Local Structure of Ferric Hydroxide $\text{Fe}(\text{OH})_3$ in Aqueous Solution by the Anomalous X-ray Scattering and EXAFS Methods

Kozo Shinoda[†], Eiichiro Matsubara^{††}, Atsushi Muramatsu
and Yoshio Waseda

Institute for Advanced Materials Processing, Tohoku University, Sendai 980-77, Japan

The atomic structure around ferric ions of the ferric hydroxide $\text{Fe}(\text{OH})_3$ in aqueous solution has been studied by the anomalous X-ray scattering (AXS) and EXAFS methods. It is found that this ferric hydroxide consists of the FeO_6 octahedral unit structure and these octahedral units are connected with the edge and double-corner sharing linkage. On the other hand, the powder of the present ferric hydroxide prepared by freeze-drying the aqueous solution was also studied by the conventional X-ray diffraction method. The atomic structure of ferric hydroxide powder is also found to consist of the FeO_6 octahedra connected with the edge and double-corner sharing linkage. Referring to the crystalline structures of other ferric hydroxides and oxides, it is predicted that the FeO_6 octahedral chains formed by the edge sharing linkage are connected with the double-corner sharing linkage in the present ferric hydroxide $\text{Fe}(\text{OH})_3$ solution and powder. The number of the double-corner sharing linkage in solution is about 60% of that in powder. This implies that the solution structure is characterized by the octahedral chains with a relatively large amount of vacant space.

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I. Introduction

Various Fe oxides, oxyhydroxides and hydroxides are widely distributed in soils, minerals, rivers, sea water, etc., and playing an important role in our environment, biological actions and industrial activities. The formation and transformation of Fe (hydrated) oxides in aqueous solutions are, for example, reviewed by Blesa and Matijevic⁽¹⁾. However, little is known about the atomic structure of ferric hydroxides in the early stage of the hydrolytic behavior of ferric ions. Experimental difficulty lies in the coexistence of a large amount of water. Thus, the atomic structure of hydroxides in water is often evaluated from the freeze-dried powder by assuming that their atomic structures are identical. Furthermore, the poor crystallinity of these dried powder also makes the structural determination more difficult since it results in the absence of sharp diffraction peaks. Therefore, the short-range atomic arrangements of these ferric hydroxides were studied by high resolution electron microscopy⁽²⁾, X-ray diffraction coupled with the radial distribution functions (RDFs) analysis⁽³⁾, EXAFS for determining the local atomic arrangements around ferric ions⁽⁴⁾ and so on.

In the present study, the ferric hydroxide of $\text{Fe}(\text{OH})_3$ in aqueous solution was studied by the anomalous X-ray

scattering (AXS) and EXAFS methods. Both methods make up for information of the local atomic structure around ferric ions. This will enable us to obtain more structural information on $\text{Fe}(\text{OH})_3$. Another purpose of the present paper is to demonstrate how effectively the simultaneous use of the AXS and EXAFS methods provides the atomic structure of the poorly crystallized system.

II. Experimental

A ferric hydroxide was precipitated from 1 kmol/m³ ferric nitrate solution by adding 3 kmol/m³ sodium hydroxide aqueous solution till the pH of the solution reaches 8. The precipitated ferric hydroxide was settled, the solution was decanted and new distilled water was added to the solution. This process was repeated several times so that free NO_3^- and Na^+ ions in the solution have been removed completely, which was confirmed by measuring the electric conductivity of the solution. The concentration of a ferric ion in the final solution which was determined by the ICP (Inductively Coupled Plasma Absorption Spectroscopy) is 1.6 kmol/m³. The density of the solution measured by the picnometer is 1.171 Mg/m³. The powder sample was also prepared by freeze-drying this solution. The density of the powder sample determined using a picnometer with isopropyl alcohol is 2.93 Mg/m³.

The AXS and EXAFS measurements were carried out at the beam line 6B in the Photon Factory (PF) of the National Laboratory for High-Energy Physics, Tsukuba,

[†] Graduate Student, Tohoku University.

^{††} Present address: Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

Japan. A double Si(111) crystal monochromator is installed in the upstream of this beam line. The anomalous X-ray scattering (AXS) intensity of solution contained in a cell with kapton windows in both sides was measured at the two incident energies of 1.091 fJ (6.811 keV) and 1.135 fJ (7.086 keV) below the Fe K absorption edge (1.139 fJ (7.111 keV)) with the transmission geometry at lower scattering angles up to 60° and with the reflection geometry at higher scattering angles from 50° to 120° . Scattering intensities observed in both geometries were corrected for absorption, and connected for further structural analysis⁽⁵⁾. The incident beam was monitored with an ionization chamber placed just in front of the sample. The higher harmonics produced by Si (333) was reduced to an insignificant level by intentionally detuning the second Si crystal by a piezo device attached to it. The thickness of the solution sample was evaluated by measuring the absorption in the transmission geometry.

The AXS intensity of at least 40,000 counts was collected at each scattering angle, the average being about 80,000 counts. The intensity corrected for air scattering and absorption was converted to electron units per atom by the generalized Krogh-Moe-Norman method⁽⁶⁾, using the X-ray atomic scattering factor⁽⁷⁾, including their anomalous dispersion terms⁽⁸⁾ theoretically calculated by the method of Cromer and Liberman⁽⁹⁾, and Compton scattering factors⁽¹⁰⁾. From the intensity difference between these scattering intensity in the absolute units, the environmental radial distribution function for ferric ions was determined. The details of the analysis of the AXS intensity has already been described⁽¹¹⁾ and then not duplicated here.

The Fe EXAFS measurements were made for samples of solution and powder form, and the $\alpha\text{Fe}_2\text{O}_3$ crystalline powder. The intensities of the incident and transmitted beams were measured by ionization chambers. The effect of the higher harmonics was also reduced in the EXAFS measurements. By analyzing the EXAFS spectrum of the $\alpha\text{Fe}_2\text{O}_3$ crystal, the performance of the EXAFS measurement was verified and the parameters required for the EXAFS analysis were evaluated. The details of the experimental settings and data processing for disordered systems have already been described elsewhere⁽¹²⁾.

The X-ray scattering intensities of the solution and powder samples were also measured with Mo $K\alpha$ radiation produced by the rotating-anode X-ray generator in operation at 45 kV and 150 mA. A monochromatic beam was obtained with a Ge (111) flat single-crystal monochromator in the incident beam. The observed intensity was corrected for air scattering, polarization and absorption, and converted to electron units per atom by the Krogh-Moe-Norman method. The RDFs of the solution and powder samples were obtained by the Fourier transformation of the interference function obtained from the scattering intensity in absolute units.

III. Results

Intensity profiles of the solution and powder samples

are shown in Fig. 1(a) and (b), respectively. The essential feature of the solution profile in Fig. 1(a) is attributed to pure water⁽¹³⁾, such as a broad first peak with a shoulder indicated with arrows. On the other hand, the profile of the powder sample in Fig. 1(b) consists of several broad peak and shoulders at about 12, 25, 30, 36, 40, 60 nm^{-1} etc. The positions of these peaks coincide with those of $\text{Fe}(\text{OH})_3$ tabulated in the JCPDS (Joint Committee Powder Diffraction Standard) file but not with those of other ferric hydroxides or oxides, such as αFeOOH , Fe_2O_3 , etc. The ordinary RDFs of solution and powder are shown with the solid and dotted curves in Fig. 2(a).

Fig. 1 Intensity profiles of hydroxide $\text{Fe}(\text{OH})_3$ solution and powder by Mo $K\alpha$ radiation. The peak positions are compared with those for $\text{Fe}(\text{OH})_3$ and αFeOOH tabulated in the JCPDS files.

Fig. 2 (a) The ordinary RDFs in aqueous ferric hydroxide $\text{Fe}(\text{OH})_3$ solution (solid) and freeze-dried $\text{Fe}(\text{OH})_3$ powder (dotted), and (b) the environmental RDF for ferric ions.

Fig. 3 Intensity profiles of aqueous ferric hydroxide $\text{Fe}(\text{OH})_3$ solution measured at 1.135 fJ (7.086 keV) and 1.091 fJ (6.811 keV) below the Fe K absorption edge and its differential profile, ΔI . The variation of real and imaginary parts of Fe anomalous dispersion terms (f''_{Fe} and f'_{Fe}) are shown near the Fe K absorption edge. **a** and **b** correspond to the incident energies used for the present AXS measurements.

Two intensity profiles of solution shown at the bottom of Fig. 3 correspond to the AXS intensities observed at 1.091 fJ (6.811 keV) and 1.135 fJ (7.086 keV) just below the Fe K absorption edge (1.139 fJ (7.111 keV)). Since their difference shown at the top of Fig. 3 results from a distinct variation of the real part of the anomalous dispersion term of Fe at **a** and **b** in the inserted figure just below the Fe K absorption edge, the peak and shoulder due to water indicated with arrows completely disappear in the differential intensity profile. Namely, by analyzing this difference, an atomic structure around a ferric ion in solution can be directly and clearly obtained. The peaks labeled **a** through **e** in Fig. 1 are also observed in the differential intensity of the solution in Fig. 3 although their relative intensities are different in detail. This indicates that the fundamental unit structure of ferric hydroxide in solution is quite similar to the powder case.

The Fourier transformation of the environmental interference function for ferric ions in solution calculated from the differential intensity in Fig. 3 gives an environmental RDF for ferric ions. The environmental RDF for ferric ions in solution is shown in Fig. 2(b). As it is seen in the differential intensity profile for solution in Fig. 3, the peak at about 0.28 nm of the ordinary RDF for solution in Fig. 2(a) which is attributed to the correlation of oxygen atoms in water molecules, disappears in the environmental RDF for ferric ions.

The EXAFS method has now recognized as a useful tool for determination of local environmental structure around a specific element in materials including solutions. This is particularly true for the nearest neighbor region. The EXAFS signals and their Fourier transforms

Fig. 4 (a) Fe K EXAFS spectra and (b) Fe K EXAFS radial distribution functions (RDFs), uncorrected for phase functions, in the ferric hydroxide $\text{Fe}(\text{OH})_3$ solution and its powder.

of RDFs for both solution and powder are shown in Fig. 4. Both samples show a similar profile consisting of three peaks indicated with arrows. By consulting the crystal-line data of some ferric hydroxides and oxides, it is found from these EXAFS data that the first and second peaks are attributed to the first nearest neighboring Fe-O and Fe-Fe pairs, respectively, and the second nearest neighboring Fe-Fe and Fe-O pairs are overlapped at the third peak. The contribution of the second neighboring Fe-O and Fe-Fe pairs at the third peak is not so significant and then it is excluded for the EXAFS analysis. Consequently, the coordination numbers and atomic distances for the nearest neighboring Fe-O and Fe-Fe pairs were determined from the EXAFS data so as to reproduce the experimental EXAFS signals as shown in Fig. 4(a). They are summarized in Table 1.

The ordinary RDF for powder and the environmental RDF for ferric ions for solution in Fig. 2(a) and (b) were analyzed with the least-squares variational method⁽¹²⁾⁽¹⁴⁾ using the structural parameters in Table 1 for the nearest neighboring pairs. In this analysis of the AXS data, the second nearest neighboring Fe-O and Fe-Fe pairs were included. The environmental interference function for ferric ions for solution and the ordinary interference

function for powder calculated with the least-squares variational method are compared with the experimental

Table 1 The coordination numbers and atomic distances determined by EXAFS in the Fe(OH)₃ solution and its powder prepared by freeze-drying.

Pairs	Solution*		Powder*	
	<i>r</i> /nm	<i>N</i>	<i>r</i> /nm	<i>N</i>
Fe–O(1st)	0.197	5.6	0.196	5.3
Fe–Fe(1st)	0.309	3.7	0.308	3.9

* The experimental errors of the atomic distances and coordination numbers are ± 0.002 nm and ± 0.6 , respectively.

Fig. 5 (a) The experimental environmental interference function for ferric ions for solution and (b) the ordinary interference function for powder are compared with the ones calculated with the least-squares variational method (dotted curves).

Table 2 The coordination numbers and atomic distances obtained from the anomalous X-ray scattering (AXS) data in the Fe(OH)₃ solution and from the X-ray diffraction data in the Fe(OH)₃ powder are compared with those calculated from the crystalline data in α -FeOOH.

Pairs	Solution*		Powder*		α -FeOOH	
	<i>r</i> /nm	<i>N</i>	<i>r</i> /nm	<i>N</i>	<i>r</i> /nm	<i>N</i>
Fe–O(1st)	0.209	5.5	0.199	5.5	0.202	5.9
Fe–O(2nd)	0.367	7.0	0.365	8.5	0.360	9.0
Fe–Fe(1st)	0.316	3.6	0.308	3.9	0.315	4.0
Fe–Fe(2nd)	0.341	2.2	0.344	3.6	0.346	4.0

* The experimental errors of the atomic distances and coordination numbers are ± 0.003 nm and ± 0.3 , respectively.

ones in Fig. 5. The resultant structural parameters are summarized in Table 2. The structural parameters except for the coordination number of the second nearest neighboring Fe–Fe pair show no significant difference between solution and powder. The coordination number for the second nearest neighboring Fe–Fe pair in solution is about 60% less than that of powder.

IV. Discussion

Careful investigation of the crystalline structures, such as goethite (α -FeOOH), akaganeite (β -FeOOH), lepidocrocite (γ -FeOOH) and hematite (α -Fe₂O₃), reveals the following important common structural features in the ferric hydroxides and oxides. First, the fundamental unit structure is FeO₆ octahedra in these crystalline materials. These octahedral units are connected in four different ways as exemplified by the schematic representation in Fig. 6. Namely, face sharing, edge sharing, double-corner sharing and single-corner sharing linkages⁽¹⁴⁾. Average distances between ferric ions vary in each linkage. They are 0.289 nm for the face sharing linkage, 0.297 to 0.308 nm for the edge sharing linkage, 0.337 to 0.370 nm for the double-corner sharing linkage and 0.390 nm for the single-corner sharing linkage.

It is found in Table 2 that 5.5 ± 0.5 oxygen atoms are located at 0.209 ± 0.003 nm in solution and 5.5 ± 0.3 oxygen atoms at 0.199 ± 0.002 nm for powder. This indicates that the fundamental unit structure is considered FeO₆ octahedra in the present hydroxide solution and powder. The atomic distances of the first and second nearest neighboring Fe–Fe pairs for solution are 0.316 ± 0.002 and 0.341 ± 0.003 nm, and 0.308 ± 0.002 and 0.344 ± 0.003 nm for powder, respectively. Thus, according to the atomic distances of the Fe–Fe pairs discussed for the Fig. 6 case, the FeO₆ octahedra in both solution and powder may be connected by sharing the edge and double-corner, but not by sharing the face or single-corner. By comparing the coordination numbers of the Fe–Fe pairs for both solution and powder in Table 2, it is

Fig. 6 The local arrangements of the FeO₆ octahedra in the ferric hydroxides and oxides; (a) face, (b) edge, (c) double-corner and (d) single-corner sharing linkages.

Fig. 7 Local arrangements around a certain octahedron drawn with thick lines in the goethite αFeOOH . E_1 and E_2 correspond to the octahedra connected to the central octahedron with the edge sharing linkage. The octahedra labeled DC are connected to the central octahedron with the double-corner sharing linkage. The atoms labeled a to f are the second nearest neighboring oxygen atoms around the ferric ion in the central octahedron.

also found that the number of the double-corner sharing octahedra increases from 2.2 ± 0.3 to 3.6 ± 0.2 by freeze-drying the solution.

An arrangement of some FeO_6 octahedra around a certain octahedron drawn with thick outlines in αFeOOH is schematically shown in Fig. 7. The octahedra labeled E_1 and E_2 in Fig. 7 are connected to the central octahedron with the edge sharing linkage. The octahedra or E_1 or E_2 form an octahedral chain normal to Fig. 7 with the edge sharing linkage and these chains are also connected by the edge sharing linkage. Namely, a double-octahedral chain is formed in αFeOOH by the edge sharing linkage. The octahedra labeled DC in Fig. 7 are connected to the central octahedron with the double-corner sharing linkage. With this double-corner sharing linkage, the double-chain of E_1 and E_2 is connected with the neighboring other double-chains. The first nearest neighboring ferric ions in the central octahedron in αFeOOH are ferric ions in the octahedra of E_1 and E_2 . The second nearest neighboring ferric ions correspond to ferric ions in the octahedra of DC. The second nearest neighboring oxygen atoms for the central ferric ion are labeled a through f. The average coordination numbers and atomic distances for these first and second nearest neighboring pairs calculated from the αFeOOH crystal are shown in Table 2. These values of αFeOOH coincide with those for the present powder case as easily found in Table 2. However, it should be mentioned the following point. The peak positions of powder do not coincide with those in αFeOOH as shown in Fig. 2 and these experimental results suggest that the local atomic arrangement of the FeO_6 octahedra remains in powder, similar to the αFeOOH case, but their crystalline symmetries are different with each other.

Assuming that the local atomic arrangement of the octahedra in powder is perfectly similar to that in αFeOOH (Fig. 7), the following features of the local atomic structure between powder and solution would be suggested. No significant difference is detected in the structural parameters of the first neighboring pairs between solu-

tion and powder. However, the structural parameters of the second neighboring pairs in solution appear to differ from those of powder. The coordination numbers of solution are smaller than the values of powder. Particularly, the coordination number of the second neighboring Fe-Fe pairs in solution is about 60% less than the powder case. As explained in Fig. 7, the second nearest neighboring Fe-Fe pairs correspond to the double-corner sharing linkage, with which the neighboring double octahedral chains are connected with each other. Therefore, the double octahedral chains in solution is not likely to present as many as in powder. Namely, the double-corner sharing linkage are partially broken and they may be replaced by water molecules in solution. By freeze-drying the solution, these water molecules are removed from the structure and the number of the double-corner sharing linkages increases. It may also be suggested the ferric hydroxide $\text{Fe}(\text{OH})_3$ in aqueous solution is transformed to crystalline αFeOOH by completing the double-corner sharing linkage through the freeze-drying process.

In conclusion, the fundamental unit structure of the hydroxide $\text{Fe}(\text{OH})_3$ in aqueous solution is the FeO_6 octahedra. They are connected in two different ways, that is, the edge and double-corner sharing linkages, so that the network of the double octahedral chains is formed. Since the number of the double-corner sharing linkage in solution is about 60% less when compared with the powder case, the network structure formed by the FeO_6 octahedra in solution may contain more vacant space where water molecules may be involved. It is worth mentioning from the present results that potential capability of simultaneous use of the AXS and EXAFS methods to investigate the atomic structure around a heavy metallic cation of a precipitated hydroxide in aqueous solution has been clearly demonstrated.

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