

## FORMATION OF HARD HEMATITE-CEMENTED SOLIDS IN STEAM GENERATORS: AN ANALOG OF LITHIFICATION OF Fe-CONTAINING SEDIMENTARY ROCKS

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**Abstract**—The formation of hard hematite in steam generators with relatively high levels (5–10 µg/L) of dissolved oxygen at temperatures around 280–290°C and pressures around 6–8 MPa can serve as an analog for the formation of hard hematite in sedimentary processes. Furthermore, in steam generators, as well as in nature, hematite is an effective cementing agent, capable of incorporating as much as twice its own weight of other solids to form a hard composite material. Laboratory simulations showed ferrihydrite to be the likely starting material for the formation of hard, dense hematite at temperatures much lower than those required for sintering of anhydrous hematite. These laboratory simulations, performed at temperatures around 260°C and pressures of ~500 MPa, resulted in the formation of hard hematite or hematite-based composite solids over periods of 3–5 h, compared with several months in steam generators and many years in nature. The amount of water present during the synthesis (10–15% of the weight of dry ferrihydrite) and the gradual removal of water proved to be key parameters in the formation of hard, dense hematite. The mechanism, studied by means of X-ray diffractometry, Mössbauer spectroscopy and infrared spectroscopy, appeared to involve build-up, then gradual condensation of OH bridges, leading to the conversion of ferrihydrite to hydrohematite with approximately 4–5% of residual water. The presence of other solids, such as copper and its oxides, alumina and silica, in large quantities, resulted in smaller grain size of the hydrohematite product but did not affect its mechanical properties. On the other hand, the use of hydrazine to provide a reducing environment produced goethite during the precursor synthesis stage and soft magnetite during the pressing stage. However, whenever hematite was produced, it could not be subsequently reduced to magnetite by hydrazine under the reaction conditions specified above. The mechanical properties as well as the spectroscopic characteristics of the product of pressing agreed with observations on sedimentary hematite-cemented rocks.

**Key Words**—Cementation, Dehydration, Ferrihydrite, Hardening, Hematite, Hydrohematite, Fe Oxides, Lithification, Oxyhydroxide, Sedimentary Rock.

### INTRODUCTION

In nature, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) occurs in some formations and sediments as a dense, fairly hard rock (Mohs hardness 5.5–6.5). In many cases the occurrence of hematite is sedimentary, implying that its formation has taken place at moderate temperatures. On the other hand, it is known that sintering of hematite powder requires very high temperatures, typically above 900°C (Bagchi and Sen, 1982; Pfaff and Feltz, 1990). These findings raise the question whether forms of Fe oxides other than dry hematite powder, in particular hydrated species, are the precursors of dense, hard hematite formed at moderate temperatures. Many researchers have studied the conversion of hydrated Fe oxides such as ferrihydrite into hematite (Cornejo, 1986; Schwertmann and Cornell, 2000; Schwertmann *et al.*, 1999). A large number of observations on the occurrence and constitution of natural and synthetic ferrihydrite, and in particular on the transformation of ferrihydrite into hematite (Stanjek

and Weidler, 1992; Eggleton and Fitzpatrick, 1988; Drits *et al.*, 1993, 1995; Campbell *et al.*, 1997; Zhao *et al.*, 1994), have been reported and reviewed (Jambor and Dutrizac, 1998; Cornell and Schwertmann, 2003). It was noted that when the 2-line or 6-line varieties of ferrihydrite were heated at 127°C for periods as long as 1180 h, a significant reduction in water content was observed, but there was no major change in the X-ray diffraction (XRD) patterns (Weidler, 1995). On the other hand, when ferrihydrite was heated at 227°C, hematite formed readily (Stanjek and Weidler, 1992). The transformation was approximately half complete at the end of 48 h and fully complete at the end of 96 h. At 327°C, the transformation was completed in 4 h (Stanjek and Weidler, 1992), and at 400°C it took 1 h (Cornell and Schwertmann, 2003, p. 380).

Although a number of studies have been performed on the conversion of ferrihydrite powder into hematite, much less information is available on the formation of hard, dense, consolidated hematite as the product of these conversion processes.

With a view to understanding the processes leading to the formation of dense, consolidated hematite, it is interesting to note that densified hematite has been

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observed in deposits of corrosion products accumulated around the heat exchanger tubes in certain steam generators (SGs) (Burns *et al.*, 1996). The speciation and structure of steam generator solids has been reviewed in detail (Varrin, 1996). In the SGs of pressurized water reactors (PWRs), the temperatures are of the order of 300°C and steam pressures are ~8 MPa. Deposits containing dense hematite as the predominant Fe oxide were recovered from SGs that were operated with water containing relatively high concentrations of dissolved oxygen, of the order of 5–10 µg/L (Burns *et al.*, 1996), while solids accumulated in the presence of low concentrations of dissolved oxygen ( $\leq 1$  µg/L) predominantly consisted of soft, non-consolidated magnetite (Fe<sub>3</sub>O<sub>4</sub>). As in the case of rocks, the processes leading to the formation of very dense hematite in SGs at relatively low temperatures have not been fully elucidated. As noted above, little information is available on the possible formation of hard, dense hematite from hydrated precursors.

Hematite-based solids incorporating large amounts of foreign species have been observed in steam generator solids (Burns *et al.*, 1996) as well as in rocks. Indeed, hematite is a common binder in sedimentary rocks. Foreign species are known to affect the conversion of ferrihydrite to hematite. For instance, in the presence of Si and Al oxides, the temperatures required for this transformation become considerably higher (Cornell and Schwertmann 2003, p. 381; Barron *et al.*, 1984; Carlson and Schwertmann, 1981). However, the effects of foreign species on the formation of a hard, densified product remain largely uncharacterized. Existing information on the effects of foreign species on the formation of dense hematite are largely confined to studies of sintering under low pressures and temperatures in excess of 600°C (Glasauer *et al.*, 2000). The study described here was intended to explore the formation of hard, dense hematite under conditions relevant to those found in SGs as an analog of the formation of hard, consolidated hematite in sedimentary rocks. In addition to the physical variables (temperature and pressure), the effects of varying chemical parameters (amount of water, redox conditions as determined by the presence or absence of hydrazine) were also investigated. The effects of the presence of foreign species and of the ratio of the amount of such species to the amount of hematite were also included in the present study. The specific objectives of the study were, first, to characterize dense hematite-based solids formed at relatively low temperatures, and then to study the conditions and processes leading to the formation of such composite solids, as well as of pure dense hematite.

## EXPERIMENTAL

### Materials

Solids recovered from the steam generators of a power plant were characterized. This power plant was

the Indian Point 2 Nuclear Power Station, a 970-MW PWR located in Buchanan, NY, which had four Westinghouse Model 44 steam generators. Different solids were obtained under three sets of conditions used in the water circulation system in the plant over a period of several years. Type A solids were formed in the presence of extensive amounts of Cu-based components (heaters, condensers), relatively high concentrations of dissolved oxygen (5–10 µg/L), and the presence of Na phosphate as a buffer. Type B solids were formed when the amount of Cu-based components was less, the concentrations of dissolved oxygen were 1–3 µg/L, and ammonia was used to control the pH. Type C solids were formed when the presence of Cu-based components was minimized, concentrations of dissolved oxygen (<1 µg/L) became very low, and the use of ammonia continued. The chemical composition and physical properties of these three types of solids are shown in Table 1.

Scanning electron microscopy (SEM)/EDS (energy dispersive spectrometry) characterization of the consolidated solids of Types A and B showed these solids to consist of a matrix of micron-sized and smaller Fe oxide grains, some of which loosely combined into larger aggregates (Figure 1). Inclusions of foreign particles, such as Cu in metal or oxide form, stainless steel debris (Cr + Ni + Fe), Al oxide, Ti (in metal or oxide form) and Zr (apparently in metal form) were observed. The exact nature of the Al oxide (anhydrous or hydrated, according to Varrin, 1996) was not determined. Calcium concentrations in the solids were always very low (<0.1%), and no solid phases associated with Ca were detected. Some of the inclusions had dimensions as large as 20–100 µm. Small (micron-size) pockets with high concentrations of trace impurities such as Mg, Pb and S were also identified. The observation that many of the oxide grains appeared to be a single micron or less in size was compatible with the results of measurements performed using Mössbauer spectroscopy. These results indicated that the predominant Fe-containing species was hematite,

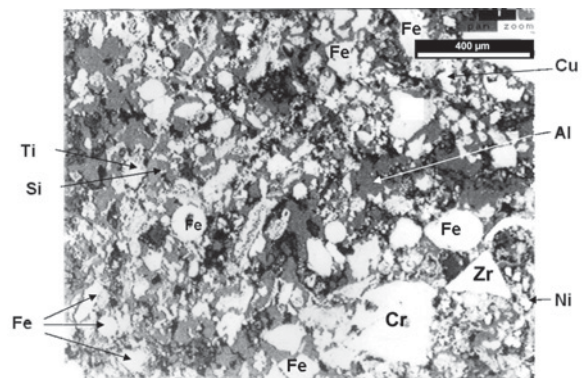


Figure 1. SEM image of a representative steam generator solid (Type A) with EDS identification of regions dominated by elements other than Fe.

Table 1. Composition and properties of steam generator solids.

Constituent or chemical parameter	Content, wt.% (except as noted)		
	Type A	Type B	Type C
Combined Fe oxides (Fe <sub>3</sub> O <sub>4</sub> + Fe <sub>2</sub> O <sub>3</sub> )	40–25	80–60	90–80
Cu and its oxides (Cu + Cu <sub>2</sub> O + CuO)	35–50	15–25	3–12
ZnO	7–12	2–3	1–1.5
Al <sub>2</sub> O <sub>3</sub>	4–10	2–3	0.1–0.2
NiO	approx. 2	approx. 1	approx. 1
Mn oxides (MnO + Mn <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> )	approx. 1	approx. 1	0.2–0.3
SiO <sub>2</sub>	approx. 1	approx. 1	0.1–0.2
P <sub>2</sub> O <sub>5</sub>	1.8–3.5	0.3–0.8	0.1–0.05
PbO	approx. 0.05	0.04–0.12	0.01
Na <sub>2</sub> O	approx. 0.02	approx. 0.03	0.01
Sulfate	0.01–0.04	0.02–0.03	0.01–0.02
Chloride	<0.01	<0.01	<0.01
Carbon	0.1–0.4	0.1–0.4	0.1–0.4
Fe <sub>2</sub> O <sub>3</sub> :Fe <sub>3</sub> O <sub>4</sub> ratio	5:1	5:1	<1:5
Major Cu species	Cu, Cu <sub>2</sub> O	CuO, Cu <sub>2</sub> O, Cu	Cu
Type of solid	consolidated	consolidated	powder
Bulk density, g/mL	4.5–5.0	4.5–5.0	n.a. <sup>a</sup>
Hardness, Rockwell T, 15-kgf load	50–80	50–80	n.a. <sup>a</sup>
Adhesion to SG tube surface (Alloy 600)	Strong	Strong	n.a. <sup>a</sup>
Specific surface area, m <sup>2</sup> /g	n.a. <sup>b</sup>	n.a. <sup>b</sup>	8.5

<sup>a</sup> not applicable (powdery material); <sup>b</sup>not applicable (bulk solid)

but a sizeable fraction of the Fe oxide exhibited the superparamagnetic character (Kündig and Bömmel, 1966) of small (<0.02 μm) particles, characterized by the presence of a quadrupole-split center doublet in addition to the typical broad six-line spectrum (Schwertmann and Cornell, 2000) of macrocrystalline hematite. Mössbauer spectroscopy also indicated that the main form of Fe oxide in Type B solids was macrocrystalline hematite, while in Type A solids the hematite grains were smaller, possibly intermixed with some ferrihydrite (Figure 2). The infrared spectra of both types of solids were compatible, according to reported data (Schwertmann and Cornell, 2000), with the identification of hematite as the major form of Fe oxide in these solids.

#### Chemical analyses

Chemical analysis of both solids recovered from steam generators and synthesized solids was performed by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) following dissolution in HCl solution. The instrument was a Perkin Elmer Plasma 400 spectrometer. The concentrations of sulfate and chloride were determined by stirring the powdered sample for 48 h in a 0.1 M aqueous solution of oxalic acid and analyzing the resulting aqueous solution by means of a Dionex DX 500 ion chromatography system. The total carbon content was determined using micro-combustion analysis.

#### Spectroscopic analyses

The identity of Fe and Cu species was determined using XRD by means of a Siemens Theta-Theta D500

diffractometer. Mössbauer spectroscopy and infrared (IR) spectroscopy were also used in the characterization of Fe species. Mössbauer spectra were obtained using a Mössbauer spectrometer Model MS-900 (Ranger Scientific) in constant-acceleration mode with moving source geometry at room temperature. The samples were ground in an agate mortar into a fine powder and used without dilution. The samples were mounted in polyethylene or polypropylene cells. The gamma-ray source consisted of 25-mCi Co-57 in a Pd foil. No orientation effects were noted. The velocity range was calibrated with Fe foil. The resulting spectra were analyzed by least-squares fitting to Lorentzian shaped lines. The Mössbauer parameters for the various Fe oxides were taken from the literature (Cornell and Schwertmann, 2003, pp. 155–156). The ratios of hematite to magnetite and maghemite were determined from the ratios of the total spectral areas for each of the oxides. Infrared spectroscopy was performed, using a Perkin-Elmer Model 1750 Fourier transform infrared spectrometer, on samples following incorporation in KBr tablets containing a ratio of 1:150 of powdered sample to pure KBr. The measured spectra were interpreted in terms of those reported in the literature, primarily by Schwertmann and Cornell (2000). In order to ensure the validity of the XRD, Mössbauer and IR measurements, measurements using these techniques were made on commercially available minerals of hematite, magnetite and goethite (acquired from Ward's Natural Science, Rochester, NY), as well synthetic pure magnetite and hematite. The results showed full agreement with the literature, and they also served to validate the

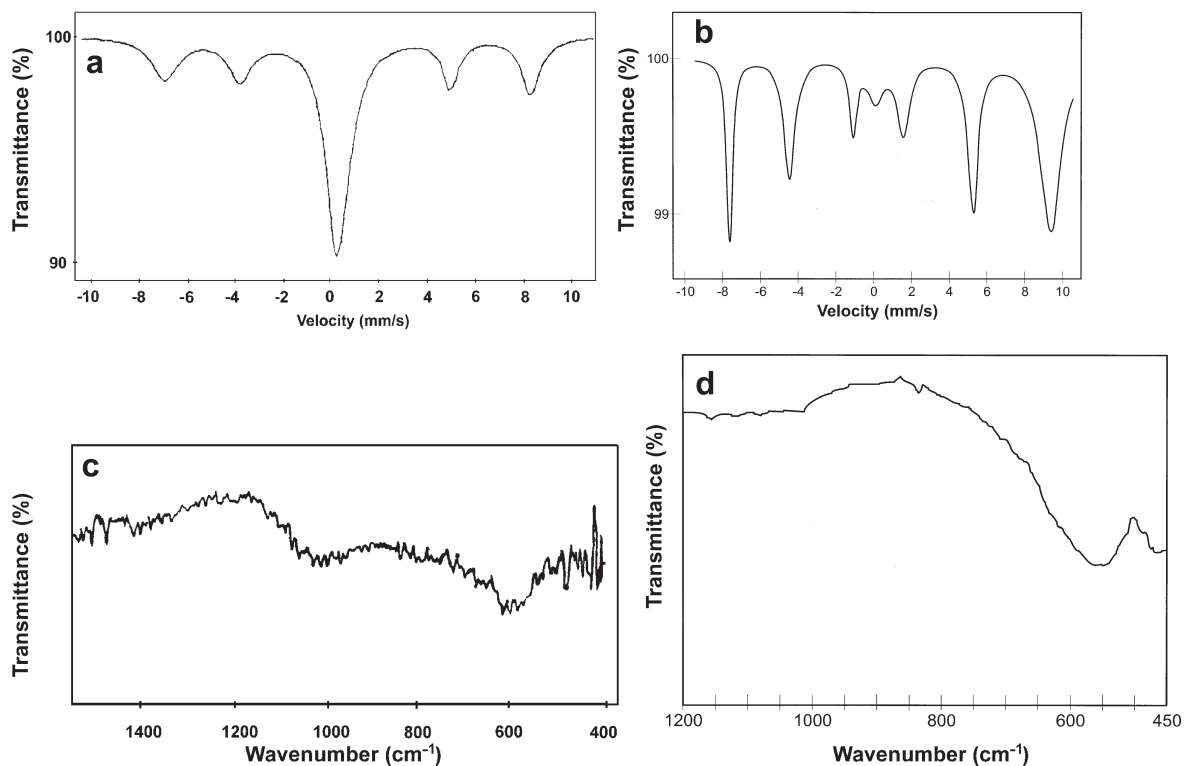


Figure 2. Spectra of steam generator solids. Mössbauer spectra: (a) Type A; (b) Type B. IR spectra: (c) Type A; (d) Type B.

estimate of the relative amounts of different species in the solids investigated or synthesized in the present study.

#### Physical properties

The hardness of both actual and synthetic SG solids was measured by means of an Ames Portable Rockwell Hardness Tester, Model 1-S, using the Rockwell T scale. Crush strength was measured by means of an Ametek AccuForce Cadet force gauge, 0–445 N (0–100 lb). Densities of pressed discs were measured by pycnometry. The adhesion of pressed oxide pellets to Alloy 600 material was qualitatively evaluated by observing the result of pressing a precursor powder onto an Alloy 600 disc inside a pellet die (see below). Strong adhesion required the use of a chisel or a screwdriver to separate the pellet from the disc. Specific surface areas were measured using a Quantasorb Quantochrome system to determine the BET nitrogen absorption.

#### Sulfate migration rates

Migration rates of sulfate through the dense solids were measured by exposing a disc-shaped sample to a volume of ~16 mL of an aqueous solution of  $\text{Na}_2\text{SO}_4$ , where the sulfur consisted of the beta-emitting S-35 isotope. The outer rim of each sample was coated with a high-temperature adhesive/sealant (Dow Corning 1-2577) in order to control the direction of sulfate migration during the exposure and to make it possible to

handle the sample during the subsequent gradual etching operation without scratching the exposed surface around the center of the disc. The activities of the test solutions were between 0.21 and 1.03 MBq/mL. Following exposure for 7–11 days in a pressure vessel at a temperature of 180°C, each solid sample was quickly rinsed with deionized water and then subjected to gradual etching by dipping it sequentially in a series of vials, each containing 10 mL of 2 M HCl. The thickness dissolved in each dipping step, based on the concentration of dissolved Fe, was ~0.010 mm. Accordingly, the total dissolved thickness was ~0.10 mm. The amount of S-35 in each of the dissolved layers was determined by adjusting the pH of each of the solutions to 6.5–7 using a mixture of NaOH and  $\text{NaH}_2\text{PO}_4$ , adding 5 mL of scintillation fluid to 1 mL of each neutralized test solution, and counting the beta activity of S-35 in the mixed solution by means of a liquid scintillation counter. The rates of sulfate migration were calculated on the basis of the beta activity and thickness of the layers.

#### Synthesis

Synthetic hard hematite was prepared starting with a solution of  $\text{Fe}(\text{NO}_3)_3$ , made by dissolving 47.04 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 100 mL of water. Hematite-based solids containing other ingredients such as  $\text{Al}_2\text{O}_3$ , ZnO,  $\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4$  and  $\text{Cu}_2\text{O}$  were prepared starting from solutions of  $\text{Fe}(\text{NO}_3)_3$  (prepared as described above), mixed with dissolved  $\text{Al}(\text{NO}_3)_3$  (made by dissolving

2.81 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 100 mL of water) and dissolved  $\text{Zn}(\text{NO}_3)_2$  (made by dissolving 1.64 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 100 mL of water) as necessary. The corresponding hydroxides, or oxyhydroxides, such as ferrihydrite, gibbsite and zinc hydroxide were precipitated by adding concentrated ammonia solution (28–30%  $\text{NH}_4\text{OH}$ ) to raise the pH to 7.5–8.0 at ambient temperature. The ferrihydrite produced according to this procedure was the poorly crystalline 2-line ferrihydrite (see Results section below). This was expected, since the synthetic procedure used here was based on bringing the pH of an  $\text{Fe}(\text{NO}_3)_3$  solution to 7.5–8 by means of adding a base at ambient temperature, similar to the procedure described by Schwertmann and Cornell (2000) for the preparation of 2-line ferrihydrite. The precipitate was filtered to separate it from the supernatant solution.  $\text{Cu}(\text{OH})_2$  was similarly prepared from a  $\text{Cu}(\text{NO}_3)_2$  solution (made by dissolving 6.58 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  in 100 mL of water) using tetramethylammonium hydroxide (26–28%  $(\text{CH}_3)_4\text{NH}_4\text{OH}$ ) as a precipitating agent. Insoluble ingredients such as silica gel,  $\text{Fe}_3\text{O}_4$  or  $\text{Cu}_2\text{O}$  were added as necessary and mixed with the wet hydroxides. All of the chemicals used in this procedure were of analytical reagent grade, and all water was deionized. The mixture (or ferrihydrite alone, when the synthesis of pure dense hematite was investigated) was filtered through a coarse-grade filter paper, and the precipitate was washed five times, each time with 200 mL of deionized water, dried in air at 110°C for 12–18 h, and ball-milled in acetone. The product was dried at 70–80°C for 24 h and then sieved in order to separate out the –200 mesh fraction. The Fe-based powder was confirmed to remain ferrihydrite following the two drying steps at 110°C and at 70–80°C (see Results section). This observation agreed with reported findings indicating that ferrihydrite retained its structure upon heating at a temperature of 127°C and was not converted to hematite even when heating at this temperature lasted for periods as long as 1180 h (Weidler, 1995). The resulting powder constituted the precursor of the dense hematite product. In some of the experiments the precursor solids consisted, entirely or partially, of pure oxides such as magnetite or of powdery deposits recovered from actual steam generators. In all cases, the dried precursor powder was mixed with a controlled amount of water, and then placed in a Perkin Elmer evacuable die (12.7 mm diameter) equipped with heating tape and a thermocouple. The die was pressed using a Carver laboratory press. Pressing was performed under a loading of approximately 500 MPa at a temperature of 260°C for a total period of 3.5 h. The die was connected to a vacuum pump after the first hour of pressing to draw off water vapor. The resulting pressed discs were 12.7 mm in diameter and 3–4 mm thick.

In addition to providing realistic simulation of the elemental composition of the steam generator solids, the procedure described here was intended to reproduce the

majority speciation of each elemental species found in Type A and Type B solids. Accordingly, this procedure was used to produce solids in which Fe was present in the form of a hematite ( $\alpha\text{-Fe}_2\text{O}_3$ )-magnetite ( $\text{Fe}_3\text{O}_4$ ) mixture, magnetite alone, or hematite alone, copper as tenorite ( $\text{CuO}$ ) or cuprite ( $\text{Cu}_2\text{O}$ ), zinc as zincite ( $\text{ZnO}$ ), aluminum as boehmite ( $\alpha\text{-AlOOH}$ ), and silicon as partially hydrated silica ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ). The key ingredient in the preparation of the synthetic solids was the brown powder, obtained upon drying the product, of neutralization of  $\text{Fe}(\text{NO}_3)_3$  solution with ammonia. This powder was used as the sole precursor in the synthesis of hard pure hematite, and also as the key ingredient in the synthesis of most of the composite hematite-based solids. The latter syntheses included those using precursors of Type A and Type B solids, as well as similar precursors doped with additional components, e.g.  $\text{Ca}_3(\text{PO}_4)_2$ . In addition, various Fe oxides and oxyhydroxides, alone or in various combinations with one another and with the brown dried precipitate, were used as starting materials. Type C powders (designated CP), which were actually recovered from steam generators, were also used as starting materials.

## RESULTS

### *Characteristics of synthetic hard hematite*

Laboratory simulation studies were performed in order to identify the cementing agent responsible for the consolidation and hardening of Type A and Type B solids. Simplified target compositions of these solids were formulated. These compositions are shown in Table 2 in terms of percentages on a dry oxide basis. The procedure developed to synthesize these solids is described in the Experimental section above.

The results of the experiments are summarized in Table 3, with AP and BP designating the precursors of Type A and Type B solids, respectively.

The grain structures of actual hard sludge and of synthetic hard sludge, respectively, appeared identical when examined by optical microscopy at a magnification of 40× (Figure 3). No voids were observed at this magnification in either of the two materials. The densities of both the actual and synthetic Type A and

Table 2. Intended compositions of synthetic hematite-based solids (percentages on dry basis).

Component	Content, wt. %	
	Type B	Type A
$\text{Fe}_2\text{O}_3$	62.3	38.2
$\text{Fe}_3\text{O}_4$	16.1	0.0
$\text{CuO}$	15.1	0.0
$\text{Cu}_2\text{O}$	0.0	38.2
$\text{ZnO}$	3.0	11.1
$\text{Al}_2\text{O}_3$	2.6	11.1
$\text{SiO}_2$	0.9	1.4

Table 3. Effects of precursor composition on properties of pressed product.

Precursor composition	Product composition	Properties of product	
		Hardness, Rockwell T, 15-kgf load	Adhesion to Alloy 600 surface
BP	B	62	Strong
BP + Ca <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	B + 3% Ca <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	75	Strong
BP + H <sub>3</sub> PO <sub>4</sub>	B + 2% P <sub>2</sub> O <sub>5</sub>	65	Strong
BP + Cu(OH) <sub>2</sub> + Cu	B + 12.5% CuO + 12% Cu	72	Strong
BP + CaSiO <sub>3</sub>	B + 3% CaSiO <sub>3</sub>	60	Moderate
BP + Co(OH) <sub>2</sub>	B + 1.2% CoO	60–85	Strong
BP + HgO	B + 10% HgO	60–85	Strong
AP	A	60–85	Strong
100% ferrihydrite	100% hematite	82	Strong
100% hematite	100% hematite	0	None
100% goethite	100% hematite	0	None
100% magnetite	100% magnetite	0	None
80% ferrihydrite + 20% magnetite	76% hematite + 24% magnetite	80	Strong
CP		0	None
60% CP + 40% ferrihydrite		54	Strong
80% CP + 20% ferrihydrite		60	Moderate

Type B solids were in the range of 4.5–5.0 g/mL. An indication of low porosity of the actual steam generator solids was the observation that these materials contained pockets in which minor components (such as SiO<sub>2</sub>, sulfate, Mg, Pb) were highly concentrated, and that these pockets had not dissipated over many years in spite of the high solubility of some of these components in hot water. Direct measurements of the rate of migration of sulfate in synthetic B solid at 180°C, using Na<sub>2</sub>SO<sub>4</sub> with the radioactive isotope S-35 as a sulfate source, showed that the effective diffusivity was  $<1.5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ , indicative of very low porosity.

According to Schwertmann and Cornell (2000), the hydrated ferric oxide most likely to form under steam generator conditions and in the laboratory studies simulating these conditions is ferrihydrite, because its



Figure 3. Optical micrographs (40 ×) of actual (above) and simulated (below) Type B solids.

formation is favored at weakly alkaline pH (~8). The Fe species present in the synthetic precursor was indeed identified as ferrihydrite, using XRD as well as Mössbauer and IR spectroscopies. The data in Table 3 show that the presence of ferrihydrite as a precursor species was essential for the formation of hard, dense hematite at moderate temperatures (~260°C). These data also showed that ferrihydrite could serve as a cementing agent even when present in small amounts, causing consolidation and hardening of a composite material having a large content of other solids.

#### *Effects of chemical composition and of pressing conditions on the products of pressing of ferrihydrite*

*Effects of pressing time.* Studies of the transformation of ferrihydrite into dense, hard hematite as a function of pressing time were performed under standard conditions (12 wt.% of water added to the dried precursor powder, 260°C, 500 MPa, no secondary binder). The products of pressing were characterized using XRD, Mössbauer spectroscopy and IR spectroscopy. Ferrihydrite samples pressed for <3 h consisted of soft hematite while samples pressed for periods of 4–5 h or longer were hard. The effects of pressing time on the hardness, crush strength, XRD pattern and IR spectrum of the product are summarized in Table 4.

*Effects of water content.* When wet ferrihydrite slurry, with water present in excess of 20% by weight, was placed in the die during pressing under the conditions described above (260–280°C, 500–530 MPa, 4–5 h), the final product was a soft powder. At the other extreme, when the ferrihydrite was pre-heated to 300°C before pressing, no consolidation and no hardening were observed. Pressing hematite powder, even upon addition

Table 4. Effect of pressing time on the characteristics of the products of pressing.

Pressing time (h)	XRD	IR	Hardness, Rockwell T (147-N load)	Crush strength (N)	Adhesion to Alloy 600 surface	Appearance
0	2-line ferrihydrite	Ferrihydrite	n.a.	n.a.	None	Powder
1.5	Hematite	n.d.	0	n.d.	Weak	Soft
2.75	n.d.	Hematite	0	116–178	None	Soft
3.0	Hematite	Hematite	73	67–445	Moderate	Moderately soft
3.5	Hematite	Hematite	85	445	Strong	Hard
24	n.d.	Hematite	93	>445	Strong	Hard

n.d. = not determined; n.a. = not applicable

of 10–15% water, did not produce a hard solid. The best results were obtained upon following the procedure detailed in the Experimental section above, *i.e.* drying the initial precipitate of ferrihydrite at 110°C for 12–18 h, ball-milling in acetone, and re-drying at 70–80°C. This procedure removed non-structural water. The ferrihydrite precursor was subsequently mixed with 10–15% by weight of water, and then pressed at an elevated temperature, while gradually removing the water in vapor form (see Experimental section). This procedure resulted in the formation of a precursor powder having a carefully controlled ratio of water to ferrihydrite. Adding water at an amount above or below the 10–15% range prior to the pressing stage resulted either in a long time to obtain a hard product or in a decrease in product hardness when the pressing period was restricted to the usual duration of 4–5 h. These findings showed that slow, gradual removal of excess water is essential to the formation of hard hematite. This conclusion agreed with observations on the formation of hard hematite in actual steam generators. Such observations suggested that in steam generators hematite formed under considerably lower pressures (~8–10 MPa) in an environment rich with respect to water vapor. In this environment, drying was expected to take place very slowly, characteristically over periods of several weeks or months, as water was gradually removed from the hottest region around the surfaces of the SG tubes.

Based on Mössbauer and IR measurements, the transition from 2-line ferrihydrite to hematite was partial at the end of 1.5 h and complete at the end of 3.5 h of pressing. Between 1.5 and 3.5 h, the product became hard. The water content of several samples was measured using two techniques. One of these techniques involved measurement of the weight loss of the samples following heating to 800°C, and the other consisted of measurement of the weight gain of a CaSO<sub>4</sub> tube absorbing water vapor evolved upon heating the sample. The results of the moisture analysis are shown in Table 5.

According to the data in Table 5, the initial water content was very similar to the total water content (including water of hydration as well as water bound in

the form of OH groups) based on the reported formulae of ferrihydrite. The formula (Russell, 1979) Fe<sub>2</sub>O<sub>3</sub>·2FeOOH·2.6H<sub>2</sub>O corresponds to a theoretical water content of 18.9%, and the formula (Towe and Bradley, 1967) Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O to a water content of 16.9%. Even after 3.5 h, when the product was already hard (see Table 4), it still contained a significant amount of moisture. This remaining water was observed to be driven out only upon heating above 350–400°C, in agreement with the observations reported for hydrohematite (Schwertmann and Cornell, 2000; Wolska and Schwertmann, 1989). Thus, the laboratory product could be more accurately described as hydrohematite (Wolska and Schwertmann, 1989; Wolska, 1981) than as anhydrous hematite. The IR spectrum of hard hematite obtained by pressing ferrihydrite was similar to the hydrohematite spectra reported by Wolska, exhibiting bands at 950 and at 630 cm<sup>-1</sup>, associated with OH groups (Wolska, 1977, 1981; Ruan *et al.*, 2002). The 950 cm<sup>-1</sup> band has been reported to be an OH-deformation band (Ruan *et al.*, 2002). The Mössbauer spectrum and the XRD pattern of hematite are not greatly altered by the presence of a small amount of water, of which a large part is believed to be incorporated at defect sites of the hematite structure (Wolska and Schwertmann, 1989).

The results in Table 5, together with the data in Table 4, showed that the hardening process was concurrent with gradual and incomplete removal of water from the solid.

Table 5. Water content of ferrihydrite during conversion to hematite.

Pressing time	Water content (%)	
	Based on weight loss	Based on absorption of evolved water vapor
0.0	20.5	17.8
2.75	6.6	n.d.
3.0	4.7	n.d.
3.5	4.3	4.5

n.d. = not determined

*Effects of secondary binders.* Experiments on pressing ferrihydrite at lower temperatures and pressures showed that hard products could be obtained at temperatures of 150–200°C, pressures as low as 100–180 MPa, and pressing times of 1.5–5.5 h, with a mixture of  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  and MgO added as a secondary binder. Increasing the content of the secondary binder mixture facilitated hardening at lower temperatures and pressures and attainment of higher product density and hardness.

*Effects of hydrazine.* Both oxidized and reduced Fe oxides appear in steam generators as well as in sedimentary rocks. Hydrazine is used to control dissolved oxygen levels in steam generators and in the laboratory. The effects of reducing environments on the precipitation of the oxyhydroxide precursor from solution and on its transformation during the pressing stage were studied. In the precursor studies, hydrazine hydrate was added to the  $\text{Fe}(\text{NO}_3)_3$  solution prior to the usual procedure of neutralization with ammonia, filtration and drying. The amount of added hydrazine corresponded to a  $\text{N}_2\text{H}_4:\text{Fe}(\text{NO}_3)_3$  mole ratio of 1:2. Precursor powders prepared with and without hydrazine were pressed according to the usual procedure, adding 12 wt.% of water to the dried precursor. In parallel experiments, pressing was performed in the presence of 12 wt.% of an aqueous solution containing 85% hydrazine instead of water. Pressing in the presence of hydrazine was also performed on hematite and goethite powders, as well as on the synthetic precursors BP and AP (see Tables 2 and 3). The results of the experiments are summarized in Table 6. The precursors and pressing products were characterized by means of Mössbauer spectroscopy, IR spectroscopy and XRD.

Based on the data in Table 6, a hard, consolidated product was obtained at 260°C only upon conversion of

ferrihydrite to hematite, and only when hydrazine was absent both during the precipitation stage and during the pressing stage. It was also noted that upon pressing dry hematite at this temperature in the presence of hydrazine, the hematite remained unchanged. Under the same conditions, ferrihydrite and goethite underwent reduction to yield magnetite. The finding that once hematite was formed it was no longer susceptible to reduction by hydrazine at temperatures of ~260°C or lower was compatible with reported observations on steam generator solids, which indicated that raising hydrazine levels caused fresh magnetite to form instead of hematite, but did not convert old hematite deposits into magnetite (Burns *et al.*, 1996).

*Effects of foreign species.* Upon pressing precursors containing as much as 60–80% of foreign species such as combinations of CuO, ZnO,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Cu}_2\text{O}$  and  $\text{SiO}_2$  (see Table 3) the mechanical properties of the product did not differ much from those of the product obtained upon pressing pure ferrihydrite. Specifically, according to the data in Table 3, the products of pressing the BP and AP precursors were similar in hardness, crush strength and adhesion to a metal surface, to the product of pressing pure ferrihydrite. Mössbauer and IR measurements showed that the product of pressing the BP precursor yielded well developed, macrocrystalline hematite, similar to the product of pressing pure ferrihydrite. On the other hand, pressing the AP precursor gave rise to microcrystalline, highly disordered hematite according to Mössbauer spectroscopy, which is sensitive to grain size (Kündig and Bömmel, 1966). In the latter case, the product contains only 38% hematite (compared with 62% in the Type B target solid), with much higher concentrations of the oxides of Cu, Zn and Al than the BP precursor. Thus, the grain size

Table 6. Effects of hydrazine on the products of precipitation and pressing.

Precursor	Mineralogical composition of Fe-based phases in precursor	Hardness and Fe-based phases in the product of pressing	
		In the absence of hydrazine	In the presence of hydrazine
$\text{Fe}(\text{NO}_3)_3$ precipitated in absence of hydrazine	Ferrihydrite (brown)	Hard, all hematite	Soft, magnetite
$\text{Fe}(\text{NO}_3)_3$ precipitated in presence of hydrazine	Goethite (major, yellow); maghemite (minor, not certain)	Soft, hematite (~80%); maghemite (~20%)	Soft, magnetite
Goethite	Goethite	Soft, hematite (major); maghemite, residual goethite (minor)	Soft, magnetite
Hematite	Hematite	Soft, hematite	Soft, hematite
BP precipitated in the absence of hydrazine	Ferrihydrite	Hard, hematite	Soft, magnetite
AP precipitated in the absence of hydrazine	Ferrihydrite	Hard, microcrystalline hematite	Soft, microcrystalline magnetite

was observed to decrease upon increasing the concentration of foreign species, but the overall mechanical properties of the product were not significantly degraded.

Upon pressing the high-Fe precursor BP in the presence of hydrazine, macrocrystalline magnetite was obtained, as in the case of pressing pure ferrihydrite (see Table 6). Upon pressing the low-Fe precursor AP in the presence of hydrazine, Mössbauer spectroscopy showed that the magnetite obtained was microcrystalline and more disordered. These findings indicated, as in the case of pressing in the absence of hydrazine, that the main effect of the presence of large amounts of foreign species was to cause a reduction in grain size of the Fe oxide matrix.

Detailed Mössbauer, XRD and IR spectra of actual steam generator solids, synthetic precursors and pressing products obtained under various conditions were reported by Labuda (1996).

## DISCUSSION

### *Conditions required for the formation of hard, consolidated hematite at moderate temperatures*

The most important result of the study described here was the observation that dense, hard hematite could be formed upon pressing ferrihydrite at relatively low temperatures (~260°C) while allowing a gradual escape of water in vapor form. It was shown that various foreign species could be incorporated in the resulting hematite matrix without significant reduction in the mechanical strength and hardness of the consolidated product, even though the presence of large amounts of foreign species could lead to the formation of a microcrystalline matrix, rather than well defined macrocrystalline hematite. Under the same conditions as those used with ferrihydrite, pressing magnetite, hematite or goethite did not result in the formation of a hard, strong solid. Pressing ferrihydrite without allowing water to escape likewise led to the formation of a soft, friable product.

In addition, based on the results in Table 6, it could be concluded that hydrated Fe oxides were readily reduced to magnetite by hydrazine at relatively low temperatures, but once hematite was formed, it was no longer susceptible to reduction under such conditions. These results agreed with observations made on actual steam generator solids (Burns *et al.*, 1996). According to such observations, magnetite, rather than hematite, was the predominant Fe oxide in solids formed when the water steam generator system contained elevated concentrations of hydrazine (Type C conditions). However, when the steam generators contained hematite-rich solids previously formed in the presence of low concentrations of hydrazine and high levels of dissolved oxygen (Type A or Type B conditions), this hematite was not reduced upon subsequent increase in hydrazine concentrations, even when elevated hydrazine levels were maintained for several years (see Table 1).

Solids recovered from SG systems as well as those obtained upon pressing in the laboratory studies described above were consistently observed to be consolidated and hard when the magnetite-to-hematite ratio was low and to consist of unconsolidated powder or crumbling, soft bodies when that ratio was high. This observation supported the conclusion that, among Fe oxides, only hematite, formed upon dehydration of ferrihydrite under pressure, formed hard, dense solids at the temperature range around 260°C.

*Effects of foreign species.* The studies described above showed that hard, dense hematite-based solids were formed even when the content of foreign, non-binder species (*e.g.* Cu, Zn, and Al oxides) was as high as 60–80%. However, it was observed that the presence of large quantities of such foreign species in actual or synthetic Type A solids impeded the transformation of ferrihydrite into well developed, macrocrystalline hematite and caused the solid product to consist of microcrystalline, highly disordered hydrohematite, possibly containing some remaining ferrihydrite.

Many metal ions, including those of Cu, Zn, Al, Ni, Mn and Co, retard the transformation of ferric oxyhydroxides such as ferrihydrite and goethite into hematite (Inouye *et al.*, 1972; Schwertmann *et al.*, 1979; Lewis and Schwertmann, 1979; Schultz *et al.*, 1987; Cornell and Giovanoli, 1988; Schwertmann and Murad, 1990). Such metal ions can stabilize the ferric oxyhydroxide structure through adsorption as well as replacement of Fe in the structure, thus interfering with the transformation of the oxyhydroxide into hematite. For instance, in the presence of Cu, the hydrolysis of ferric salts produces a stable amorphous product (Inouye *et al.*, 1972). In the case of Type A solids, large amounts of oxides and hydroxides of Cu and other foreign metals were mixed with the initial, water-saturated ferric oxyhydroxide precipitate before drying, and, later, heated together in the presence of added water at the beginning of the pressing stage. In this case, Cu, Zn, Al and silicate ions were likely to be released into the water and then taken up on OH surface sites (Inouye *et al.*, 1972; Cornell and Giovanoli, 1988), obstructing subsequent condensation of OH groups. Silicate and phosphate ions present in Type A solids are also known to interfere with the transformation of ferrihydrite into well defined hematite (Cornell *et al.*, 1989). Even though the presence of large amounts of Cu, Zn, Al, silicate and phosphate ions obstructed the transformation of ferrihydrite in Type A solids, the product, probably consisting of a mixture of microcrystalline hematite, hydrohematite and unaltered semi-amorphous ferrihydrite grains, still formed a hard, strong solid. The effects of incomplete conversion into hematite on the strength of the product were apparently cancelled out by the denser packing of the very small size of the grains formed under these conditions.

*Steam generator solids as analogs of hematite-cemented sedimentary rocks.* In both steam generators and simulation experiments, lowering the dissolved oxygen levels in the water (through the use of hydrazine) causes hematite-to-magnetite ratios in the newly formed sludge to plunge. Similarly, in sedimentary systems the relative amounts of ferric and ferrous Fe are determined by the amount of available oxygen, *i.e.* the excess of oxygen over oxidizable organic matter. Indeed, it is known that, upon heating under reducing conditions, ferrihydrite is not transformed into hematite, but into magnetite and even into wüstite (Drits *et al.*, 1995). Very significantly, hardening of solids is suppressed upon reduction of dissolved oxygen concentrations, and the solids formed at very low oxygen levels (<1 µg/L) are soft and powdery (Type C solids). This observation is fully compatible with the known fact that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, unlike Fe<sub>3</sub>O<sub>4</sub>, constitutes a common cementing agent in sedimentary rocks. Magnetite, unlike ferrihydrite, is an anhydrous species, and thus unable to undergo consolidation through condensation of OH groups.

The ability of hematite, formed from ferrihydrite, to act as a cement is reflected in the finding that a hematite matrix can incorporate about half its weight (in Type B solids), and about twice its weight (in Type A solids), of other oxides (including SiO<sub>2</sub>) and metal particles, and yet remain as hard as pure hematite. In nature, hematite sorbs on and coats grains, even coarse ones, of other solids such as sand. In sedimentary formations, cementation by hematite results in consolidation of these heterogeneous solid mixtures into hard rock types such as certain shales and sandstones. The microstructure of Type B and Type A solids, consisting of relatively large foreign inclusions of metallic and oxide impurities embedded in a matrix of fine hematite grains, closely resembles the microstructure of red siltstone, which consists of large quartz particles (typically 50–500 µm in size) set in a cryptocrystalline matrix of hematite (Friedman and Sanders, 1978). Unlike silicate ions (Zhao *et al.*, 1994; Cornell *et al.*, 1987; Vempati and Loeppert, 1989), solid silica particles are apparently unable to block the transformation of ferrihydrite into hematite.

The transformation of ferrihydrite into hematite was found in the experiments described above to require addition of a controlled amount of liquid water to the dried ferrihydrite, in agreement with previous findings (Torrent *et al.*, 1982). This observation, which can be attributed to the need to form bridging OH groups for the transformation to occur, has been taken into account in considering the rates of transformation in various types of soil (Stanjek and Weidler, 1992). It has been suggested that, in the presence of chemisorbed water molecules, condensation of the resulting reactive surface sites is responsible for the transformation of ferrihydrite to hematite at relatively low temperatures (Zhao *et al.*, 1994).

In sediments, hematite is thought to be the end-product of an ageing process that involves progressive, spontaneous dehydration of an initially X-ray amorphous ferric hydroxide gel, precipitated from hydrous solutions, often through bacterial action (Lunden and Dean, 1979; Fischer, 1988; Childs, 1992; Wightman, 2002). This ageing process (Crosby, 1891; Van Houten, 1972; Van Houten, 1973; Walker, 1967; Walker, 1974; Turner, 1980) is analogous to the process of silica dehydration, and it is accompanied by hardening. The dehydration of hematite in geological environments is often incomplete, and the resulting product is hydrohematite (Wolska and Schwertmann, 1989; Wolska, 1981; Dang *et al.*, 1997), which retains several percent (by weight) of water. The same phenomenon was observed in the studies reported above, where the hard hematite produced upon pressing ferrihydrite at 260°C and 500 MPa for 3.5 h was found to contain 4.5% of residual water (Table 5). The formation of macrocrystalline hematite in nature may occur, over long periods of time, at lower temperatures and pressures than those prevailing in steam generators and in the simulation experiments.

## CONCLUSIONS

Hard, dense solids are obtained when ferrihydrite undergoes gradual dehydration under pressure at moderate temperatures (below 300°C) while excess water vapor is allowed to escape. The pressure required is lower the longer the time available for dehydration. Under the same mild conditions, pressing goethite, hematite, magnetite, or wet ferrihydrite produces compacted powders without significant strength or hardness. In contrast, the bulk solids formed from ferrihydrite in the presence of a controlled amount of moisture are hard and strong even when they contain large amounts of foreign substances. Formation, retention, and, subsequently, gradual condensation of hydroxyl bridges during the partial dehydration of ferrihydrite under moderate pressures and temperatures are responsible for the cohesion and strength of the hydrohematite product.

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## REFERENCES

- Bagchi, T.P. and Sen, P.K. (1982) Kinetics of densification of powder compacts during the initial stage of sintering with constant rates of heating. A thermal analysis approach. *Thermochimica Acta*, **56**, 269–283.

- Barron, V., Rendon, J.L., Torrent, J. and Serna, C.J. (1984) Relation of infrared, crystallochemical, and morphological properties of Al-substituted hematites. *Clays and Clay Minerals*, **32**, 475–479.
- Burns, R., Cherepakhov, G., Mark, J.T. and Skulte, P. (1996) Strategic water chemistry plan – Indian Point 2 Station. Pp. A-43–A-47 in: *PWR Secondary Water Chemistry Guidelines – Revision 4*, EPRI TR-102134-R4, (A. McIlree, P. Millett and C.J. Wood, editors). Electric Power Research Institute, Palo Alto, California, USA.
- Campbell, A.S., Schwertmann, U. and Campbell, P.A. (1997) Formation of cubic phases on heating ferrihydrite. *Clay Minerals*, **32**, 615–622.
- Carlson, L. and Schwertman, U. (1981) Natural ferrihydrites in surface deposits from Finland and their association with silica. *Geochimica et Cosmochimica Acta*, **45**, 421–429.
- Childs, C.W. (1992) Ferrihydrite: A review of structure, properties and occurrence in relation to soils. *Zeitschrift fuer Pflanzenernaehrung und Bodenkunde*, **155**, 441–448.
- Cornejo, J. (1986) The effect of heat treatment on textural evolution of ferrihydrite. *Materials Chemistry and Physics*, **15**, 369–377.
- Cornell, R.M. and Giovanoli, R. (1988) The influence of copper on the transformation of ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) into crystalline products in alkaline media. *Polyhedron*, **7**, 385–391.
- Cornell, R.M. and Schwertmann, U. (2003) *The Iron Oxides*, 2<sup>nd</sup> edition. Wiley-VCH, Weinheim, Germany.
- Cornell, R.M., Giovanoli, R. and Schindler, P.W. (1987) Effect of silicate species on the transformation of ferrihydrite into goethite and hematite in alkaline media. *Clays and Clay Minerals*, **35**, 21–28.
- Cornell, R.M., Giovanoli, R. and Schneider, W. (1989) Review of the hydrolysis of iron(III) and the crystallization of amorphous iron(III) hydroxide hydrate. *Journal of Chemical Technology and Biotechnology*, **46**, 115–134.
- Crosby, W.O. (1891) On the contrast in color of the soils of high and low latitudes. *American Geologist*, **8**, 77.
- Dang, M.-Z., Rancourt, D.G., Dutrizac, J.E., Lamarche, G. and Provencher, R. (1997) Protohematite-hydrohematite-hematite: structuro-chemical phase relationships in hematite-like materials. *Clays Our Future, Proceedings of the 11th International Clay Conference*, 265–270.
- Drits, V.A., Sakharov, B.A., Salyn, A.L. and Manceau, A. (1993) Structural model for ferrihydrite. *Clay Minerals*, **28**, 185–207.
- Drits, V.A., Gorshkov, A.I., Sakharov, B.A., Salyn, A.L., Manceau, A. and Sivtsov, A.B. (1995) Ferrihydrite and its phase transformations during heating in the oxidizing and reducing environments. *Lithology and Mineral Resources*, **1**, 76–84.
- Eggleton, R.A. and Fitzpatrick, R.W. (1988) New data and a revised structural model for ferrihydrite. *Clays and Clay Minerals*, **36**, 111–124.
- Fischer, W.R. (1988) Microbiological reactions of iron in soils. Pp. 715–748 in: *Iron in Soils and Clay Minerals* (J.W. Stucki, B.A. Goodman and U. Schwertmann, editors). NATO ASI Series, **217**. D. Reidel Publishing Company, Dordrecht, The Netherlands.
- Friedman, G.M. and Sanders, J.E. (1978) *Principles of Sedimentology*. Wiley, New York, NY, p. 235.
- Glasauer, S.M., Hug, P., Weidler, P.G. and Gehring, A.U. (2000) Inhibition of sintering by Si during the conversion of Si-rich ferrihydrite to hematite. *Clays and Clay Minerals*, **48**, 51–56.
- Inouye, K., Ishii, S., Kaneko, K. and Ishikawa, T. (1972) Effect of copper(II) on the crystallization of  $\alpha$ -iron oxide hydrate [ $\alpha$ -FeOOH]. *Zeitschrift für Anorganische und Allgemeine Chemie*, **391**, 86–96.
- Jambor, J.L. and Dutrizac, J.E. (1998) Occurrence and constitution of natural and synthetic ferrihydrite, a widespread iron oxyhydroxide. *Chemical Reviews*, **98**, 2549–2585.
- Kündig, W. and Bömmel, H. (1966) Some properties of supported small  $\alpha$ - $\text{Fe}_2\text{O}_3$  particles determined with the Mössbauer effect. *Physical Review*, **142**, 327–333.
- Labuda, E. (1996) Reactions of iron oxides at elevated pressures and temperatures. PhD dissertation, The Catholic University of America, Washington, D.C., 262 pp.
- Lewis, D.G. and Schwertmann, U. (1979) The influence of aluminum on the formation of iron oxides. IV. The influence of aluminum concentration, hydroxide concentration, and temperature. *Clays and Clay Minerals*, **27**, 195–200.
- Lunden, D.G. and Dean, W. (1979) Biochemistry of iron. Pp. 211–251 in: *Biogeochemical Cycling of Mineral-forming Elements* (P.A. Trudinger and D.J. Swaine, editors). Elsevier, Amsterdam.
- Pfaff, G. and Feltz, A. (1990) Solid-state reactivity and mechanisms in oxide systems. VI. Sintering behaviour of hematite prepared by the hydrothermal method. *Solid State Ionics*, **38**, 25–29.
- Ruan, H.D., Frost, R.L., Klopogge, J.T. and Duong, L. (2002) Infrared spectroscopy of goethite dehydroxylation: III. FT-IR microscopy of *in situ* study of the thermal transformation of goethite to hematite. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, **58A**, 967–981.
- Russell, J.D. (1979) Infrared spectroscopy of ferrihydrite: Evidence for the presence of structural hydroxyl groups. *Clay Minerals*, **14**, 109–114.
- Schultz, M.F., Benjamin, M.M. and Ferguson, J.F. (1987) Adsorption and desorption of metals on ferrihydrite: Reversibility of the reaction and sorption properties of the regenerated solid. *Environmental Science and Technology*, **21**, 863–869.
- Schwertmann, U. and Cornell, R.M. (2000) *Iron Oxides in the Laboratory*, 2<sup>nd</sup> edition. Wiley-VCH, Weinheim, Germany.
- Schwertmann, U. and Murad, E. (1990) The influence of aluminum on iron oxides: XIV. Aluminum-substituted magnetite synthesized at ambient temperatures. *Clays and Clay Minerals*, **38**, 196–202.
- Schwertmann, U., Fitzpatrick, W.R., Taylor, R.M. and Lewis, D.G. (1979) The influence of aluminum on iron oxides. Part II. Preparation and properties of aluminum-substituted hematites. *Clays and Clay Minerals*, **27**, 105–112.
- Schwertmann, U., Friedl, J. and Stanjek, H. (1999) From Fe(III) ions to ferrihydrite and then to hematite. *Journal of Colloid and Interface Science*, **209**, 215–223.
- Stanjek, H. and Weidler, P.G. (1992) The effect of dry heating on the chemistry, surface area, and oxalate solubility of synthetic 2-line and 6-line ferrihydrites. *Clay Minerals*, **27**, 397–412.
- Torrent, J., Guzman, R. and Parra, M.A. (1982) Influence of relative humidity on the crystallization of Fe(III) oxides from ferrihydrite. *Clays and Clay Minerals*, **30**, 337–340.
- Turner, P. (1980) *Continental Red Beds*. Developments in Sedimentology, Vol. **29**. Elsevier, Amsterdam.
- Towe, K.M. and Bradley, W.F. (1967) Mineralogical constitution of colloidal hydrous ferric oxides. *Journal of Colloid and Interface Science*, **24**, 384–392.
- Van Houten, F.B. (1972) Iron and clay in tropical savanna alluvium, Northern Colombia. Contribution to the Origin of Red Beds. *Geological Society of America Bulletin*, **83**, 2761–2772.
- Van Houten, F.B. (1973) Origin of Red Beds. A review. 1961–1972. *Annual Review of Earth and Planetary Science*, **1**, 39–61.
- Varrin, R.D., Jr. (1996) *Characterization of PWR Steam Generator Deposits*, EPRI TR-106048. Electric Power

- Research Institute, Palo Alto, California, USA.
- Vempati, R.K. and Loeppert, R.H. (1989) Influence of structural and adsorbed Si on the transformation of synthetic ferrihydrite. *Clays and Clay Minerals*, **37**, 273–279.
- Walker, T.R. (1967) Formation of Red Beds in modern and ancient deserts. *Ganz-mavag Bulletin* **78**, 353–368.
- Walker, T.R. (1974) Formation of Red Beds in moist tropical climates. Hypothesis. *Geological Society of America Bulletin*, **85**, 633–638.
- Weidler, P.G. (1995) Surfaces of iron oxides. Dissertation, Technical University of Munich, Germany, 108 pp.
- Wightman, P.G. (2002) New insights into bacteria-related geochemical processes: co-adsorption, temperature dependence of protonation, and effects on iron-hydroxide precipitation. Dissertation, University of Notre Dame, Indiana, USA, 104 pp.
- Wolska, E. (1977) The significance of aluminum traces in the elimination of the goethite phase during the ageing of amorphous iron(III) hydroxide. *Monatshefte für Chemie*, **108**, 819–828.
- Wolska, E. (1981) The structure of hydrohematite. *Zeitschrift für Kristallographie*, **154**, 69–75.
- Wolska, E. and Schwertmann, U. (1989) Nonstoichiometric structures during dehydroxylation of goethite. *Zeitschrift für Kristallographie*, **189**, 223–237.
- Zhao, J., Huggins, F.E., Feng, Z. and Huffman, G.P. (1994) Ferrihydrite: surface structure and its effect on phase transformation. *Clays and Clay Minerals*, **42**, 737–746.

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