

EVALUATION OF CRYSTALLINITY IN HYDRATED FERRIC OXIDES*

EDWARD R. LANDA and ROBERT G. GAST†
University of Minnesota, St. Paul, Minnesota 55101, U.S.A.

(Received 15 November 1972)

Abstract—The nature of freshly-precipitated and aged hydrated ferric oxides prepared by the addition of ferric chloride to KOH was investigated by the use of scanning and transmission electron microscopy, X-ray diffraction, i.r. absorption, and pH 3.0 ammonium oxalate extraction. The results show the fresh material to be essentially non-crystalline hydrated ferric oxide, which when aged at 60°C and high pH rapidly crystallizes as goethite, without any indication of coexisting hematite. The various methods were evaluated as indices of crystallinity for aging materials. The acid ammonium oxalate method was shown to extract selectively only the non-crystalline portion of such mixtures. The use of X-ray diffraction analysis for estimating aging stage requires elimination of the preferred orientation of the goethite crystals. While both the oxalate and X-ray methods can detect as little as 2 per cent crystallinity, the oxalate method is probably superior for quantitative determinations as it depends directly on an inherent difference in the solubility of the crystalline and non-crystalline materials, rather than on a technique dependent intensity measurement. The use of the intensity of the O-H bending vibrations of the infrared absorption spectra can also potentially detect as little as 2 per cent crystallinity, but the procedure is probably less useful for quantitative determinations than the oxalate or X-ray methods because of the problem of evaluating the area under the peaks.

INTRODUCTION

THE WIDESPREAD occurrence in soils and sediments of ferric oxides and their hydrates, as discrete bodies and as coatings on other particles, makes a knowledge of their properties a valuable adjunct to any physical, chemical or genetic study of the material as a whole. Also, mixtures of amorphous hydrated ferric oxide and crystalline goethite, similar to those which will be described here, are found suspended in some groundwaters of the coastal plain (Langmuir and Whittemore, 1971).

The common naturally occurring ferric oxides and hydrous oxides may be grouped into two polymorphic series. The α -series, which will be examined in this study, consists of hematite, the anhydrous oxide, and goethite, the monohydrate, and is based on hexagonal close packing of the layers of oxygen atoms. The γ -series, consisting of the anhydrous oxide, maghemite, and the monohydrate, lepidocrocite, exhibits oxygens in a cubic close packed array.

The hematite (α -Fe₂O₃) structure consists of Fe³⁺ ions arranged interstitially between oxygen layers in octahedral groupings which are slightly distorted by the size of the cation (Blyholder and Richardson, 1962). Goethite (α -FeOOH) consists essentially of the same distorted Fe³⁺-centered octahedra with the edges of the octahedra shared so as to yield strips two-octahedra wide, running parallel to the *c*-axis (Deer, Howie and Zussman, 1962; Ewing, 1935).

The object of this study was to establish procedures for identifying and quantitatively determining the amounts of these materials in freshly prepared, and aged hydrated ferric oxide precipitates.

EXPERIMENTAL

Materials

Standard crystalline materials. The natural, well crystallized, fibrous goethite was obtained from the Hanna Mining Company. X-ray diffraction showed a small peak at 2.30 Å (high quartz?) as the only crystalline impurity. The hematite was reagent grade Mallinckrodt ferric oxide. X-ray diffraction revealed no crystalline impurities.

Synthetic hydroxy-iron materials. The synthetic, fresh, hydrated ferric oxide gel was prepared by the dropwise addition of an equivalent amount of ferric chloride to 250 ml of 2.0 N KOH while stirring rapidly. The flocculated dark reddish-brown precipitate was washed with deionized water by centrifuging and decanting until it began

*Paper N. 8140 Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul, Minnesota 55101. This work was supported by the Graduate School, University of Minnesota and by a National Science Foundation Traineeship to the senior author.

†Research Assistant and Professor of Soil Science, respectively, University of Minnesota, St. Paul, Minnesota 55101, U.S.A.

to disperse. This freshly-precipitated, washed gel was either used immediately, or aged for various lengths of time in 0.2 N KOH at 60°C in polyethylene bottles.

Methods

Acidified ammonium oxalate extraction. The acidified ammonium oxalate extraction method of Schwertmann (personal communication) was used for the selective dissolution of iron oxides. The procedure consists of shaking a 50–100 mg sample of iron oxide with 100 ml of a pH 3.0 mixture of 0.2 M ammonium oxalate and 0.2 M oxalic acid for 2 hr in the dark, filtering and determining the iron in solution. A duplicate sample is dissolved completely by gently heating in concentrated HCl to ascertain the total iron content. The iron concentration in solution was determined by the colorimetric orthophenanthroline method (Jackson, 1956) using a Coleman Junior Model II-A linear absorbance spectrophotometer read at 510 μm . Since oxalate does interfere with the color development (Sandell, 1944), it was important to include appropriate oxalate concentrations in the standard solutions.

The iron extractions were carried out in the dark due to the photosensitive nature of the reaction. Schwertmann (as cited by Blume and Schwertmann, 1969) has shown that in the dark, only the noncrystalline portion (as determined by D.T.A. and X-ray diffraction) of the iron oxides was oxalate-soluble. The method has been used (Schwertmann, Fischer and Papendorf, 1968) to characterize the aging stage of hydrous ferric oxide gels, using the ratio of oxalate-soluble to warm, concentrated HCl-soluble iron (total Fe) as a measure of the crystallinity of the gel.

I.R. analysis. I.R. spectra were obtained using a pellet containing 1 mg of sample dispersed in 400 mg of spectroscopic grade KBr, and pressed at 100,000 psi. The spectrophotometer was a Beckman model I.R.-12 spectrophotometer operated in the double beam mode.

Transmission and scanning electron microscopy. Specimens for transmission electron microscope analysis were sedimented onto a Formvar-coated copper grid and examined, without further treatment, using a Phillips model E.M.-300 microscope. For scanning electron microscopy, specimens were sedimented onto a stainless steel stub, coated with carbon and then gold, and examined with a Cambridge Stereoscan Mark IIA S.E.M.

X-ray diffraction analysis. For X-ray diffraction analysis, 5 mg of material was distributed uniformly from aqueous suspension over a one square inch area of a glass microslide and allowed to air-dry. The specimens were examined on a G. E. model X.R.D.-5 diffractometer with nickel-filtered

CuK α radiation generated at 50 kV and 15 mA. The intensity of a given reflection was assessed by point counting the counts-per-sec over background of the strongest X-ray line of the sample in question. Sufficient counts were recorded to maintain a less than 5 per cent counting error. The relative intensity (I_x/I_s) of any such reflection is given by the ratio of the intensity of the diffraction line of the crystalline component of the sample (I_x) to the intensity of the same line in a standard wholly crystalline material (I_s).

RESULTS AND DISCUSSION

Freshly-precipitated hydrated ferric oxide

The freshly-precipitated and washed hydrated ferric oxide gel was found to be amorphous to X-rays, and completely soluble ($\text{Fe}_{\text{ox}}/\text{Fe}_{\text{HCl}} = 1.0$) in pH 3.0 ammonium oxalate. Infrared analysis showed no evidence of goethite or hematite (Fig. 5). Scanning electron micrographs (Fig. 1) revealed no crystallinity in this material. However, transmission electron microscopy does show the presence of some distinct rod-shaped particles in the otherwise granular matrix of the salt-free (negative AgNO_3 test) freshly prepared gel (Fig. 2). These particles apparently represent the first crystalline products of natural aging, since there was no visible evidence of this material crystallizing during the examination (i.e. due to heating of the sample by the electron beam).

The evidence thus suggests that the initially precipitated material is essentially amorphous within the detection limits of X-ray, infrared and ammonium oxalate analysis. The traces of crystallinity which are observed with the transmission electron microscope are presumably goethite since, as will be seen later, the particles are similar in morphology to the particles in aged

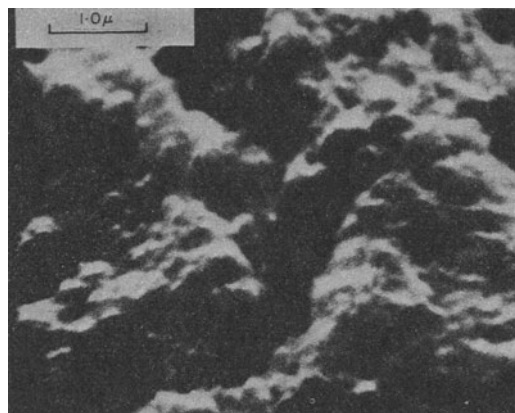


Fig. 1. Scanning electron micrograph of X-ray amorphous hydrated ferric oxide.

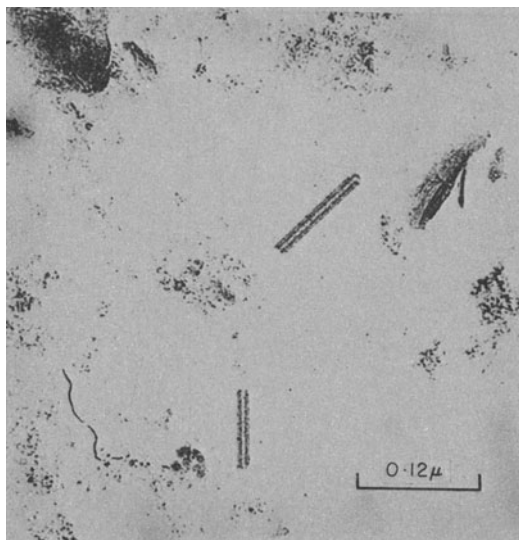


Fig. 2. Transmission electron micrograph of X-ray amorphous hydrated ferric oxide.

gels which can be positively identified as goethite by X-ray and i.r. analysis.

Fully-aged hydrated ferric oxide

Aging the freshly prepared gel at pH 13 and 60°C resulted in a gradational color change from dark reddish-brown (Munsell color 10 R 3/3) to a bright yellow (2.5Y 7/8) in a matter of hours. Material aged for more than 24 hr at pH 13 and 60°C was found to be insoluble ($Fe_{ox}/Fe_{HCl} = 0.0$) in pH 3.0 ammonium oxalate, as was the natural goethite and the reagent-grade hematite. While Pawluk (1972) has shown that prolonged and repeated ammonium oxalate extractions of soil samples do remove the crystalline as well as the amorphous iron oxides, the residues remaining after a single 2 hr extraction of partially crystalline synthetic gels in this study were found to be essentially insoluble in subsequent extractions.

Transmission electron micrographs (Fig. 3) show the aged material to be composed of apparently needle-like crystals, approximately 1 μm long and 0.04 μm wide with no evidence of the granular material observed in the freshly prepared gels. Scanning electron micrographs (Fig. 4) reveal a more-marked flattening in one plane, producing a blade-shaped crystal. Such a platy habit has also been observed by Stoops (1970), under the scanning electron microscope, for goethite crystals lining the walls of voids in a laterite soil. These elongated crystals, characteristic of goethite, are readily distinguished from the hexagonal to rounded crystals of hematite (Schwertmann *et al.*, 1968).

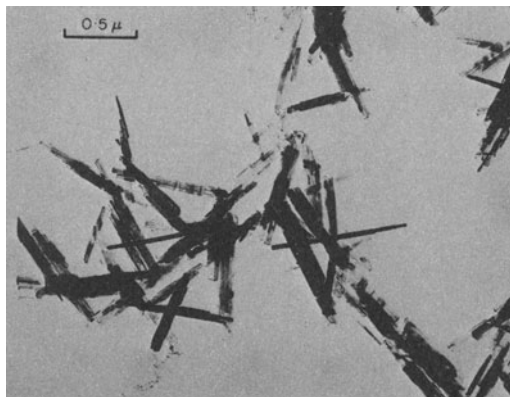


Fig. 3. Transmission electron micrograph of fully-aged, synthetic goethite.

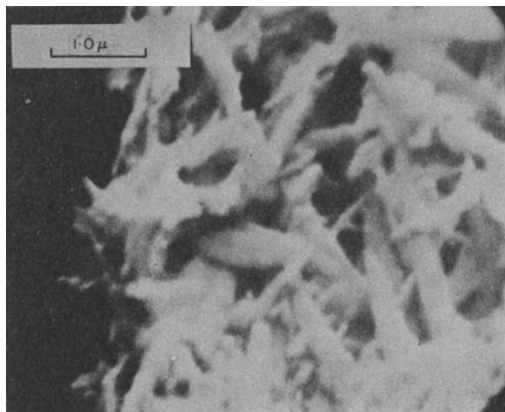


Fig. 4. Scanning electron micrograph of fully-aged, synthetic goethite.

The aged material showed strong infrared absorption bands at 650, 795, 890 and 3150 cm^{-1} in addition to the sorbed water bands at 1630 and 3450 cm^{-1} (Fig. 5). The 795 and 890 cm^{-1} bands have been previously reported for goethite and are assigned to lattice O-H bending vibrations (Glemser and Hartert, 1953; Marshall and Rutherford, 1971). The 3150 cm^{-1} band apparently represents a strongly hydrogen-bonded O-H stretch. The 650 cm^{-1} band has been reported (Roy and Roy, 1957) without specific assignment.

Infrared analysis can be used to distinguish clearly between α -FeOOH (goethite) and its polymorphs, β -FeOOH (akaganeite), and γ -FeOOH (lepidocrocite) since differences in the structural relationships of the hydrogens to the oxygens result in differences in the O-H bending vibrational frequencies. These vibrations are at 795 and 890 cm^{-1} for α -FeOOH, at 680 and

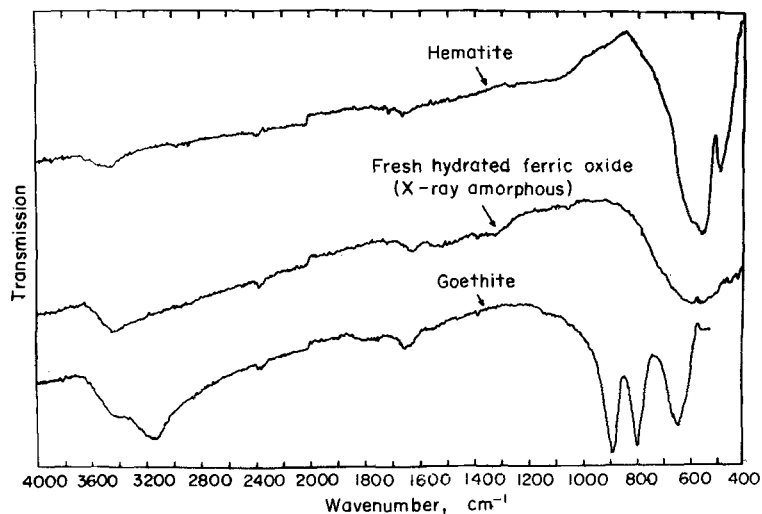


Fig. 5. I.R. absorption spectra of hematite, goethite, and X-ray amorphous hydrated ferric oxide.

804 cm^{-1} for $\beta\text{-FeOOH}$, and at 730 and 1025 cm^{-1} for $\gamma\text{-FeOOH}$ (Marshall and Rutherford, 1971).

The goethite spectrum is also easily distinguished from those of freshly precipitated hydrated ferric oxide and hematite (Fig. 5). These spectra, aside from the sorbed water deformation and stretching bands, are similarly featureless in the 700–4000 cm^{-1} region, in agreement with Kumada and Aizawa (1959). The 400–700 cm^{-1} region of the amorphous material is dominated by a single strong, broad band at 580 cm^{-1} , while that of hematite shows distinct absorption at 485, 550, and 585 cm^{-1} , in general agreement with the spectra reported by Bentley *et al.* (1968).

The fully-aged crystalline material gave an X-ray diffraction pattern corresponding to that of goethite. As in the case of infrared spectroscopy, X-ray diffraction can be used to distinguish clearly between the various iron oxides and hydrous oxides (Rooksby, 1961). Thus it appears that aging at high pH and elevated temperature results in the synthesis of wholly crystalline goethite. X-ray diffraction also showed that aging of the freshly prepared material at pH 8 and 11 likewise resulted in the development of goethite as the only crystalline phase. However at these lower pH values, only partial crystallization was evident after four weeks of aging.

Other studies have shown goethite (Mackenzie and Meldau, 1959; Sims and Bingham, 1968; Smith and Kidd, 1949), or hematite (Milligan, 1952) or both (Schwertman *et al.*, 1968) to be the aging products of similarly prepared gels.

Garrels (1959) suggests that upon aging, the amorphous hydrous ferric oxide crystallizes to

either hematite or goethite depending upon minor compositional differences in solution. This hypothesis is supported by several studies which have shown that low pH, Mg^{2+} , Ca^{2+} , and Al^{3+} promote hematite formation, while high pH, CO_3^{2-} , SO_4^{2-} , and Fe^{2+} favor the crystallization of goethite. Furthermore, silicate, phosphate and certain organic compounds may inhibit crystallization of both goethite and hematite (Gastuche, Bruggenwert and Mortland, 1964; Langmuir and Whittemore, 1971; Schwertmann *et al.*, 1968; Taylor and Graley, 1967). The major impurity in the reagent grade KOH used in our aging gels was K_2CO_3 (2.0 per cent maximum). This impurity perhaps explains the occurrence of only goethite at pH values where other workers (Schwertmann *et al.*, 1968) report coexisting hematite.

Mixtures of amorphous and crystalline hydrated ferric oxides

Having demonstrated that we could prepare both essentially amorphous hydrated ferric oxide, and wholly crystalline goethite, we then evaluated the relative merits of the oxalate extraction, X-ray diffraction analysis, and infrared absorption analysis for quantitatively measuring the degree of crystallinity of various mixtures of these materials. The mixtures studied included.

- (1) An artificial mixture of natural, well crystallized goethite and amorphous material.
- (2) An artificial mixture of reagent hematite and amorphous material.
- (3) An artificial mixture of wholly crystalline, synthetic goethite and amorphous material.

(4) An aging series with increasing crystallinity (goethite).

Acid ammonium oxalate extraction. As indicated previously, the fresh, essentially amorphous material was completely soluble ($Fe_{ox}/Fe_{HCl} = 1.0$), and the fully-aged goethite was insoluble ($Fe_{ox}/Fe_{HCl} = 0.0$) in pH 3.0 ammonium oxalate with a two hour extraction time.

Figure 6 shows the X-ray diffractograms of the goethite (110) reflection both for the members of an aging series and for their respective post-oxalate extraction residues. The similar residue intensities, despite divergent initial oxalate solubilities, support the use of this method in the selective removal of noncrystalline components from mixtures.

A series of artificial mixtures of synthetic goethite and amorphous material, of known composition, were then used as a check on extraction. The measured oxalate-soluble fraction of each of the artificial mixtures is plotted against the known weight fraction of amorphous material (Fig. 7). The high r^2 Value and the small deviation of the slope of the regression line from unity shows the close, 1:1 relationship between oxalate solubility and crystallinity.

X-ray diffraction analysis. A plot of oxalate-soluble fraction vs. the relative intensity of the goethite (110) X-ray reflection (normalized to the intensity of the post-oxalate residue) for the aging series shows a marked attenuation of the relative intensity at all intermediate stages of crystallinity (Fig. 8a). To determine if a change in some physical property of the individual crystals (size, imperfections, changes in stacking order, etc.), which might accompany the increase in numbers of crystals with aging, were responsible for the X-ray attenuation at lower levels of cry-

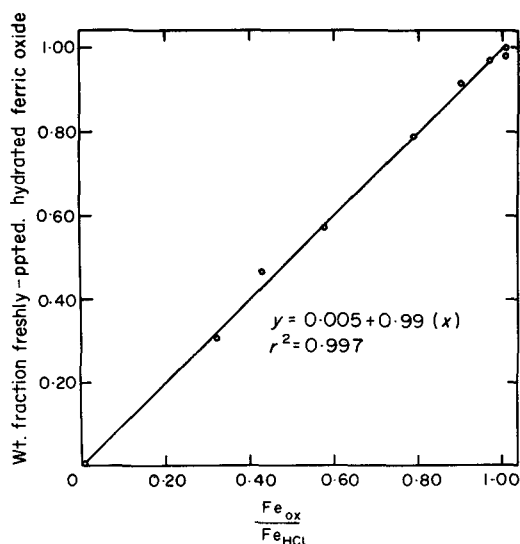


Fig. 7. Effect of pH 3.0 ammonium oxalate extraction on artificial mixtures of synthetic X-ray amorphous hydrated ferric oxide and goethite.

stallinity, mixtures of both natural goethite (Fig. 8b) and synthetic goethite (Fig. 8c) with the freshly prepared amorphous material were examined. Because the properties of the crystalline material in such mixtures are invariant, any deviation of the plot from linearity must reflect a matrix effect involving the non-diffracting, fresh material. Both Figs. 8b and c show this attenuation, although to a somewhat lesser extent than does the aging series. A matrix effect, probably involving variations in the absorption of X-radiation, and/or in particle orientation, is thought to be responsible. The greater attenuation observed

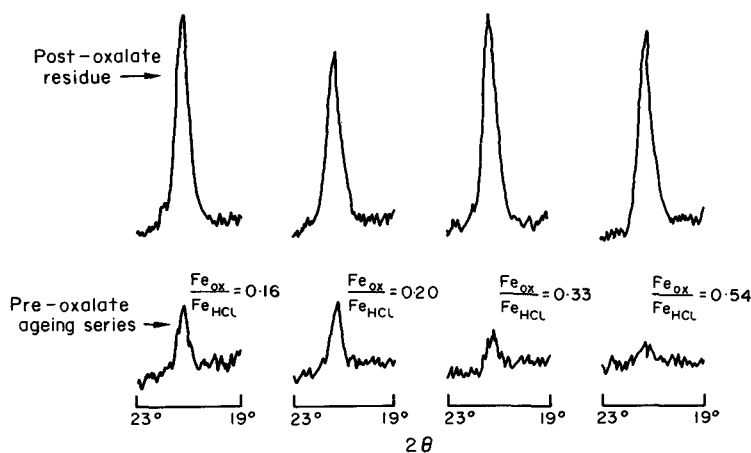


Fig. 6. X-ray diffraction intensity of goethite 4.18 \AA (110) peak before and after pH 3.0 ammonium oxalate extraction of aging materials.

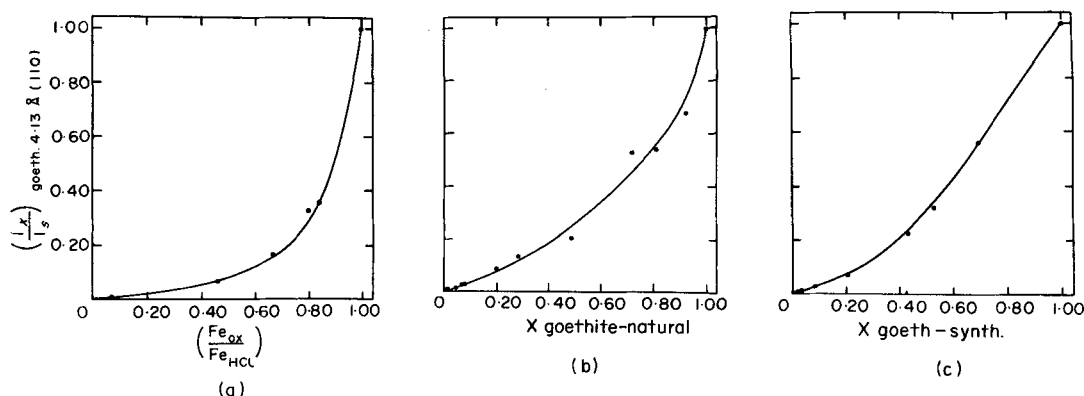


Fig. 8. Relative intensity (I_x/I_s) of goethite 4.13 Å (110) X-ray diffraction line as a function of oxalate-soluble fraction, Fe_{ox}/Fe_{HCl} , for aging materials (b) artificial mixtures of natural goethite and X-ray amorphous hydrated ferric oxide (c) artificial mixtures of synthetic goethite and X-ray amorphous hydrated ferric oxide.

in the aging series of samples is perhaps due to the continuum of crystallinity, from initial nuclei to final crystals, which exists in the aging series but not in the artificial mixtures.

The mass absorption coefficient (μ^*) of a given material for X-radiation, is a measure of the reduction of the intensity of the incident beam on passing through a thickness of the material. The large values of μ^* for $CuK\alpha$ radiation for high iron content materials ($\mu_{Fe_2O_3} = 230.8$, $\mu_{FeOOH} = 208.4$) indicate that such materials will absorb much of the incident radiation, thus reducing the intensity of the diffracted radiation, and increasing the background radiation level by non-directional fluorescence. The value of μ^* for a given X-ray wavelength depends only on the chemical composition of the material and is not

affected by polymorphic variations (Brindley, 1961; Whittig, 1965). Klug and Alexander (1954) have shown that the relationship between intensity and concentration of a given component is linear for binary mixtures of materials with similar coefficients. On the other hand, for a binary mixture of a strongly absorbing and weakly absorbing species, the reflections of the weak absorber are attenuated, while those of the strong absorber are enhanced.

To see if differences in the X-ray absorption and scattering properties of the crystalline goethite and the freshly prepared material were responsible for the reduced intensity shown in Figs. 8a, b and c, a similar concentration/intensity plot was prepared for mixtures of reagent hematite and freshly prepared material (Fig. 9a). In contrast to the

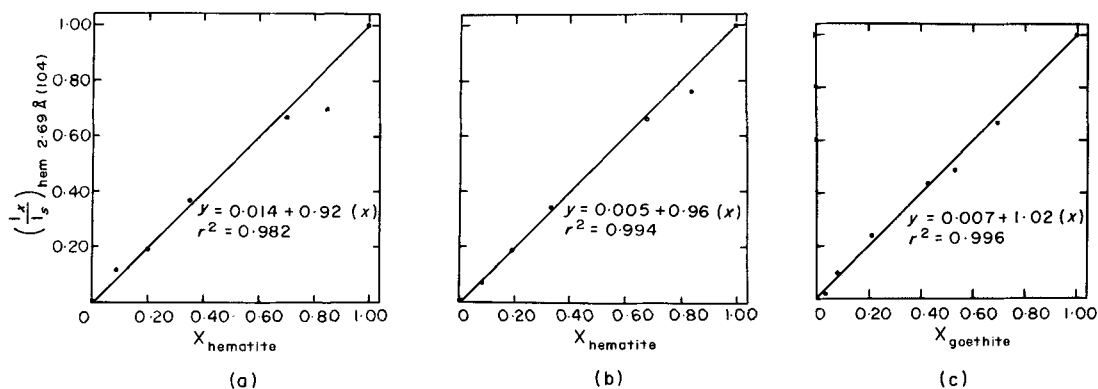


Fig. 9. Relative intensity (I_x/I_s) of strongest X-ray diffraction line as a function of weight fraction crystalline material for sedimented diffractometer specimens of: (a) artificial mixtures of hematite and X-ray amorphous hydrated ferric oxide (b) artificial mixtures of hematite, X-ray amorphous hydrated ferric oxide, and glass powder (c) artificial mixtures of synthetic goethite, X-ray amorphous hydrated ferric oxide, and glass powder.

results for goethite (Figs. 8a, b, c), the hematite series shows a linear relationship (Fig. 9a), indicating that the absorption coefficients (μ^*) for hematite and the amorphous material are approximately the same. Since μ^* (Brindley, 1961) for hematite, Fe_2O_3 , is close to that for goethite, FeOOH , it follows that the value of μ^* for the amorphous material is also close to that of goethite. Therefore, we conclude that absorption effects are not responsible for the non-linear concentration/intensity plots found for the goethite-fresh material mixtures.

The fibrous to platy habit revealed by electron microscopy for both natural and synthetic goethites suggests the possibility of a preferred orientation on settling from suspension onto an X-ray slide. A comparison of the X-ray diffractogram intensities (peak heights) obtained from the pure materials, dried down in this manner, with those obtained from random powder patterns (Rooksby, 1961), reveals a strong degree of enhancement in the intensity of the goethite (110) relative to the other planes, while no such effect is observed for hematite (Table 1).

To test this hypothesis, X-ray amorphous fine glass powder was ground together with the mixtures of freshly-prepared and crystalline hydrated ferric oxides in an attempt to randomize the particle orientation in the mixtures. From the chemical analysis of the glass, a μ^* of 43.5 was calculated. Because this coefficient is much less than that of Fe_2O_3 or FeOOH , one must maintain a constant ratio of glass to ferric oxide in samples for X-ray diffraction analysis in order that orientation effects, rather than inequalities in the absorbing

power of the ferric oxide specimen and the glass powder diluent, be reflected by the X-ray intensities recorded. Indeed, where such a constant ratio was used with the presumably non-oriented hematite-fresh material mixtures (Fig. 9a), a similar linear concentration vs X-ray intensity plot was obtained (Fig. 9b).

Randomly packed specimens of the previously-examined mixtures of synthetic goethite and fresh material were prepared for X-ray diffractometer study by incorporating one part of the hydrated ferric oxide mixture with two parts of the glass powder (by weight). By using the same amount of glass in each, the mass absorption coefficient of the specimens is kept relatively uniform, leaving only orientation as a possible variable. A comparison of the concentration/intensity plots of the same mixtures with (Fig. 9c) and without glass powder (Fig. 8c) reveals both the efficacy of the glass powder procedure, and the pronounced effect of preferred orientation on the X-ray diffraction intensity of goethite admixed with fresh material.

Thus it appears that the wholly crystalline goethite samples display a strong degree of preferred orientation which greatly enhances the (110) X-ray reflection. With increasing amounts of amorphous material, the degree of orientation, and thus the (110) intensity, is apparently reduced. Likewise, the lack of any strong preferred orientation in the sedimented hematite crystals results in a linear crystallinity vs. relative intensity plot. So, while Rooksby (1961) discounts the effect of preferred orientation in X-ray diffraction analysis of iron oxides and hydrous oxides, in the case

Table 1. Comparison of X-ray diffraction intensities of various crystallographic planes for sedimented diffractometer and randomized powder specimens of goethite and hematite

Material	$d(\text{\AA})$	$(hkl)^*$	Relative intensity of X-ray reflection		Ratio $\frac{I_{\text{diff.}}}{I_{\text{powd.}}}$
			diffractometer*	powder†	
Natural goethite	4.98	020	6	15	0.40
	4.18	110	100	100	
	3.38	120	4	10	0.40
	2.69	130	11	30	0.33
	2.49	040	3	15	0.20
	2.19	140	6	20	0.30
Synthetic goethite	4.18	110	100	100	
	2.69	130	9	30	0.30
	2.45	111	8	25	0.32
Reagent hematite	3.67	102	33	35	0.94
	2.69	104	100	100	
	2.51	110	74	75	0.99
	2.20	113	22	25	0.88

*Rooksby (1961).

†Normalized peak height.

of goethite at least, our results show it to be an important consideration.

I.R. absorption analysis. The strength and sharpness of the O–H deformation bands of goethite suggested their use as a measure of the goethite content of partially crystalline gels. To test this, the mixtures of the fresh precipitate ($Fe_{ox}/Fe_{HCl} = 1.0$) with well-aged goethite ($Fe_{ox}/Fe_{HCl} = 0.0$) were examined.

Figure 10 shows the 400–1000 cm^{-1} region of the i.r. absorption spectra of mixtures containing 0, 2, 8, 21, 43, 69 and 100 per cent crystalline goethite. The results show that the diagnostic goethite bands are masked to different extents by the freshly-prepared material. The very strong 890 cm^{-1} band is first evident at 2 per cent crystallinity, the slightly weaker 795 cm^{-1} band at 8 per cent and the moderately strong 650 cm^{-1} band at 43 per cent crystallinity.

Potentially, the intensity of the 890 cm^{-1} absorption band may be a good measure of the degree of crystallinity in these mixtures. However, difficulty in accurately locating the peak shoulders at lower levels of crystallinity, and the resulting uncertainty in establishing the baseline of the peaks, makes quantitative measurements less certain than in the case of oxalate extraction or X-ray diffraction analysis.

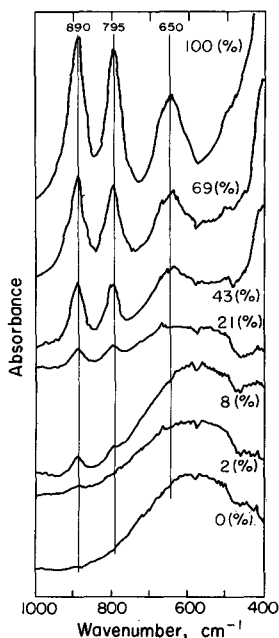


Fig. 10. Intensity of diagnostic goethite i.r. bands as a function of weight percent synthetic goethite in artificial mixtures with X-ray amorphous hydrated ferric oxide.

SUMMARY AND CONCLUSIONS

By the methods outlined, it is possible to prepare essentially non-crystalline hydrated ferric oxide, wholly crystalline goethite, and mixtures of the two, without coexisting hematite. The apparent contradictions in the literature as to the identity of the initial and aged products are thought to result from subtle differences in preparatory techniques and materials, and from kinetic factors.

The acid ammonium oxalate extraction method, and the non-oriented X-ray diffraction method are both satisfactory ways of quantitatively estimating the degree of crystallinity of such gels in which goethite crystallizes during the aging process. While no attempt was made to assess absolute detection limits, both methods appear capable of detecting 2 per cent crystalline material. However, the oxalate method is probably superior since it depends directly on an inherent difference in the solubility of the crystalline and non-crystalline materials, rather than on a technique-dependent intensity measurement.

The use of the intensity of the O–H bending vibrations of the infrared absorption spectra can potentially detect as little as 2 per cent crystallinity, but the procedure is probably less useful for quantitative determinations, than ammonium oxalate extraction or X-ray diffraction analysis.

Acknowledgements—The assistance of Dr. R. J. Zeyen in obtaining the electron micrographs, and Dr. R. H. Dowdy in obtaining and interpreting the i.r. spectra is gratefully acknowledged.

REFERENCES

- Bentley, F. F., Smithson, L. D. and Rozek, A. L. (1968) *Infrared Spectra and Characteristic Frequencies 700–300 cm^{-1}* . Interscience, New York.
- Blume, H. P. and Schwertmann, U. (1969) Genetic evaluation of profile distribution of aluminum, iron and manganese oxides: *Soil Sci. Soc. Am. Proc.* **33**, 438–444.
- Blyholder, G. and Richardson, E. A. (1962) Infrared and volumetric data on the adsorption of ammonia, water and other gases on activated iron (III) oxide: *J. Phys. Chem.* **66**, 2597–2602.
- Brindley, G. W. (1961) Quantitative analysis of clay minerals: in *X-ray Identification and Crystal Structures of Clay Minerals* (Edited by G. Brown) pp. 489–516. Mineral Soc. London.
- Deer, W. A., Howie, R. A. and Zussman, J. (1962) *Rock Forming Minerals, Non-silicates* Vol. 5. Longmans, London.
- Ewing, F. J. (1935) The crystal structure of diaspore: *J. Chem. Phys.* **3**, 203–207.
- Garrels, R. M. (1959) Rates of geochemical reactions at low temperatures and pressures: *Researches in Geochemistry* (Edited by P. H. Abelson) Wiley, New York.
- Gastuche, M. C., Bruggenwert, T. and Mortland, M. M.

- (1964) Crystallization of mixed iron and aluminum gels: *Soil Sci.* **98**, 281–289.
- Glemser, O. and Hartert, E. (1953) Knickschwingungen der OH-gruppe im gitter von hydroxyden: *Naturwissenschaften* **40**, 552–553.
- Jackson, M. L. (1956) *Soil Chemical Analysis-Advanced Course*. Publ. by author, Dept. of Soils, Univ. of Wisconsin, Madison 6, Wisconsin.
- Klug, H. P. and Alexander, L. E. (1954) *X-ray Diffraction Procedures*. Wiley, New York.
- Kumada, K. and Aizawa, K. (1959) The infrared absorption spectra of soil components: *Soil Plant Food (Tokoyo)* **4**, 181–188.
- Langmuir, D. and Wittermore, D. O. (1971) Variations in the stability of precipitated ferric oxyhydroxides: In *Non-equilibrium Systems in Natural Water Chemistry* (Adv. in Chem. series, No. 106) (Edited by R. F. Gould) pp.209–234. Am. Chem. Soc., New York.
- Mackenzie, R. C. and Meldau, R. (1959) The aging of sesquioxide gels. (I) Iron oxide gels: *Mineral Mag.* **32**, 153–165.
- Marshall, P. R. and Rutherford, D. (1971) Physical investigations on colloidal iron-dextran complexes: *J. Colloid Interface Sci.* **37**, 390–402.
- Pawluk, S. (1972) Measurement of crystalline and amorphous iron removal in soils: *Can. J. Soil Sci.* **52**, 119–123.
- Rooksby, H. P. (1961) Oxides and hydroxides of iron and aluminum: In *X-ray Identification and Crystal Structures of Clay Minerals* (Edited by G. Brown) 354–392. Mineral Soc. London.
- Roy, D. M. and Roy, R. (1957) Hydrogen-deuterium exchange in clays and problems in the assignment of infra-red frequencies in the hydroxyl region: *Geochim. Cosmochim. Acta* **11**, 72–85.
- Sandell, E. B. (1944) *Colorimetric Determination of Traces of Metals*. Interscience, New York.
- Schwertmann, U., Fischer, W. R. and Papendorf, H. (1968) The influence of organic compounds on the formation of iron oxides: *Trans. 9th Intern. Congr. Soil Sci. (Adelaide)* **1**, 645–655.
- Sims, J. R. and Bingham, F. T. (1968) Retention of boron by layer silicates, sesquioxides, and soil materials (II). Sesquioxides: *Soil Sci. Soc. Am. Proc.* **32**, 364–373.
- Smith, F. G. and Kidd, D. J. (1949) Hematite-goethite relations in neutral and alkaline solutions under pressure: *Am. Mineralogist* **34**, 403–412.
- Stoops, G. (1970) Scanning electron microscopy applied to the micromorphological study of a laterite: *Pedologie (Ghent)* **20**, 268–280.
- Taylor, R. M. and Graley, A. M. (1967) The influence of ionic environment on the nature of iron oxides in soils: *J. Soil Sci.* **18**, 341–348.
- Whittig, L. D. (1965) X-ray diffraction techniques for mineral identification and mineralogical composition: In *Methods of Soil Analysis* (Edited by C. A. Black) Am. Soc. Agronomy (Monogr. 9), Madison, Wis., 671–698.

Résumé—La nature d'oxydes ferriques hydratés fraîchement précipités et vieillis, préparés par addition de chlorure ferrique à KOH, a été étudiée au moyen des microscopies électroniques à balayage et par transmission, de la diffraction des rayons X, de l'absorption infrarouge et de l'extraction par l'oxalate d'ammonium à pH 3, 0. Les résultats montrent que le matériel frais est essentiellement un oxyde ferrique hydraté non cristallisé, qui, lorsqu'il vieillit à 60°C et à pH élevé cristallise rapidement en goethite, sans aucune indication d'une coexistence d'hématite. Les différentes méthodes ont été testées en vue de fournir des indices de cristallisation pour les matériaux en cours de vieillissement. La méthode à l'oxalate d'ammonium acide s'est révélée capable d'extraire sélectivement la seule fraction non cristalline de tels mélanges.

L'utilisation de l'analyse aux rayons X pour estimer le degré de vieillissement requiert l'élimination de l'orientation préférentielle des cristaux de goethite. Alors que les méthodes à l'oxalate et aux rayons X peuvent chacune détecter un degré de cristallinité aussi petit que 2%, la méthode à l'oxalate est probablement supérieure pour des déterminations quantitatives car elle dépend directement d'une différence inhérente à la solubilité des matériaux cristallins et amorphes, plutôt que d'une mesure d'intensité dépendant d'une technique. L'utilisation de l'intensité des vibrations de déformation O-H du spectre d'absorption infrarouge permet aussi potentiellement de détecter un degré de cristallinité aussi petit que 2%, mais le procédé est probablement moins utile pour des déterminations quantitatives que les méthodes à l'oxalate ou aux rayons X à cause du problème posé par l'évaluation de la surface des pics.

Kurzreferat—Die Beschaffenheit von frisch gefällten und gealterten hydratisierten Ferrioxiden, die durch Zugabe von Ferrichlorid zu KOH hergestellt worden waren, wurden unter Einsatz der Raster- und der Durchlichtelektronenmikroskopie, der Röntgenbeugung, der IR-Absorption und einer Extraktion mit Ammoniumoxalat bei pH 3 untersucht. Die Ergebnisse zeigen, daß das frische Material im wesentlichen aus nichtkristallinem, hydratisiertem Ferrioxid besteht, das bei Alterung (60°C) und hohem pH schnell zu Goethit kristallisiert ohne daß Anzeichen für die Koexistenz von Hämatit auftreten. Die verschiedenen Methoden wurden ausgewertet, um ein Maß für die Kristallinität des alternen Materials zu erhalten. Es zeigte sich, daß die Extraktion mit saurem Ammoniumoxalat selektiv nur den nichtkristallinen Anteil solcher Gemische erfaßt. Die Anwendung der Röntgenbeugungsanalyse zur Abschätzung des Alterungszustandes erfordert die Beseitigung einer bevorzugten Orientierung der Goethitkristalle. Während sowohl die Oxalat- als auch die Röntgenbeugungsmethode eine Kristallinität von nur 2% nachzuweisen vermag, ist die Oxalatmethode wahrscheinlich bei quantitativen Bestimmungen überlegen, da sie sich direkt auf die spezifischen Löslichkeitsunterschiede zwischen

kristallinem und nichtkristallinem Material und nicht auf eine Intensitätsmessung gründet, die von der jeweiligen Technik abhängt. Bei Verwendung der Intensität der O-H-Deformationsschwingung des IR-Spektrums kann ebenfalls eine Kristallinität von nur 2% nachgewiesen werden. Jedoch ist dieses Verfahren vermutlich deswegen weniger für quantitative Bestimmungen brauchbar als die Oxalat- oder Röntgenbeugungsmethode, weil sich das Problem der Auswertung von Peak-Flächen ergibt.

Резюме — Электронной микроскопией со сканированием и просвечиванием, рентгенографией, ИК-абсорбцией и экстракцией рН 3,0 щавелекислого аммония исследовался характер свежосажденной и состарившейся гидратированной окиси железа, приготовленной путем прибавления хлорида железа к КОН. По результатам видно, что свежий материал является по существу некристаллической гидратированной окисью железа, которая подвергаясь старению при 60°C и при высоком рН быстро превращается в кристаллы гетита без всякого намека на спутника гематит. Рассматривались различные методы вызова кристаллического состояния для подвергавшихся старению материалов. Щавелекислый метод селективно экстрагировал только некристаллическую часть таких смесей. Рентгенографический метод для определения стадии старения требует устранения ориентации кристаллов гетита. В то время как обоими методами — щавелекислым и рентгенографией — можно детектировать такое незначительное кристаллическое состояние как 2%, но щавелекислый метод все таки лучше для количественного определения, так как он зависит непосредственно от растворимости кристаллических и некристаллических материалов, а не от техники зависящей от измерения интенсивности. ИК-абсорбцией можно также детектировать такое малое кристаллическое состояние как 2%, но эта процедура не так пригодна для количественного определения, как щавелекислый метод, вследствие трудности оценки площади под пиком.