

CHARACTERISTICS OF FERRIHYDRITES FORMED BY OXIDATION OF FeCl_2 SOLUTIONS CONTAINING DIFFERENT AMOUNTS OF SILICA

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Abstract—Well-crystallized ferrihydrite as indicated by its X-ray powder diffraction pattern and low solubility in acidified oxalate ($\text{Fe}_o/\text{Fe}_t = 0.27$) was formed by the oxidation of FeCl_2 solution containing $\text{Si}/\text{Fe} = 18 \times 10^{-3}$. The crystallinity of ferrihydrites formed from the solutions containing $\text{Si}/\text{Fe} > 18 \times 10^{-3}$ was lowered as indicated by weaker and broader XRD lines and increased oxalate solubility. Ferrihydrites formed in the presence of silica did not give the differential thermal analysis exothermic peak between 350° and 450°C that is found for ferrihydrites prepared from the hydrolysis of Fe(III) salts. The transformation of ferrihydrite (formed at $\text{Si}/\text{Fe} = 18 \times 10^{-3}$) to hematite was inhibited by the presence of 1.48% SiO_2 in the oxidation products.

Key Words—Ferrihydrite, Hematite, Iron, Lepidocrocite, Oxidation, Silica.

INTRODUCTION

Ferrihydrite, a brown, poorly crystalline Fe oxide, has been reported in nature by several workers (e.g., Jackson and Keller, 1970; Chukhrov *et al.*, 1973; Schwertmann and Fischer, 1973; Henmi *et al.*, 1980; Karim *et al.*, 1981; Schwertmann *et al.*, 1982). Natural ferrihydrites cover a range of crystallinities and usually contain significant amounts of Si, part of which is un-polymerized as indicated by Si–O–Fe bonds and part of which is polymerized (Carlson and Schwertmann, 1981). It can be synthesized in the laboratory by the rapid hydrolysis of Fe(III) solution (Towe and Bradley, 1967) and the oxidation of Fe(II) ions in the presence of Si (Schwertmann and Thalmann, 1976; Karim, 1977). Ferrihydrites prepared by the above procedures show broad X-ray powder diffraction lines indicating a hexagonal unit cell with $a = 5.08 \text{ \AA}$ and $c = 9.4 \text{ \AA}$. If Si is added, the ferrihydrite produced does not show an exothermic differential thermal analysis (DTA) peak between 350° and 450°C on DTA as does synthetic ferrihydrite prepared by the method of Towe and Bradley (1967).

Jackson and Keller (1970) and Chukhrov *et al.* (1973) used this DTA peak for detection of ferrihydrite in soils. This exothermic peak has been observed for natural ferrihydrite when the DTA was performed in air but not when it was carried out in N_2 and is therefore presumably due to the oxidation of organic matter and not to the recrystallization of hematite (Taylor, 1959; Schwertmann and Fischer, 1973).

The present paper presents further data on the X-ray diffraction powder pattern, oxalate solubility, and differential thermal analysis of ferrihydrite formed by oxidation of FeCl_2 solutions containing different amounts of Si. The data may aid in the characterization of ferrihydrites in nature.

MATERIALS AND METHODS

Ferrihydrites were prepared by bubbling CO_2 -free air at a rate of 1–2 bubbles per second into 100 ml of an aqueous solution of 0.05 M FeCl_2 (pH 7) having a range of initial atomic Si/Fe ratios between 0 and 53.5×10^{-3} (Schwertmann and Thalmann, 1976; Karim, 1977). During oxidation the pH decreased to 4.0 (± 0.3). The rate of oxidation, measured by the decrease of pH was faster in the presence of Si; solutions containing Si/Fe ratios of 18×10^{-3} and 53.5×10^{-3} took 36 and 32 min, respectively, whereas Si-free solution took about 48 min. After complete oxidation the oxides were dialyzed against distilled H_2O until the H_2O gave a negative test for Cl^- with AgNO_3 , and then dried at 70°C.

X-ray powder diffraction (XRD) patterns were obtained with a Philips diffractometer from samples packed in aluminum holders using $\text{CoK}\alpha$ radiation. Differential thermal analysis was accomplished in an inert (N_2) atmosphere with a Stanton Redcroft DTA 673-4. Specific surface areas were measured by the BET single-point method using nitrogen as the adsorption gas and a technique developed by Greene-Kelly and Gallavan (unpublished) at the Rothamsted Experimental Station.

To test the solubility of ferrihydrite in oxalate (Fe_o), a preliminary experiment was conducted shaking 25, 50, and 100 mg of ferrihydrite formed at $\text{Si}/\text{Fe} = 18 \times 10^{-3}$ in 100 ml of a NH_4 -oxalate/oxalic acid mixture (pH 3.0) for 2 hr in the dark (Schwertmann, 1964). A duplicate sample was dissolved completely by gentle heating in a few milliliters of approximately 12 N HCl to determine total iron (Fe_t). For the above solid-solution ratios the Fe_o/Fe_t values varied only from 0.30 to 0.28; therefore, 100 mg of sample was used throughout.

Iron was determined by atomic absorption spec-

Table 1. Properties of synthetic ferrihydrites prepared by oxidation of 0.05 M FeCl₂ solutions.

| Si/Fe × 10 ⁻³ of initial solution | Minerals formed | Uncorrected width at half height | | Specific surface m ² /g | Fe _o /Fe _t | Si _t | Si _o /Si _t |
|--|--|-----------------------------------|----------------------------------|------------------------------------|----------------------------------|-----------------|----------------------------------|
| | | (020) line of lepidocrocite (°2θ) | (112) line of ferrihydrite (°2θ) | | | | |
| 0 | Lepidocrocite | 0.50 | — | 57 | 0.42 | — | 0 |
| 8.3 | Lepidocrocite, some ferrihydrite | 0.64 | Not detected | 108 | 0.36 | 0.29 | 0.38 |
| 18.0 | Well-crystallized ferrihydrite, some ferroxihite, trace lepidocrocite + goethite | 0.73 | 1.25 | 146 | 0.27 | 0.69 | 0.30 |
| 35.6 | Poorly crystallized ferrihydrite | — | 1.67 | 167 | 0.47 | 1.19 | 0.31 |
| 53.5 | Poorly crystallized ferrihydrite | — | Very weak peak | 291 | 0.82 | 1.85 | 0.89 |

trospecty. Silica was determined in the HCl and oxalate extracts photometrically (Boltz and Mellon, 1947). HCl extracts were neutralized with NaOH to minimize polymerization, and oxalate extracts were filtered before the determinations. The concentrations of Fe in these extracts were always determined first, and the silica standard solutions were made up containing the same concentration of iron. For oxalate, the standard solution also contained an equal concentration of ammonium oxalate.

RESULTS AND DISCUSSION

X-ray powder diffraction pattern

The oxidation of the 0.05 M FeCl₂ solution yielded lepidocrocite (Table 1). The lepidocrocite formed at Si/Fe = 8.3 × 10⁻³ was less well crystalline as seen from diffraction line broadening. The specific surface of the products was also higher (Table 1). At Si/Fe = 18 × 10⁻³, the most well-crystalline ferrihydrite was formed and gave rise to six distinct lines at 2.54 (110), 2.24 (112), 1.98 (113), 1.73 (114), 1.51 (115), and 1.47 Å (300) (Figure 1a). This sample contained small amounts of lepidocrocite and goethite and possibly some ferroxihite. At Si/Fe = 35.6 × 10⁻³, all of the ferrihydrite lines were weaker and broader, and the lines at 1.98 and 1.73 Å could hardly be detected. No lepidocrocite, ferroxihite, or goethite was present (Figure 1c, Table 1). At Si/Fe = 53.5 × 10⁻³, lines at 1.98, 1.73, and 1.51 Å were not detected, and the line at 2.24 Å was very weak; only two broadened lines at 2.54 and 1.47 Å were noted.

Natural ferrihydrites usually give broad reflections at 2.50, 2.24, 1.97, 1.72, and 1.53 Å (Schwertmann and Fischer, 1973; Chukhrov *et al.*, 1973). Carlson and Schwertmann (1981) described ferrihydrites from Fe-bearing waters in Finland whose crystallinity varied from a reasonably well-developed structure to a highly

disordered one with only two prismatic reflections at 2.5 and 1.5 Å.

The XRD pattern of the well-crystallized ferrihydrite formed at Si/Fe = 18 × 10⁻³ fairly well agrees with that of the best crystalline ferrihydrite formed on the wall of an open pit in a sulfide mine where water flows from a fissure in a black schist in Finland (Carlson and Schwertmann, 1981). The ferrihydrite formed at Si/Fe = 53.5 × 10⁻³ was similar to the highly disordered material described by these authors and gave mainly two reflections at 2.5 and 1.5 Å.

Oxalate solubility

At Si/Fe = 18 × 10⁻³, well-crystallized ferrihydrite was formed possibly with some ferroxihite and small amounts of lepidocrocite and goethite (Figure 1a). This oxide mixture contained 0.69% Si. The Fe_o/Fe_t ratio was 0.27, lower than that of lepidocrocite (0.42) formed in the Si-free system. The XRD patterns of this sample did not change after oxalate treatment (Figure 1a, 1b), indicating that the well-crystallized, Si-containing ferrihydrite was only partly soluble in oxalate. These findings are in agreement with those of Carlson and Schwertmann (1981) who found that even after three extractions with oxalate, some ferrihydrite remained.

As the Si/Fe in solution increased, the Si content of the oxide as well as its Fe_o/Fe_t ratio increased (Table 1). The role of Si in the oxalate solubility of ferrihydrite is not well understood. The solubility of ferrihydrite seems to be closely related to the specific surface. Ferrihydrite formed at Si/Fe = 53.5 × 10⁻³ containing 1.85% Si in the oxide and having the largest specific surface (291 m²/g) had a Fe_o/Fe_t ratio of 0.82. The Si_o/Si_t values for the oxides formed between Si/Fe of 8.3 × 10⁻³ and 35.6 × 10⁻³ varied from 0.30 to 0.38, indicating that a large fraction of the precipitated Si was associated with the oxalate-insoluble residue. Silica as-

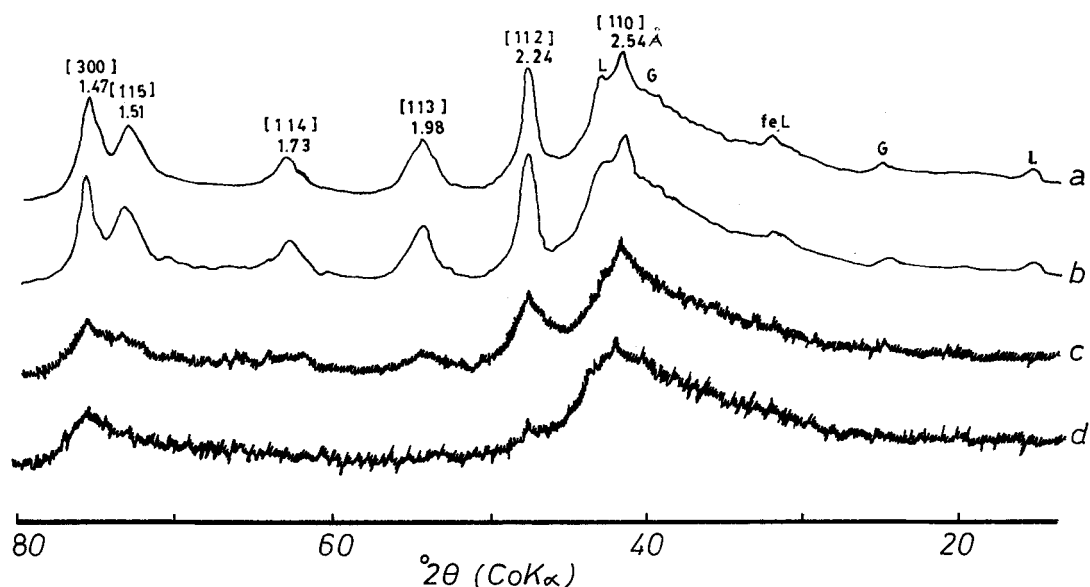


Figure 1. X-ray powder diffraction patterns of ferrihydrite (L = lepidocrocite, G = goethite, fe = feroxyhite). (a) Ferrihydrite from oxidation of FeCl₂ solution with Si/Fe = 18×10^{-3} ; (b) same as (a) but after extraction with acidified oxalate; (c) same as (a) but with Si/Fe = 35.6×10^{-3} ; (d) same as (a) but with Si/Fe = 53.5×10^{-3} .

sociated with ferrihydrites may be partly polymerized and partly unpolymerized (Carlson and Schwertmann, 1981), thereby affecting its solution in oxalate.

Thermal analysis

DTA (in N₂) of ferrihydrite formed at Si/Fe = 18×10^{-3} did not give the exothermic peak between 350° and 450°C (Figure 2a) that was found for the sample prepared from Fe(NO₃)₃ by the method of Towe and Bradley (1967). On the contrary, it gave a broad endothermic peak at ~100°C due to adsorbed water, as well as a weak endothermic peak at ~130°C which is probably due to the presence of a small amount of feroxyhite. A natural ferrihydrite, from an ochreous deposit formed in a plastic pipe in areas where water has drained through peaty, pyrite-containing fen soils in England (supplied by G. Brown at Rothamsted Experimental Station) also gave no exothermic peak; rather it gave only one broad endothermic peak at ~100°C. Iwasa (1965), Jackson and Keller (1970), and Chukhrov *et al.* (1973) used the exothermic peak between 300° and 400°C for the detection of ferrihydrite in soils; however Taylor (1959) and Schwertmann and Fischer (1973) observed this exothermic peak only when the DTA was performed in air but not under N₂.

XRD patterns were obtained for a synthetic ferrihydrite formed at Si/Fe = 18×10^{-3} and heated between 230° and 750°C. No hematite was formed below 650°C, but the transformation was complete at 750°C. The main weight loss, about 11.2% of the initial weight, occurred below 230°C. Discrete steps were not noted

above 230°C. A ferrihydrite sample prepared by the method of Towe and Bradley (1967) and converted to hematite by heating, produced a sharp DTA peak at

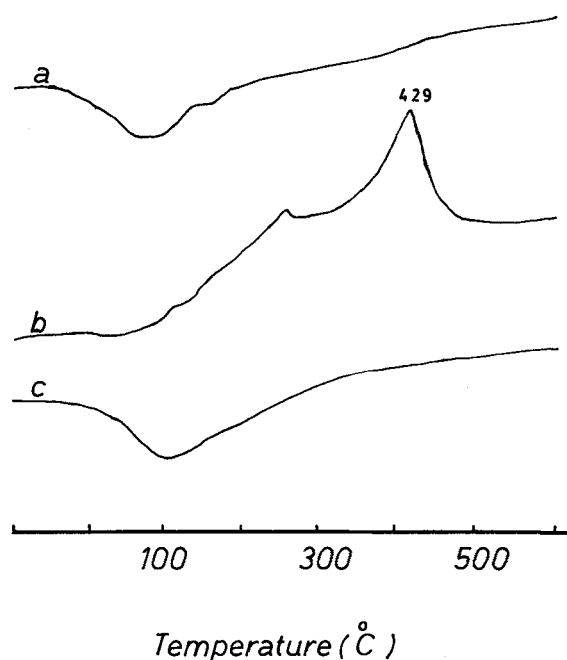


Figure 2. Differential thermal analysis curves of ferrihydrite. (a) Ferrihydrite from oxidation of FeCl₂ solution with Si/Fe = 18×10^{-3} ; (b) ferrihydrite from hydrolysis of Fe(III) salts by the method of Towe and Bradley (1967); (c) natural ferrihydrite containing 1.9% Si.

429°C. These results indicate that the transformation reaction was strongly inhibited by Si associated with ferrihydrite. These data are in good agreement with the results from Carlson and Schwertmann (1981) who found that a natural ferrihydrite persisted to 600°C. Natural ferrihydrite always contains some silica (Chukhrov *et al.*, 1973); Si–O–Fe bonds are probably responsible for its stabilization (Carlson and Schwertmann, 1981).

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Резюме—Хорошо кристаллизированный железогидрит формировался путем окисления раствора FeCl₂, содержащего Si/Fe = 18 × 10⁻³, что показано при помощи рентгеновских порошковых дифрактограмм (РПД) и низкой растворимости в подкисленном оксалате (Fe_o/Fe_t = 0,27). Кристалличность железогидритов, формирующихся из растворов с Si/Fe = 18 × 10⁻³ уменьшалась, что показано при помощи более слабых и широких линий РПД и увеличивающейся растворимости в оксалате. Железогидриты, формирующиеся в присутствии кремнезема, не давали экзотермических пиков между 350° и 450°C (по дифференциальному термическому анализу), которые находились в случае железогидритов, подготовленных путем гидролиза соли Fe(III). Трансформация железогидрита (образованного при Si/Fe = 18 × 10⁻³) в гематит задерживалась при присутствии 1,48% кремнезема в продуктах окисления. [E.G.]

Resümee—Gut kristallisierter Ferrihydrit, wie durch seine Röntgenpulverdiagramme und seine niedrige Löslichkeit in angesäuertem Oxalatlösung angezeigt wird (Fe_o/Fe_t = 0,27), wurde durch die Oxidation von FeCl₂-Lösungen, die ein Si/Fe-Verhältnis von 18 × 10⁻³ aufwiesen, hergestellt. Die Kristallinität von Ferrihydriten, die aus Lösungen mit Si/Fe > 18 × 10⁻³ gebildet wurden, wurde verringert, wie durch schwächere und breitere Röntgendiffraktometerpeaks und gestiegene Löslichkeit in Oxalatlösung hervorgeht. Ferrihydrite, die sich in Gegenwart von SiO₂ bildeten, ergaben bei der Differentialthermoanalyse keinen exothermen Peak zwischen 350° und 450°C, den man bei Ferrihydriten findet, die durch Hydrolyse von Fe(III)-Salzen hergestellt wurden. Die Umwandlung von Ferrihydrit (gebildet bei Si/Fe = 18 × 10⁻³) in Haematit wurde durch die Anwesenheit von 1,48% SiO₂ in den Oxidationsprodukten verhindert. [U.W.]

Résumé—La ferrihydrite bien cristallisée, indiquée par son cliché de diffraction aux rayons-X et par sa basse solubilité dans l'oxalate acidifiée (Fe_o/Fe_t = 0,27) a été formée par l'oxidation d'une solution FeCl₂ contenant Si/Fe = 18 × 10⁻³. La cristallinité de ferrihydrites formées de solutions contenant Si/Fe > 18 × 10⁻³ était plus basse comme l'ont indiqué des lignes XRD plus faibles et plus larges, et une plus grande solubilité dans l'oxalate. Les ferrihydrites formées en présence de silice n'ont pas donné le sommet exothermique d'analyse thermique différentielle entre 350° et 450°C que l'on trouve pour les ferrihydrites préparées à partir de l'hydrolyse de sels Fe(III). La transformation de ferrihydrite (formée à Si/Fe = 18 × 10⁻³) en hématite a été inhibée par la présence de 1,48% SiO₂ dans les produits d'oxidation. [D.J.]