

THE USE OF COLOR TO QUANTIFY THE EFFECTS OF pH AND TEMPERATURE ON THE CRYSTALLIZATION KINETICS OF GOETHITE UNDER HIGHLY ALKALINE CONDITIONS

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Abstract—The crystallization kinetics of goethite were studied colorimetrically under highly alkaline conditions (pH 10.1–12.2) at temperatures from 40° to 85°C. Color changes during crystallization from fresh precipitates, plotted on a^*b^* colorimetric diagrams, were used to discriminate between pure goethite and mixtures of goethite and hematite. Only the b^* value increased as goethite crystallization proceeded, and even a minor increase in the a^* value revealed the existence of hematite. The rate of goethite crystallization, estimated from the b^* value, could be modeled by a pseudo-first-order rate law. This rate depended both on pH and on temperature. Apparent activation energies for the reactions of 56.1 kJ/mol at pH 11.7 and 48.2 kJ/mol at pH 12.2 were estimated from Arrhenius plots.

Key Words—Color, Colorimetry, Crystallization, Goethite, Hematite, Kinetics, $L^*a^*b^*$ color space.

INTRODUCTION

Poorly ordered iron hydroxides (e.g., ferrihydrite) are known to transform into crystalline phases such as goethite, akaganeite, and hematite depending on different synthetic and natural conditions. In nature, most ferrihydrite transforms to goethite (Lewis and Schwertmann, 1980; Cornell and Giovanoli, 1985), to hematite (Johnston and Lewis, 1983; Combes *et al.*, 1990), or to mixtures of the two phases (Schwertmann and Murad, 1983). The most likely reaction pathway of the transformation to goethite is thought to be dissolution of ferrihydrite and subsequent reprecipitation as goethite. Hematite is thought to form through internal rearrangement (i.e., direct dehydration) (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966). Although kinetic studies are one of the useful methods to clarify the mechanisms of these transformations, which are influenced by temperature and pH as well as pressure, ionic strength, and impurities, few of these studies have been reported in the literature (Cornell *et al.*, 1989).

Color is one of the most distinguishing features of the oxidized iron compounds, which are largely responsible for the vivid colors of soils and rocks (Schwertmann and Cornell, 1991). Ferrihydrite typically is dark-brown, goethite is yellow, and hematite is red. Since crystallization of the iron compounds is accompanied by color changes, the color is considered to be a useful indicator for following the transformations. However, studies using color to quantify the iron compounds have been scarce (Barron and Torrent, 1984; Kosmas *et al.*, 1986). Recently rapid and quan-

titative color measurements using a colorimeter have been successfully applied to rocks (Nagano and Nakashima, 1989; Nakashima *et al.*, 1992) and marine sediments (Nagao and Nakashima, 1991). We showed that the color, described using the second CIE (Commission Internationale d'Eclairage) 1976 color space (generally referred to as $L^*a^*b^*$ color space), was a simple and quantitative parameter for the crystallization progress of goethite (Nagano *et al.*, 1992). In the present study, we examined colorimetrically the kinetics of goethite crystallization under highly alkaline conditions, and the color changes occurring during hematite crystallization were quantified. In the kinetic study, we focused on the effects of the aging temperature (40° to 85°C) and the initial pH of the solutions (pH 10.1–12.2) on the crystallization rates.

EXPERIMENTAL METHODS

Synthesis

Poorly ordered iron hydroxides were precipitated from 0.1M ferric nitrate solutions by adding 2M NaOH until an initial pH 10.1, 11.2, 11.7 and 12.2 had been reached. During the pH adjustment, the solutions were stirred at least for 15 min until the pH became stable. The solution temperature was $19.5 \pm 0.5^\circ\text{C}$. Portions of the fresh precipitates were centrifuge-washed twice with deionized water, freeze-dried, and slightly crushed with an agate mortar. The dried precipitates were identified as two-line ferrihydrite by X-ray diffractometry (XRD). Residual ferric precipitates were transferred into 12-ml transparent bottles and were kept at 40°,

55°, 70°, and 85° ± 1.0°C in an electric oven. The bottles were not agitated during the aging because the agitating causes a change in the transformation rate. Colors of the precipitates were measured on the colorimeter at selected intervals. The color measurements can be made directly by reflecting light at the bottom of the samples through transparent glass.

Hematite was synthesized from a mixture of 0.1 M ferric nitrate solution and 0.002 M oxalic acid solution. The pH of the mixture was raised to pH 6.5 by adding 2 M NaOH. The incubation temperature was 95°C (Schwertmann and Cornell, 1991). The initial precipitates at the start of the incubation period were also identified as two-line ferrihydrite. The color measurements were conducted in a manner similar to that described as above. The samples were then washed in dialysis tubes in 1 liter deionized water at 10°C for two days and freeze-dried.

Apparatus

Color measurements were conducted using a colorimeter (Minolta Chroma Meter, CR-200). The colorimeter is equipped with a pulsed lighting system for stable and uniform illumination of the specimen, photocells with filters to match the CIE standard observer spectral response, and electronic circuitry to determine accurate tri-stimulus values (Sugiyama, 1986). The colorimeter allows rapid, quantitative description of colors in terms of the values of standard color systems (Munsell, Yxy, XYZ, L*C*H* and L*a*b* color space).

The Munsell notation, which consists of three dimensions of hue, value, and chroma, has been the conventional method to describe the colors of soils or iron oxides. However, in this study we follow the recommendations of the CIE and use the L*a*b* color space to describe the colors of the precipitates. This system is considered to be more uniform, in which the coordinate scales are chosen with the intention of making equal intervals represent as nearly as possible equal steps of discrimination for colors of the same luminance at all parts of the diagram (Hunt, 1980). The L* axis represents psychometric lightness; L* = 0 and L* = 100 correspond to black and white, respectively. The a* and b* axes represent psychometric chromaticness (+a* = red, -a* = green; +b* = yellow, -b* = blue) (Hunt, 1980). A white plate (Minolta) was measured as a reference.

Before every color measurement, the bottle was shaken to attain a homogeneous color of the precipitate and was centrifuged (1000 rpm, 1 minute) for rapid sedimentation. The precision of this measurement method was ±0.7% for L*-value, ±1.5% for a*, and ±1.0% for b*, including the deviations arising from differences in the incubation bottles.

Crystalline phases of the resulting freeze-dried precipitates were characterized by X-ray diffractometry

using a Rigaku powder diffractometer (CuK α radiation, 50 kV, 35 mA) equipped with the SUN data processing system. Infrared spectra of the samples were measured by diffuse reflectance spectroscopy using JEOL 3505 FT-IR spectrometer.

RESULTS AND DISCUSSION

Color changes of goethite and hematite

Figure 1 shows color variations over time that are associated with the formation of goethite and hematite. The initial precipitate, identified as two-line ferrihydrite by XRD, exhibited a dark-brownish color (5YR 2/4 by Munsell chips) (Munsell Book of Color, 1976). On the other hand, the end product was brownish-yellow (10YR 5/8) for goethite and dark red (10R 3/8) for hematite. Color changes occurred continuously during the incubation from the initial precipitates to the end products. The XRD analyses showed that the end products of both the goethite and hematite crystallization reactions did not contain any other crystalline phases. Infrared spectroscopy analyses revealed that hematite contained a small amount of goethite (790 and 890 cm⁻¹), as well as water incorporated into the structure (3400 cm⁻¹), so this phase is generally called hydrohematite (Wolska, 1981).

The crystallization of goethite seems to proceed colorimetrically parallel to the +b* axis, whereas that for hematite shows increases in both a* and b* values. This difference corresponds to the yellow appearance of goethite and the red appearance of hematite to the naked eye. Figure 1 demonstrates that the b* value can be used to measure the progress of goethite crystallization and that production of hematite can be detected by the increase in the a* value.

In the incubation experiments in which hematite was synthesized, there was a positive correlation between color changes and X-ray diffraction patterns (Figure 2) over time. These changes corresponded to nucleation and growth of hematite crystals. A peak height of the XRD 104 line of hematite (2.70 Å) was determined after smoothing the diffraction patterns and removing the backgrounds. During the first 2 hr, an induction period in which nuclei of hematite are thought to be forming (Cornell *et al.*, 1989), the peak heights were equal to zero. From 2–8 hr, the intensity of the XRD peaks rapidly increased. Peak intensity was almost constant after 8 hr.

Equivalent changes were observed colorimetrically during the experiment. In the first 2 hr, there was virtually no change in color of the precipitates, followed by a pronounced change in color from 2–8 hr during which both a* and b* values increased accordingly. After 8 hr, little color change was observed.

The distinct colorimetric paths of crystallization for goethite and hematite that are shown on Figure 1 suggest that a mixture of the two phases would be indicated

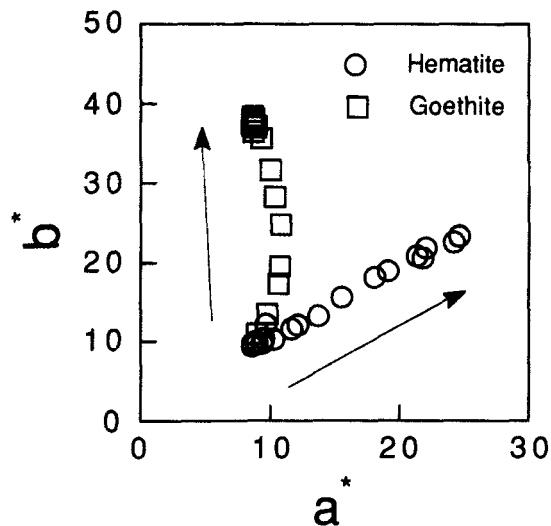


Figure 1. Color variations on an a^* - b^* diagram associated with crystallization of ferrihydrite to goethite at pH 12.2 and 40°C and to hematite at pH 6.5 and 95°C. The crystallization of goethite seems to proceed almost parallel to b^* axis, whereas that for hematite shows increases in both a^* and b^* values. Arrows indicate increases in incubation time.

by a value in the region between the lines defined by the single phases. As presented in the next section, we can use this method to describe the formation of pure goethite, pure hematite, or mixtures of the two phases on the a^* - b^* diagram.

Effects of temperature and pH

The effect of temperature between 40° and 85°C on the crystallization paths of ferrihydrite to the iron compounds is shown in Figures 3a to 3d for four separate solutions with pH 10.1, 11.2, 11.7 and 12.2, respectively. In the solution at pH 12.2 (Figure 3d), temperature did not influence the direction of color change with the incubation time, which indicates formation of the single phase goethite. Goethite formation also appears to predominate at pH 11.7 between 40° and 70°C (Figure 3c). At pH 10.1 and 11.2, higher temperatures result in larger a^* values, suggesting the formation of an appreciable amount of hematite in the mixture. All the curves in Figure 3 can be plotted between those of goethite and hematite shown in Figure 1.

Data shown in Figure 3 are replotted in Figure 4 to show the effect of initial pH levels between 10.1 and 12.2 on the crystallization path at temperatures of 40°, 55°, 70°, and 85°C. The pH effect on the direction of color change was not recognized in any of the solutions at 40°C except at pH 10.1, nor was it noted at 55°C and 70°C for the solutions above pH 11.2. Development of hematite was noted in the solutions above pH 10.1 at 85°C. A dependence of the color change on pH, in which lower pH leads to larger a^* values, corresponds to the formation of hematite, which is favored at lower pH.

The direction of crystallization paths tends to shift toward the hematite line at higher temperatures and lower pHs. To determine the relative contents of goe-

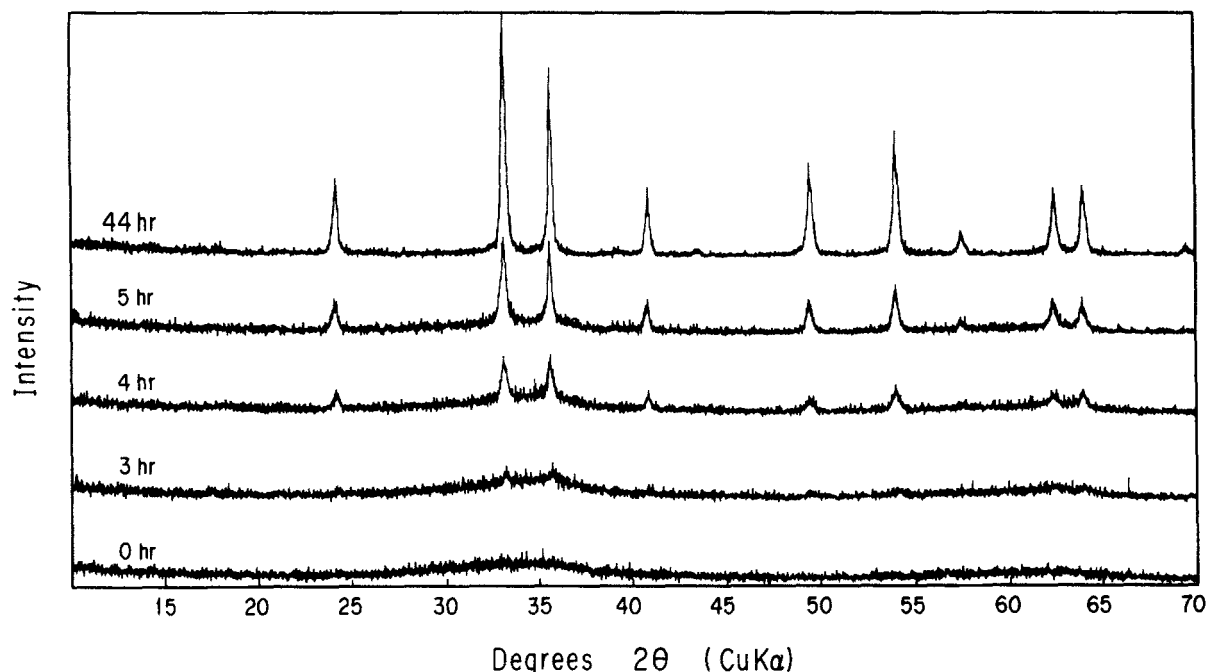


Figure 2. X-ray diffraction patterns of the iron hydroxide crystallized to hematite with an aging time of 0, 3, 4, 5, and 44 hr.

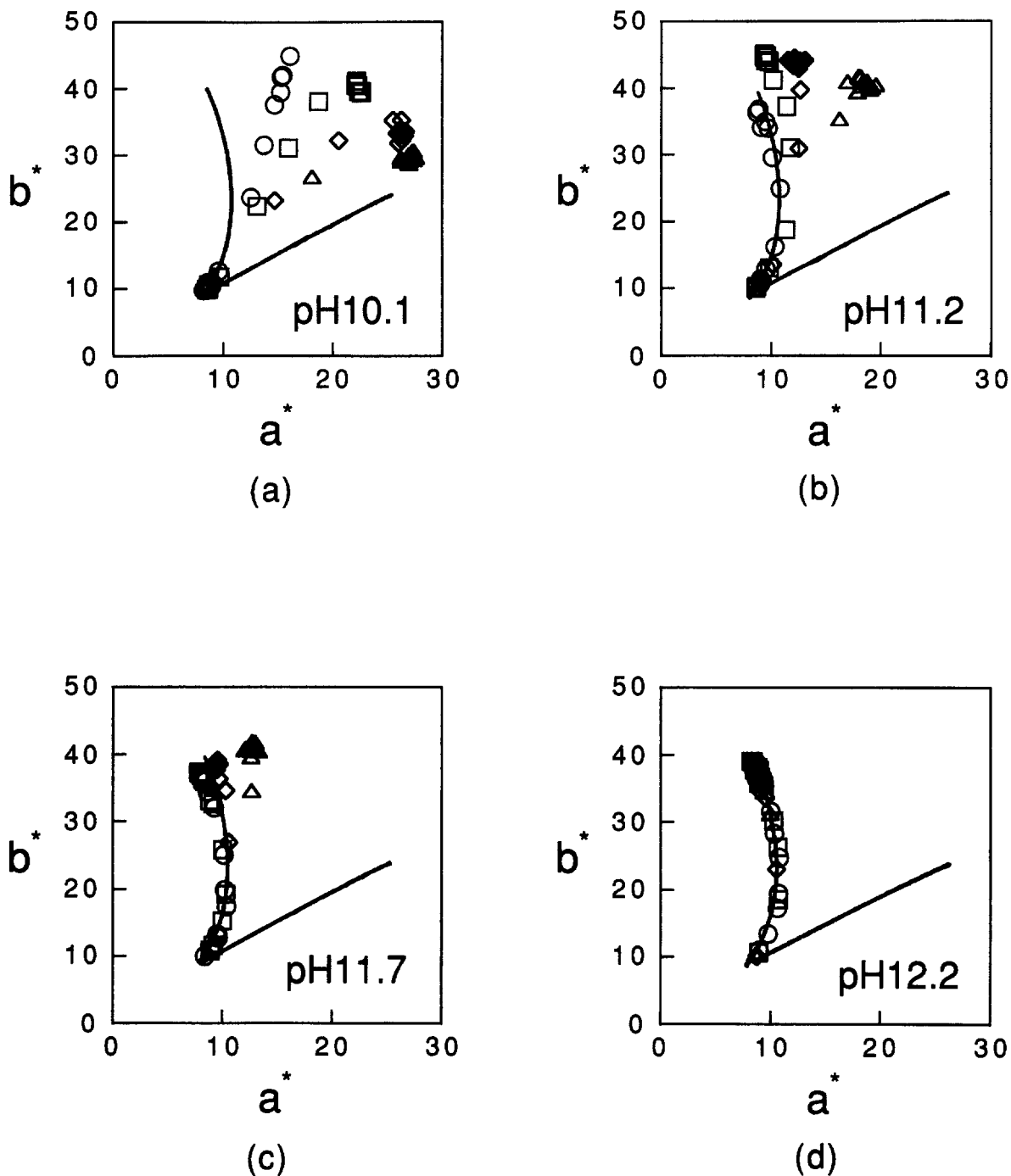


Figure 3. Temperature effects on color variations during crystallization from ferrihydrite to goethite or hematite: a) pH 10.1, b) pH 11.2, c) pH 11.7, d) pH 12.2. \circ = 40°C, \square = 55°C, \diamond = 70°C, \triangle = 85°C. Solid lines show the goethite and hematite lines from Figure 1.

thite and hematite in the end products an XRD analysis was made (increment: $0.02^\circ 2\theta$, counting time: 10 s/increment) for 20° to $25^\circ 2\theta$, which includes the strongest reflection of goethite at $21.2^\circ 2\theta$ (110) and of hematite at $24.2^\circ 2\theta$ (012) among non-overlapping peaks

with goethite. Table 1 shows the integrated intensity (peak height times width at half height) of the 100 line of goethite and the integrated intensity of the 012 line of hematite. The greatest intensity was given by the sample at pH 11.2 and 55°C for goethite and at pH 6.5

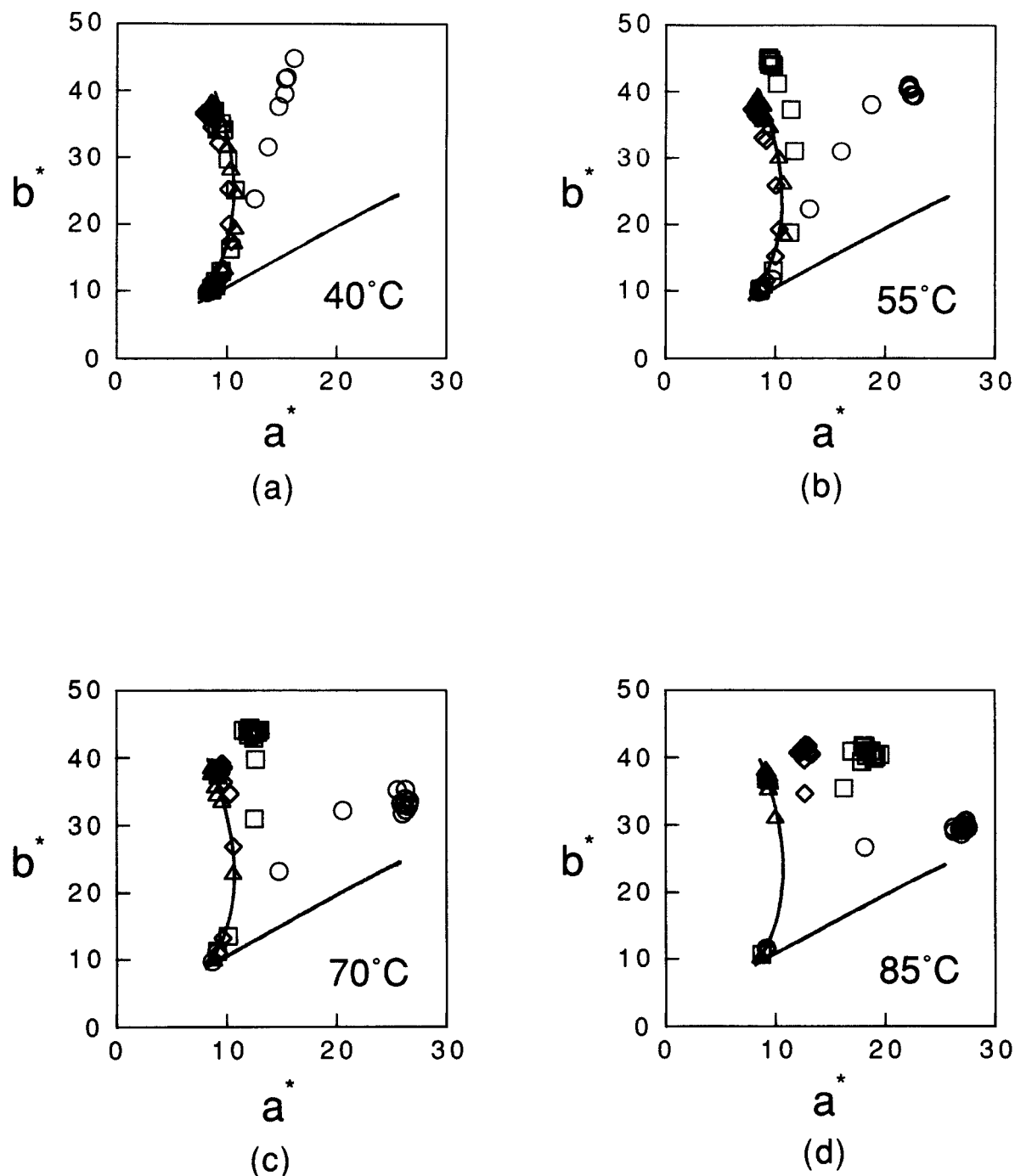


Figure 4. Effects of pH on color variations during crystallization from ferrihydrite to goethite or hematite: a) 40°C, b) 55°C, c) 70°C, d) 85°C. \circ = pH 10.1, \square = pH 11.2, \diamond = pH 11.7, \triangle = pH 12.2. Solid lines show the goethite and hematite lines from Figure 1.

and 95°C for hematite, and so the relative goethite or hematite content in these samples was set equal to 100. Based on hematite/goethite ratios (Hm/Gt) calculated from the relative contents (Table 1), a diagram of the fields of formation of goethite and mixtures of goethite

and hematite was constructed as a function of the incubation temperature and the initial pH (Figure 5). Higher temperatures and lower pHs in this study are obviously favorable for the formation of hematite. This tendency is also recognized by the color change. The

Table 1. Nature of crystalline products after aging at various pH and temperature conditions.

Condition pH, T (°C)	Goethite		Hematite		Hm/Gt	Final		
	WHH ₁₁₀	Intensity (%)	WHH ₀₁₂	Intensity (%)		a*	b*	
12.2	40	0.62	86	—	—	9	38	
	55	0.64	85	—	—	8	39	
	70	0.66	74	—	—	9	38	
	85	0.64	71	—	—	9	37	
11.7	40	0.64	80	—	—	8	37	
	55	0.64	79	—	—	8	37	
	70	0.66	75	—	—	9	38	
	85	0.58	83	0.44	2	0.02	13	42
11.2	40	0.66	79	—	—	9	36	
	55	0.40	100	—	—	9	45	
	70	0.50	92	0.36	2	0.02	13	44
	85	0.56	99	0.54	9	0.09	19	40
10.1	40	0.56	66	0.52	3	0.05	16	45
	55	0.58	81	0.48	15	0.19	23	40
	70	0.56	68	0.52	43	0.63	27	33
	85	0.58	41	0.54	70	1.71	27	30
6.5	95	—	—	0.52	100	∞	25	23

sequence of the Hm/Gt ratios corresponds to that of directions of color changes represented by final a* and b* (Table 1). Although the color change direction for pH 11.2 and 55°C is clearly different from goethite line, the relative content of hematite is 0. As shown in Table 1, pure goethites show similar widths of the 110 line (0.62–0.66) except at pH 11.2 and 55°C (0.40). A thinner width of the 110 line indicates the formation of different types of goethite, e.g., acicular crystals of smaller width (Schwertmann and Murad, 1983), which may lead to the shift from the goethite line of color change at pH 11.2 and 55°C. Since mixtures of goethite and hematite show the widths of the 110 line between

0.50 and 0.58 (Table 1), the directions of color change of the mixtures are considered to be controlled by the formation of hematite rather than that of goethite with different morphology.

Kinetics of goethite crystallization

In our previous study on the color variations associated with goethite crystallization, the b* values were related to the goethite proportion determined both by an XRD peak intensity of the 110 line and by an infrared peak area at 890 cm⁻¹ (Nagano *et al.*, 1992). Figure 6 shows goethite crystallization curves con-

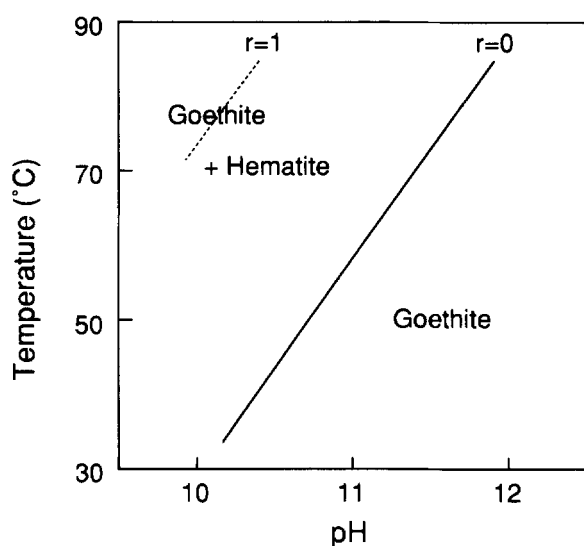


Figure 5. Fields of formation of goethite and mixtures of goethite and hematite as a function of the initial pH and the aging temperature. r = Hm/Gt ratio in Table 1.

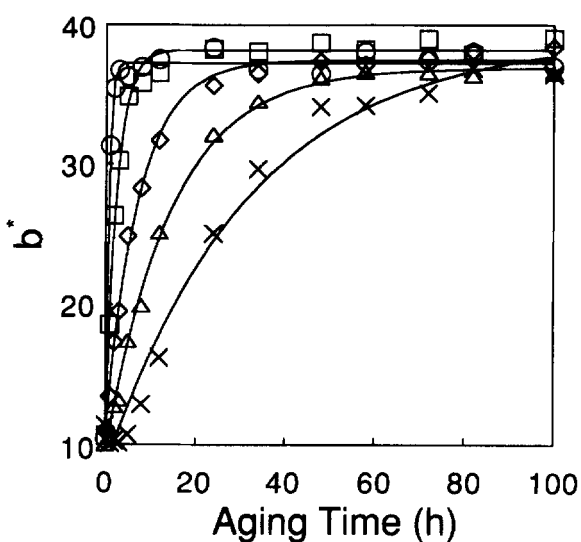


Figure 6. Crystallization curves of goethite based on the b* values. These curves appear to follow a pseudo-first-order rate law. \circ = pH 12.2, 85°C; \square = pH 12.2, 55°C; \diamond = pH 12.2, 40°C; \triangle = pH 11.7, 40°C; \times = pH 11.2, 40°C.

Table 2. Pseudo-first-order rate constants for goethite crystallization.

pH, Temperature (°C)	k (hr ⁻¹)
12.2, 85	1.46 ± 0.104
12.2, 70	0.72 ± 0.057
12.2, 55	0.40 ± 0.024
12.2, 40	0.13 ± 0.006
11.7, 70	0.45 ± 0.073
11.7, 55	0.18 ± 0.018
11.7, 40	0.07 ± 0.003
11.2, 40	0.03 ± 0.005

structured based on the variations of b^* value. The b^* value increases with the incubation time and remains constant. The crystallization of ferrihydrite to goethite was shown by Schwertmann and Murad (1983) to follow a pseudo-first-order reaction rate law; the rate of crystallization at any time is proportional to the amount of residual ferrihydrite in the precipitates. The positive relationship between goethite crystallinity and the b^* value also indicates an exponential increase in the b^* values. The crystallization curves shown in Figure 6 follow the following type of equation:

$$b^* = C_1 - C_2 \cdot \exp(-k \cdot t) \quad (1)$$

where t is the incubation time (h), and C_1 , C_2 and k are constants. We fit the colorimetric data to Eq. 1 by a least-squares fitting method to estimate k , the rate constant of the overall reaction. The results are summarized in Table 2 for the samples with the color change directions corresponding to goethite.

Temperature effects on the crystallization kinetics of goethite are expressed in the form of the Arrhenius plots (Figure 7). The positive temperature effect on the crystallization kinetics is obvious. Effects of pH on the goethite crystallization kinetics are shown in Figure 8. Higher pH conditions apparently result in higher rate constants, and a positive effect of pH on the kinetics is also obvious.

Rates of goethite crystallization are significantly influenced by aging temperature and by the initial pH of solutions. With respect to the goethite crystallization mechanism, Misawa *et al.* (1974) stress a solid state transformation on the basis that both ferrihydrite and goethite consist of hexagonal close-packed oxygen frameworks. However, the generally accepted model for the goethite crystallization consists of two steps: dissolution of ferrihydrite and reprecipitation of the Fe as goethite (Feitknecht and Michaelis, 1962; Schwertmann and Fischer, 1966). In the present study, we follow the two-step crystallization model to explain both the pH- and the temperature-dependence of the rate as below.

According to a more refined model of the two-step model, goethite is strongly favored where the concentration of monovalent Fe(III) ions such as $\text{Fe}(\text{OH})_2^+$

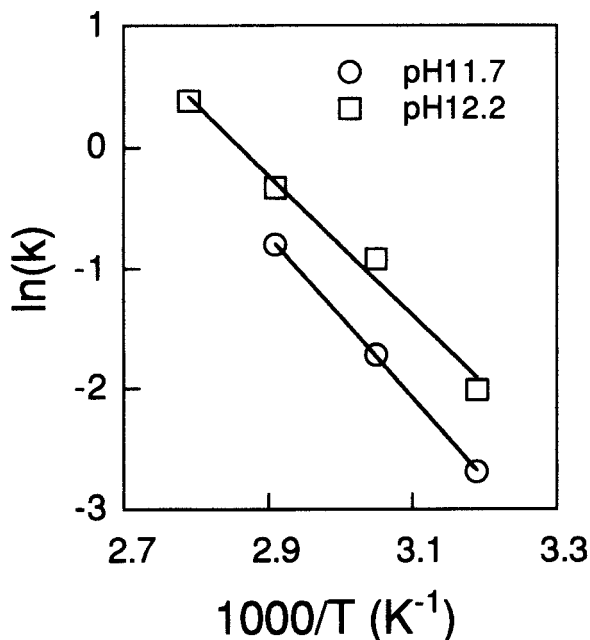


Figure 7. Arrhenius plots for the samples at pH 11.7 (40°–70°C) and pH 12.2 (40°–85°C), where only goethite formed. Apparent activation energies of overall reactions were calculated to be 56.1 kJ/mol for pH 11.7 and 48.2 kJ/mol for pH 12.2.

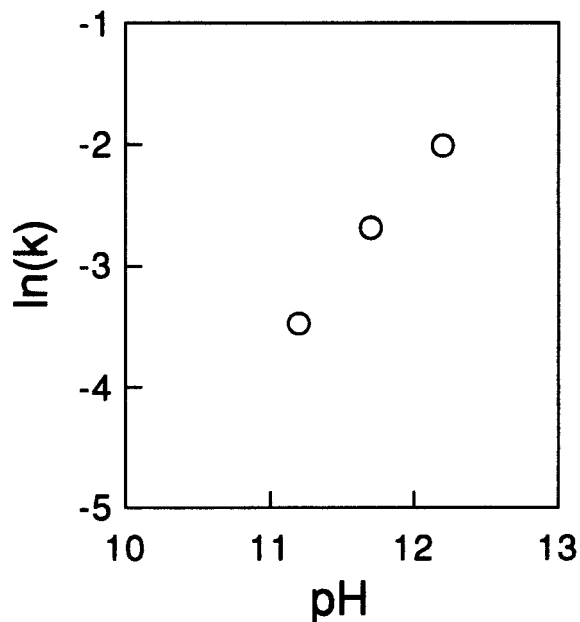
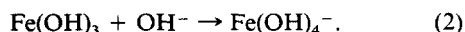


Figure 8. Effects of pH on the crystallization rates of goethite at 40°C and pH 11.2–12.2. Positive effects of $[\text{OH}^-]$ shown in this figure indicate that goethite crystallization is the OH^- -promoted reaction.

or $\text{Fe}(\text{OH})_4^-$ is at a maximum (Schwertmann and Murad, 1983). $\text{Fe}(\text{OH})_4^-$ is the dominant dissolved species in highly alkaline aqueous solutions (Stumm and Morgan, 1981) and, therefore, could be the species controlling goethite precipitation. In considering the pH-dependence of the rate (Figure 8), we can consider the dissolution of ferrihydrite for the present condition to be the OH^- promoted reaction as,



The apparent activation energies of the overall reaction were calculated from the slope of the Arrhenius plots to be 56.1 ± 0.6 kJ/mol for pH 11.7 and 48.2 ± 4.1 kJ/mol for pH 12.2. These values are within the range of mineral-solution alteration processes such as dissolution of some silicates (Lasaga, 1981; Schott and Petit, 1987).

CONCLUSION

The crystallization progress of goethite, hematite, and mixtures of the two phases was investigated in alkaline aqueous solutions by measuring their colors. The direction of color changes a^* - b^* diagrams allows us to discriminate between goethite and a goethite-hematite mixture. Goethite was indicated by parallel colorimetric changes to the b^* -axis, and hematite was indicated by increases in both the a^* and b^* values. Mixtures of the two phases had colorimetric values that plotted between the lines defined by goethite and by hematite alone. Crystallization curves for goethite based on the b^* values indicated exponential time evolution. Pseudo-first-order rate constants were obtained from the curves. Arrhenius plots showed the apparent activation energies to be about 56.1 kJ/mol at pH 11.7 and 48.2 kJ/mol at pH 12.2. The temperature and pH dependence of the goethite crystallization rate supported the published two-step model consisting of dissolution of ferrihydrite and subsequent precipitation of goethite.

ACKNOWLEDGMENTS

The authors would like to thank Drs. K. Sekine and S. Nagao of Japan Atomic Energy Research Institute (JAERI) for useful discussions and encouragement during the course of this work and Dr. T. Sato of JAERI for the technical support of XRD analyses. Review of the manuscript for English style by Dr. J. McMurry is greatly appreciated. Critical reviews and comments by Drs. U. Schwertmann and J. Amonette are also gratefully acknowledged.

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(Received 3 August 1993; accepted 23 November 1993; ms. 2408)