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STIRRING EFFECTS ON PROPERTIES OF Al GOETHITE FORMED FROM FERRIHYDRITE

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Abstract—Minerals in surface environments form in both turbulent and non-turbulent systems. This study compares the properties of Al goethite formed from ferrihydrite at 60 °C in 0.3 *M* KOH with and without mechanical stirring. Compared to the static system, stirring increased crystal order and needle thickness, decreased unit cell edge length *a*, but not *b* and *c*, reduced the separation between the 2 OH-bending vibrations, increased Al substitution and promoted hematite formation.

Key Words—Al Goethite, Crystallinity, Hematite, Stirring, Unit Cell Parameters.

INTRODUCTION

A widely used method to synthesize Al-substituted goethite and hematite is the transformation of ferrihydrite under alkaline conditions in the presence of Al in a non-stirred system (Böhm 1925; Schwertmann and Cornell 1991). The oxides obtained this way vary widely in crystal perfection, Al substitution and goethite/hematite ratio depending on temperature, pH and original valence of Fe (Cornell and Schwertmann 1996). In a natural environment, mineral formation may take place under both static or turbulent conditions, such as in the weathering mantle versus streams and coastal areas (Aller and Michalopoulos 1996).

It can be expected that turbulence may have an effect on the properties of the end product, as is well known from industrial crystallization processes (Söhnel and Mullin 1987; Mullin et al. 1989). This study investigates the effect of stirring on the properties of Al goethite (Al substitution, crystal size, unit-cell edge lengths, surface area, OH-bending vibration) formed from ferrihydrite.

METHODS

Aluminum-substituted goethites were produced following the procedure of Schwertmann and Cornell (1991). In brief, aluminum-containing 2-line ferrihydrites were precipitated with 5 *M* KOH from mixed 0.05 *M* $Fe(NO_3)_3$-$AlCl_3$ solutions with Al/(Al+Fe) mole ratios between 0 and 0.273 mol mol^{-1} and then aged at 60 °C in 1- or 2-L polyethylene bottles under an [OH] of 0.3 *M* for 9 d. Aging in an oven without stirring was compared with stirring in a 60 °C water bath using either a Teflon-coated magnet or a milkshake-blender type stirrer. We used the 2 types of stirring to ascertain that the stirring effects could be attributed at least predominately to agitation and also to avoid any possible contamination of Teflon abraded from the coating of the magnetic stirrer. After termination of the synthesis, the samples were washed salt-free with distilled water and freeze-dried. They were characterized by step-scanned X-ray diffractograms as described elsewhere (Stanjek and Schwertmann 1992) and the unit cell edge lengths *a*, *b* and *c* of goethite were calculated using up to 20 fitted lines and Si as an internal standard. The average standard deviation for *a*, *b* and *c* is 1×10^{-3}; 2×10^{-3} and 5×10^{-4} nm. The mean coherence length along the *a*-axis for goethite, MCL_a, was obtained from the linearly corrected full width at half height of the 110, 120, 130, 111 and 140 peaks using the Scherrer formula (Schulze and Schwertmann 1984). MCL_a will be taken as the needle thickness. The hematite/goethite ratio (weight basis) was obtained from the integral intensities of the 012 peak of hematite (I_{012}^{Hm}) and of the 110 of goethite (I_{110}^{Gt}) (Kämpf and Schwertmann 1982) according to:

$$\frac{\mathrm{Hm}}{\mathrm{Gt}} = \frac{3.5 I_{012}^{\mathrm{Hm}}}{3.5 I_{012}^{\mathrm{Hm}} + I_{110}^{\mathrm{Gt}}} \qquad [1]$$

Oxalate-soluble Fe and Al (Al_0, Fe_0) were determined after Schwertmann (1964). Total Al and Fe (Al_t, Fe_t) in the oxalate-treated solids were determined after dissolving 10–20 mg in 5 mL conc. HCl by atomic absorption spectroscopy (average error 2%). Where both goethite and hematite occurred, the Al substitution of goethite was corrected for that of hematite by using the calculated amount of hematite and its Al substitution obtained from the unit-cell edge length *a* using the equation $Al/(Al+Fe) = 33.14 - 65.79\,a$ (in nm) (Schwertmann et al. 1979). Surface area was measured by N_2 adsorption in a static system using the BET relation. Transmission electron micrographs were obtained with a Zeiss EM 10A/B instrument operated at 80 or 100 kV using carbon-coated copper grids. FTIR spectra of KBr pellets were obtained with a Nicolet Magna 550 instrument.

RESULTS

The ferrihydrite was essentially converted into crystalline Fe oxides as indicted by XRD and low Fe_0/Fe_t ratios (average 0.033) which increased as [Al] in the

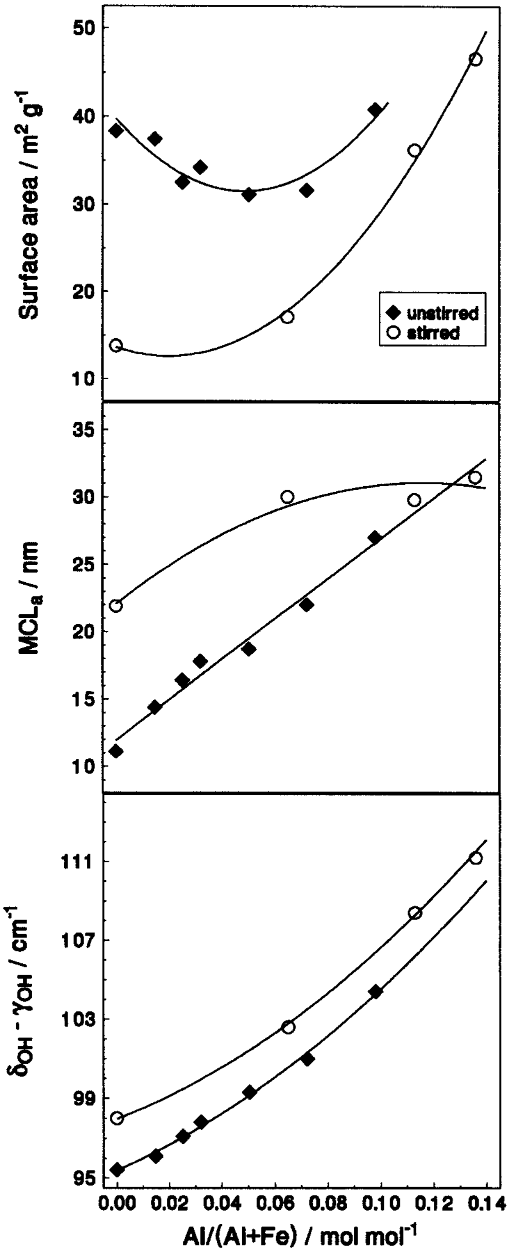

Figure 1. Surface area (upper), mean coherence length (middle), and difference between the 2 IR bending modes (lower) in relation to Al substitution of goethites without stirring and with magnetic stirring.

system increased. All unstirred preparations consisted of goethite only. In contrast, hematite occurred in most of the stirred samples. Its proportion increased as [Al] in the system increased and depended also on the mode of stirring (see above). As Al/(Al+Fe) in the system increased, the proportion of hematite was 0, 0.11, 0.14 and 0.32 in the 4 magnetically stirred samples and 0; 0; 0; traces and 0.10 in the 5 milkshake-blender stirred ones. Solution ratios of Al/(Al+Fe) of 0.086, 0.200 and 0.273 mol mol^{-1} gave structural Al/(Al+Fe) in goethite of 0.033, 0.072 and 0.095 mol mol^{-1} for the unstirred system, 0.065, 0.113 and 0.135 mol mol^{-1} for the magnetically stirred system and 0.049, 0.071 and 0.11 mol mol^{-1} for the milkshake-blender stirred system.

The surface area (SA) of the stirred samples was consistently lower at the same Al substitution (Figure 1, upper). Crystal morphologies as seen from TEM photos (not shown), MCL$_a$ and surface area were related and differed in the stirred and non-stirred system. For a non-stirred system, the relationship was described before (Schulze and Schwertmann 1984, 1987) and the present results agreed with those: at zero and low substitution, TEM showed rather thin (low opaqueness), 1–5 mm long needles consisting of several crystal domains along the needle axis with jagged needle ends (see also Figures 4.10 and 4.11 in Cornell and Schwertmann 1996). HRTEM investigations gave evidence that these domains scatter X-rays coherently (Mann et al. 1985). MCL$_a$ was low (Figure 2, middle) and SA (Figure 1, upper) was correspondingly high. As structural Al increased to <0.08 Al/(Al+Fe) mol mol^{-1}, the needles became more opaque, less domainic and thicker (MCL$_a$ increases) and SA dropped by 25%. Above this substitution the needles were increasingly shorter (several tenths of a micron) and SA increased again by 25%, although MCL$_a$ was still increasing.

In principle, the crystal development as a function of structural Al was the same in both the stirred and unstirred system. However, the needles in the stirred system not only showed MCL$_a$ values twice as high as in the non-stirred system, but they appeared generally more opaque under the TEM. Its increase at higher Al substitution can mainly be attributed to a strong reduction in needle length (from several μm to <0.3 μm) and width (<0.1 μm) whereas its thickness (MCL$_a$) did not increase anymore (Figure 1, middle). In summary, Al in the system retards crystallization (Cornell and Schwertmann 1996), hinders growth along [001], favors growth along [100] and suppresses multidomainicity.

Figure 1 (lower part) shows the separation of the 2 OH-bending vibrations at 900 (δ_{OH}) and 800 (γ_{OH}) cm^{-1} which can be attributed to the strength of the H-bond in the structure. As shown before (Schulze and Schwertmann 1984, 1987) both move to higher wave numbers as Al substitution increases but their separation also increases. The δ_{OH} and γ_{OH} band positions ranged from 890.0 to 902.9 cm^{-1} and from 893.4 to 912.3 cm^{-1} for the unstirred and stirred samples. At any given Al substitution, the band separation was significantly higher by 2–3 cm^{-1}. A similar change in position occurred for the band at 640 cm^{-1} assigned to symmetric Fe-O stretching in the *ab*-plane (Cambier

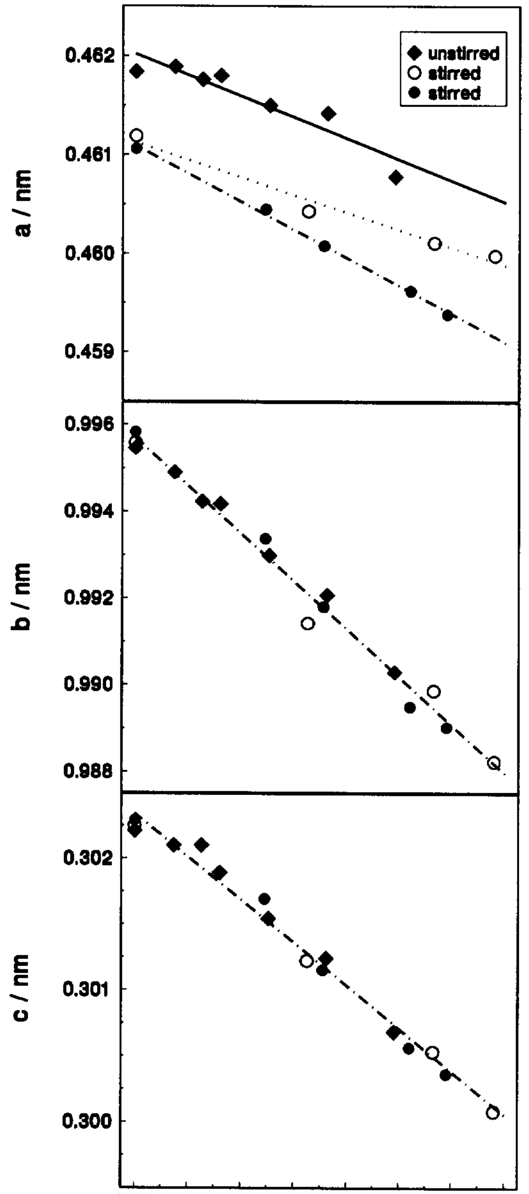

Figure 2. Unit-cell edge lengths *a* (upper), *b* (middle) and *c* (lower) in relation to Al substitution of goethites without stirring (◆), with magnetical stirring (○) and with milkshake-blender stirring (●).

1986a). At a given Al substitution, stirring lowered the band position by 5–7 wave numbers. A similar shift due to improved crystallinity was observed by Cambier (1986b) with a hydrothermally treated goethite. All 3 vibrations were also slightly sharper in the stirred than in the unstirred samples.

Figure 2 shows that stirring had no effect on the relationship between the unit cell length *b* and *c* and Al substitution, However, *a* was significantly smaller and better correlated with structural Al when stirred (r^2: 0.87; 0.98; 0.997 for unstirred, magnetically stirred and milkshake-blender stirred, respectively). Also, the *a* value for the stirred, unsubstituted goethite was much closer to the lowest value given for a well-crystalline goethite (see Discussion). This effect was slightly stronger with milkshake-blender stirring than with magnetical stirring. It is obvious that stirring had effectively suppressed the structural defects which cause a significant dilatation of the unit cell along [100].

DISCUSSION

Important factors influencing Al substitution, crystallinity and the proportion of goethite and hematite in our system are [Al], [OH] and temperature (Cornell and Schwertmann 1996). As [Al] increases, Al substitution rises, overall crystal size decreases and hematite is favored over goethite. In the alkaline range, increasing [OH] promotes goethite over hematite, lowers Al substitution and improves crystallinity. Increasing temperature favors crystal perfection and hematite formation but lowers Al substitution. Schwertmann and Schulze (unpubl.) observed that at 25 °C an Al/(Al+Fe) molar ratio as low as 0.025 is sufficient to completely suppress goethite formation at pH ≤ 7.

The unit edge lengths *b* and *c* of the goethite unit cell usually follow strictly the amount of structural Al, whereas all 3 factors mentioned above have a marked effect on *a* (Schulze 1984; Schulze and Schwertmann 1984, 1987; Fazey et al. 1991; Ruan and Gilkes 1995). The factors may or may not act independently. The *a* length for a well-crystalline goethite is given as 0.4608 nm (JCPDS No 29-133, starred). Using 17 peaks between 0.5 and 0.145 nm of a well-crystalline goethite from Cornwall, UK, Si as an internal standard and a Guinier diffractometer, we obtained a value of 0.46016(4) nm. In synthesis work, higher temperatures produce low-*a* goethites. Thiel (1963) obtained an *a* value for an unsubstituted goethite of as low as 0.4605 nm (read from Thiel's Figure 5) under hydrothermal conditions (2 *M* KOH; 155 °C; 12 h). The *a* value of goethites made from ferrihydrite at an [OH] of 0.3 *M* increased from 0.4610 to 0.4630 nm as the synthesis temperature fell from 80 ° to 25 °C and a hydrothermal treatment at 180 °C for 7 d resulted in a value of 0.4607 nm (Schwertmann et al. 1985). High *a* values of 0.4632 nm were also obtained for goethites produced by aerial oxidation of a Fe^{2+} solution at neutral pH and room temperature (Schulze 1984).

The causes for higher *a* values are most likely structural defects and/or site vacancies leading to extra OH in the structure (Schulze 1984; Wolska and Schwertmann 1993). This can be seen from a decrease in the distance between the 2 OH-bending vibrations at ~900 and ~800 cm^{-1}, which can be interpreted as a weakening of the H-bond between the double chains of octahedra (Schulze and Schwertmann 1984; Schwertmann et al. 1985; Cambier 1986b; Glasauer 1995). This bond has its strongest vector in the crystallographic *a* direction. Consequently, by heating goethite to temperatures below its transformation to hematite, *a* can be lowered (Schwertmann and Carlson 1994), for example, from 0.4635 to 0.4626 nm at 220 °C (Ruan and Gilkes 1995).

The mechanisms behind the observed effects of stirring are not clear, so we have to speculate on them. Agitation usually speeds up crystallization in a supersaturated solution (Mullin 1993). This can be explained by mass transfer either away from the surface of dissolving ferrihydrite or towards the surface of the growing goethite crystal, whichever determines the overall reaction rate. In an agitated system, these processes are no longer controlled solely by bulk diffusion, whereas in an unstirred system, a static diffusion-controlled layer may form at the surface which may retard surface diffusion of dissolved species because of smaller concentration gradients. Such a layer is likely to be minimized on stirring. On the goethite side, this may improve the chance to prevent defects by rearranging the surface-attached building units and produce better order in the growing crystal, which in turn could result in a higher incorporation of Al into the structure. More structural Al may also result from a higher [Al] in solution because stirring could lead to a faster selective dissolution of Al as $Al(OH)_4^-$ from the ferrihydrite. It has been shown that the extent of Al substitution of goethite increased with increasing $Al^{3+}/Fe(OH)_4^-$ in solution (Lewis and Schwertmann 1979). The selective dissolution of Al, in turn, would purify the remaining solid ferrihydrite and, thus, facilitate its internal transformation to hematite rather than to goethite via solution, the 2 competing processes.

Our results appear of relevance for producing Fe oxides with defined crystal properties (Schwertmann and Cornell 1991) for adsorption studies and such alike. It may also be significant for Fe oxide and, in general, for mineral formation in a natural aqueous system, may be stationary as in the weathering mantle, or turbulent as in streams or at shores.

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