Schwertmann *et al.*, 1979).

Effect of temperature

Table 4 gives data for systems kept for 16 days in 0.1 M KOH at levels of Al which were chosen to span the 'critical' range of Figure 3 at 70°C. In all cases increasing the Al concentration increased the extent of Al incorporation into the goethite. Variations in temperature

Table 4. Effect of temperature and Al concentration on the nature of the product after 16 days in 0.1 M KOH.

Temp. (°C)	Al (mM)	Fe _{oxl} ¹	Products ²		Al in goethite (mole %)
			G	H	
25	6	0.43	100	—	9
	8	0.52	100	—	10
	10	0.59	100	—	13
	12	0.60	100	—	13
50	6	0.05	100	—	9
	8	0.11	99	1	11
	10	0.12	90	10	14
	12	0.16	82	18	14
70	6	0.003	100	—	8
	8	0.012	99	1	11
	10	0.018	86	14	12
	12	0.025	77	23	13
90	6	0.002	97	3	9
	8	0.001	91	9	11
	10	0.002	75	25	11
	12	0.002	65	35	13

¹ Ratio of oxalate soluble to total Fe.

² G = goethite, H = hematite, as percentage of the crystalline material produced.

evidently had no effect on the level of Al incorporation at a fixed Al concentration, but did influence the rate of formation of crystalline products. However, increasing the temperature of storage enhanced hematite formation, particularly at the higher levels of Al. Whereas hematite was detected at all Al levels at 90°C, no hematite could be found in any of the 25°C preparations, although at the low temperature full crystallization had not occurred within 16 days. This was evident from the X-ray diffractograms and was also confirmed by the level of Fe extractable by oxalate. The latter also show that at the same temperature crystallization tended to be slower as the Al level increased. The measurements of the widths at half height of the 110 and 111 peaks of goethite indicated that at all temperatures the crystal size was similar for all Al levels. Since at 25°C hematite had not been produced, even at 0.012 M Al, while the level of Al incorporation into the goethite was equally as high as in the samples from higher temperatures, pure goethites of reasonably high Al substitution would be best formed at low temperatures, although the rate of crystal growth is slower. If the trends exhibited in Figure 3 are extrapolated to lower pH values and low temperatures it seems likely that at pH values found in soils and at extremely low concentrations of Al in solution, Al-substituted goethites could be formed, although crystallization may be extremely slow.

GENERAL DISCUSSION

The results have shown that the goethite/hematite ratio in the end product is determined by temperature, [OH], and [Al]. That an increasing temperature favors hematite appears logical because during the transfor-

mation of ferrihydrite to hematite, dehydration is involved which is favored by higher temperature.

The effect of [OH] and [Al] on the goethite/hematite ratio may be explained on the basis of somewhat different mechanisms for the formation of the two forms from ferrihydrite as proposed earlier (Fischer and Schwertmann, 1975). Whereas goethite forms through dissolution of ferrihydrite and crystallization of goethite from solution, hematite formation is preceded by an aggregation of the ferrihydrite and a nucleation within these aggregates. These two processes compete with each other. The increasing tendency for goethite formation with increasing [OH], as well as the incorporation of Al into the structure supports the contention that goethite crystallization proceeds via solution because (1) the solubility of ferrihydrite increases with [OH], and (2) *soluble* Al is the only available form.

The influence of Al is more difficult to explain. Probably, Al retards the otherwise rapid nucleation of goethite, thereby indirectly favoring the competing hematite formation which is less retarded. This is supported by the observation that preliminary storage of ferrihydrite in KOH without Al speeds up the subsequent goethite formation after Al addition to such an extent that hematite formation is prevented. The same retarding effect on goethite formation, which can be overcome by seeding the system, is exerted by silicate (Schwertmann and Taylor, 1972) as well as by oxalate (Fischer and Schwertmann, 1975).

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Резюме—Ферригидрит был преобразован в гетит и/или гематит при разных температурах, [Al] и [OH]. Повышение температуры и [Al] благоприятствует гематиту, а повышенное [OH] благоприятно для гетита. При данном [Al] образование гематита происходит эффективно при низком [OH]. Замещение Al в гетите возрастало линейно с log[Al], но не зависело от температуры. При данном [Al] замещение возрастало с убыванием [OH]. На графике соотношения Al/Fe в гетите и [Al]/[Fe(OH)₄⁻] в растворе была получена прямая линия для всех препаратов независимо от [OH].

Resümee—Ferrihydrit wurde bei verschiedener Temperatur, [OH], und [Al] in Goethit und/oder Hämatit umgewandelt. Hämatit wurde durch steigende Temperatur und [Al], Goethit durch steigendes [OH] gefördert. Bei gegebenem [Al] wird Hämatit daher umso stärker gefördert, je niedriger [OH] ist. Der isomorphe Al-Ersatz in Goethit steigt linear mit log [Al] und war unabhängig von der Temperatur. Bei gegebenem [Al] steigt der Ersatz mit abnehmendem [OH]. Bei Auftragung von Al/Fe in Goethit gegen [Al]/[Fe(OH)₄⁻] in der Lösung ergibt sich eine Gerade für alle Produkte unabhängig von [OH].

Résumé—De la ferrihydrite a été transformée en goethite et/ou en hématite à des températures, [OH], et [Al] variés. Une augmentation de température et de [Al] a favorisé l'hématite, une augmentation d' [OH] a favorisé la goethite. Un [Al] donné induit l'hématite plus effectivement à un bas [OH]. La substitution d'Al dans les goethites a augmenté linéairement avec log [Al], mais était indépendant de la température. A un [Al] donné, la substitution a augmenté avec la diminution d' [OH]. Dans un graphe représentant Al/Fe dans la goethite par rapport à [Al]/[Fe(OH)₄⁻] en solution, une droite a été obtenue pour toutes les préparations indépendantes d' [OH].