JOURNAL OF MATERIALS SCIENCE 19 (1984) 3341–3346

Characterization of brown ferric oxide hydrate xerogel

A. C. VAJPEI, UMA, I. P. SARASWAT
Chemistry Department, University of Roorkee, Roorkee-247667, India
KAILASH CHANDRA
USIC, University of Roorkee, Roorkee-247667, India

Ferric chloride solution was neutralized using sodium hydroxide as the precipitant to the extent that the final pH of the suspension was ~7. After thorough washing the precipitated gel was dried in air at 60° C for 24 h to yield brown ferric oxide hydrate xerogel. The xerogel was examined at room temperature using infrared (IR) spectroscopy, powder X-ray diffraction (XRD), electron optical measurements, magnetometry and Mössbauer resonance spectroscopy. It has been concluded that the structural, morphological and magnetic characteristics of the xerogel are identifiable with those of the protoferrihydrite phase.

1. Introduction

Brown ferric oxide hydrate gels have been studied by countless workers. Despite this, differences of opinion still persist as regards the structure of the gels and the nature of the primary particles that constitute them. Weiser and Milligan [1, 2] have inferred that the gels consist of extremely minute crystals of ferric oxide which hold varying amounts of water by adsorption and capillary forces. Mackenzie and co-workers [3, 4] indicated formation of α-, β- and γ-FeOOH or α-Fe_2O_3 phases in the gels while Kobayashi and Uda [5] inferred that the structure of the gel in the short range is very similar to that of γ-FeOOH. On the other hand, X-ray scattering studies by Magini [6] support Weiser and Milligan's view that the ferric sols and gels consist of agglomerates of extremely minute primary particles previously formed in solution, rather than an amorphous body constituted by a continuous network of polynuclear complexes linked by oxygen and hydroxy bridges. According to van der Giessen [7, 8] the iron(III) oxide hydrate gels contained hydroxyl groups within their structure and the primary particles constituting the gel showed a close resemblance to both $FeOOH{\cdot}nH_2O$ and $Fe_2O_3{\cdot}nH_2O$ type species. Almost similar structural features were suggested for the gel studied by Okamoto *et al.* [9] and a quasi amorphous structure based on a hexagonal close packed oxygen lattice with ferric ions randomly distributed in the octahedral interstices was proposed. This is in conformity with the Towe–Bradley structure model for the gel [10] related to the haematite structure and with a unit cell content of approximately $Fe_5HO_8{\cdot}4H_2O$.

For naturally occurring ferric oxide hydrate gels showing similar crystallochemical features as were initially indicated by Towe and Bradley [10], the name ferrihydrite was proposed by Chukhrov *et al.* [11, 12]. This was confirmed by the commission on new minerals [13, 14] of the IMA (International Mineralogical Association). Studies reported by Chukhrov *et al.* [11, 12], Jackson and Keller [15] and Schwertmann and Fischer [16] provided initial structural data for identification and characterization of ferrihydrite phases on the basis of IR spectrum and X-ray and electron diffraction measurements. The term protoferrihydrite was used by Chukhrov *et al.* [12] to describe a slightly less ordered precursor of ferrihydrite. According to Schwertmann *et al.* [17], the ferrihydrite phase should be regarded as being made up of layers of octahedra with iron in the centre and O, OH and OH_2 as ligands, the octahedra being arranged similarly to those in haematite, α-Fe_2O_3. The protoferrihydrite consists of

0022–2461/84 $03.00 + .12

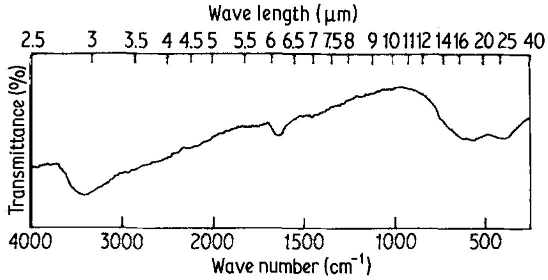


Figure 1 IR spectrum at 300 K of ferric oxide hydrate gel.

planar arrangements of $Fe(OOH,OH_2)_6$ octahedra without any stacking perpendicular to that plane and can be considered to have the most primitive arrangement of $Fe(OOH, OH_2)_6$ octahedra. The Mössbauer spectrum of synthetic ferrihydrite and its relationship to other more crystalline iron oxide forms has been analysed by Murad and Schwertmann [18].

The studies reported here are a continuation of our previous investigations [19–21] on the structure and stability of brown ferric oxide hydrate gels. IR spectroscopy, XRD, electron optical studies, magnetometry and Mössbauer resonance spectroscopy studies aimed at examining the xerogel obtained by neutralization of ferric chloride solution with sodium hydroxide at room temperature, and oven drying at 60° C for 24 h, are presented and discussed with a view to providing a coherent picture of the structure of the gel.

2. Experimental procedure

Brown ferric oxide hydrate gel was prepared by dropwise addition of sodium hydroxide (A.R.) solution to a freshly prepared and well stirred solution of ferric(III) chloride (G. R. Merck) until the pH of the suspension was ~ 7. The precipitated gel was washed with distilled water until free from electrolyte and was dried at 60° C in air in an oven for 24 h and was stored in a desiccator. The IR spectrum of the gel dispersed in the KBr disc was obtained in the range 250 to 4000 cm^{-1} using a Beckman Model IR-20 spectrometer. The X-ray diffraction pattern of the sample sieved through BSS 350 mesh sieve was obtained using a Philips PW 1140/90-X-ray diffractometer using Zr-filtered Mo$K\alpha$ radiation. Electron optical measurements were recorded with Philips EM-400 transmission electron microscope operated at 60 to 80 kV. A small quantity of gel ultrasonically dispersed in absolute alcohol on to 200 mesh copper grids covered with a thin film of formvar was taken for electron optical examination. Magnetic measurements were performed using a vibrating sample magnetometer VSM model 155, the calibration being achieved with high purity nickel showing the saturation moment 55 emu g^{-1} with a saturation flux of about 8000 G. Mössbauer measurements were made at room temperature with a ^{57}Co source in a rhodium matrix in standard transmission geometry. For the calibration of velocity and as a standard for isomer shift values, metallic iron foil was used as reference.

3. Results and discussion

Fig. 1 shows an IR spectrum of the gel in the region 250 to 4000 cm^{-1}, while Fig. 2 shows the powder XRD features for the gel. In Fig. 3 the electron diffraction features and electron microphotographs obtained from the gel are presented. The values of the specific magnetization, σ, plotted against magnetic field, H, and of magnetic susceptibility per gram, χ_g, calculated are given in Table I. The Mössbauer resonance spectrum of the gel at room temperature is given in Fig. 4. The IR spectrum in Fig. 1 shows broad absorption bands centred at 3450 and 1640 cm^{-1}, respectively characterizing the stretching and bending modes of

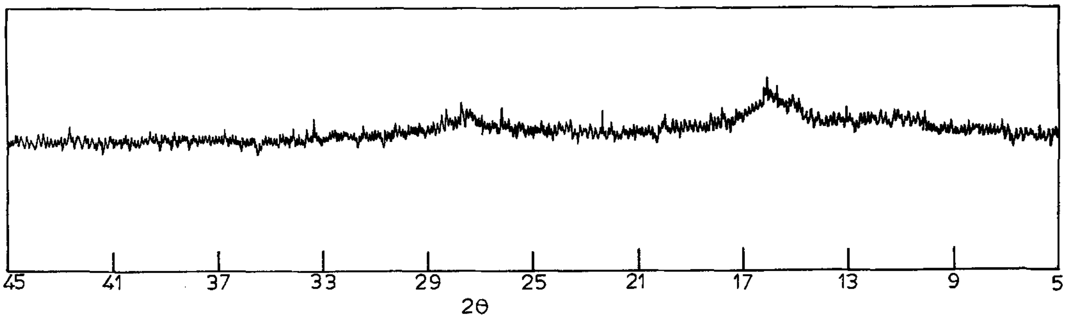
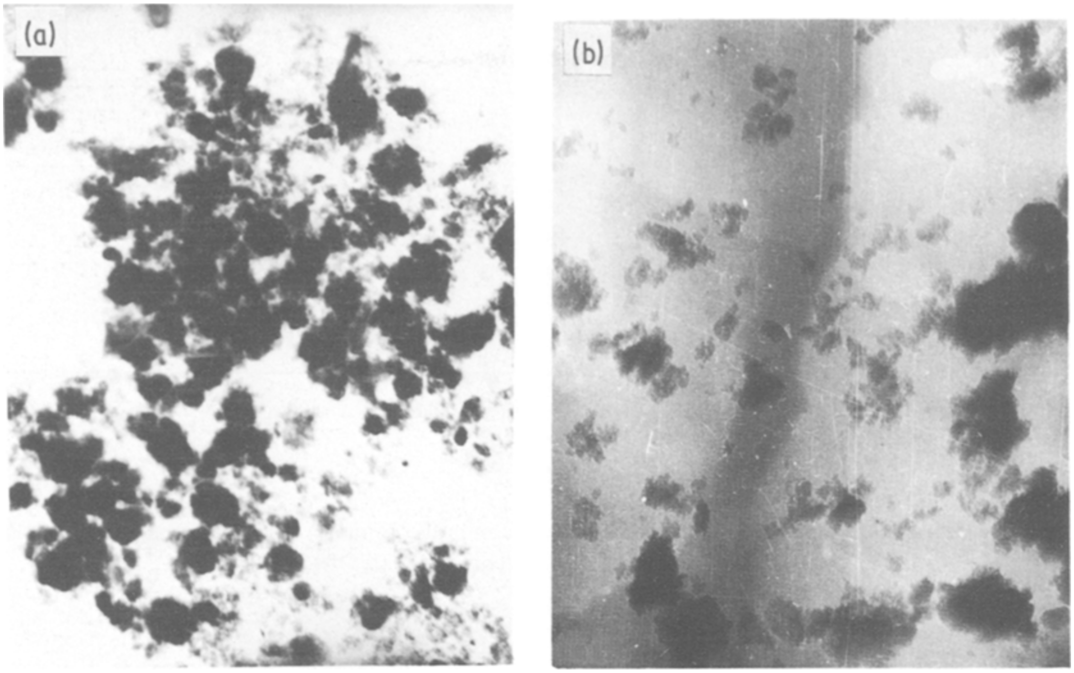


Figure 2 Powder X-ray diffraction pattern at 300 K of ferric oxide hydrate gel. Mo$K\alpha$ radiation.



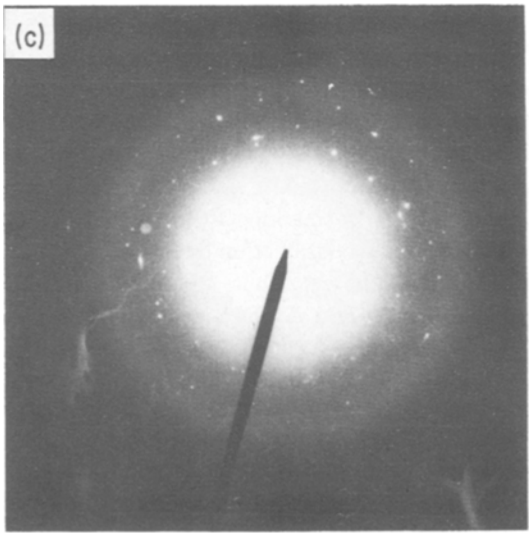


Figure 3 (a), (b) Electron micrographs of ferric oxide hydrate gel. (a) ×81 000: (b) ×135 000. (c) Electron diffraction pattern of ferric oxide hydrate gel.

vibrations for water and structural hydroxyl groups [22, 23]. In the 300 to 700 cm^{-1} region, strong broad absorption bands due to iron–oxygen lattice vibrations are observed centred around 580 cm^{-1}. It is interesting to observe that in the same region α-Fe_2O_3 exhibits distinct bands located around 560, 452 and 345 cm^{-1} [24, 25]. These features suggest that the gel consists of a hexagonal close packed arrangement of oxygen sublattice similar to that present in α-Fe_2O_3 but with little degree of order among the iron ions as indicated by the broad IR bands. The IR spectrum of the gel under investigation is devoid of any feature in the region 600 to 1100 cm^{-1}, which corresponds to bending vibrations of different ferric oxyhydroxide modifications i.e. α-, β- and γ-FeOOH [26]. Rather it shows a close resemblance to the IR characteristics reported for protoferrihydrite and ferrihydrite by Chukhrov *et al.* [12] and Russel [27].

The powder XRD pattern (Fig. 2) shows only two broad bands having *d*-values of 0.256 and 0.149 nm. In the selected-area electron diffraction pattern of the gel (Fig. 3), two sharp rings with *d*-spacings equal to 0.257 and 0.152 nm are observed. These features are diagnostic of protoferrihydrite [12]. The average crystallite size of

TABLE I Values of specific magnetization, σ, with varying magnetic field, H, for brown ferric oxide hydrate xerogel

Field, H (G)	Specific magnetization, σ (emu)
1700	0.481
3750	0.827
5500	1.190
6600	1.530

χ_g, magnetic susceptibility per gram, calculated from the linear plots of σ against H, is 220.0×10^{-6} emu g^{-1}.

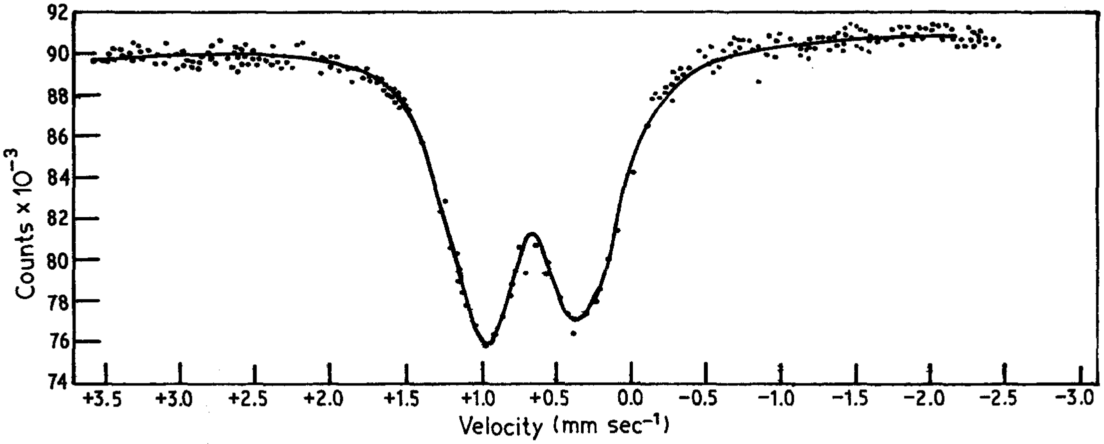


Figure 4 Mössbauer spectrum at 300 K of ferric oxide hydrate gel.

the gel as determined by X-ray line broadening is of the order of 25 nm. As shown by electron microscopy, the gel is composed of large aggregates and small discrete subunit particles with well separated edges. The discrete subunit particles in the size range 7 to 10 nm have hexagonal to rounded morphology. The aggregates which make up the bulk of the gel have a sheet-like appearance with a fibrous morphology and flaky microstructure.

Magnetization data and magnetic susceptibility per gram, χ_g, as given in Table I, characterize the gel to consist of incompletely compensated antiferromagnetic particles in the superparamagnetic state. This agrees well with the pseudohexagonal structure of the gels, based on partial occupation of Fe^{3+} octahedra in a hexagonal close packed oxygen sublattice which is essentially the structure proposed by Towe and Bradley [10] and by Chukhrov *et al.* for ferrihydrite [12]. Field-dependent magnetization and χ_g obtained from this are in good agreement with the results obtained by van der Giessen [7, 8] and also with those reported by Matzen and Poix [28] in a recent study.

Mössbauer spectrum of the gel at room temperature consists of broad quadrupole split doublet pattern with a shift δ/Fe of 0.37 mm sec^{-1} and a splitting ΔE_Q of 0.64 mm sec^{-1}. These parameters characterize Fe^{3+} ions in distorted octahedral sites with a considerable degree of randomness in relation to the distribution and incorporation of iron ions in the gel phase as reflected by the broadening of the resonance lines. The spectrum was resolved into two doublets having Lorentzian peak shapes using a least-squares computer program and the parameters extracted from them are:

$$\delta_1 = 0.36\,\text{mm sec}^{-1},\ \Delta E_{Q1} = 0.95\,\text{mm sec}^{-1}$$

$$\delta_2 = 0.38\,\text{mm sec}^{-1}\text{ and }\Delta E_{Q2} = 0.50\,\text{mm sec}^{-1}$$

These results compare well with the Mössbauer studies reported by Murad and Schwertmann for synthetic ferrihydrite [18] and with those of Childs and Johnston [29] for synthetic protoferrihydrite. The two doublet patterns obtained in protoferrihydrite and ferrihydrite can be accounted for as marking the two extreme situations for the coordination spheres of the Fe^{3+} octahedra in the gel. Thus, the different quadrupole splittings in the doublet spectra arise from the different extents of chain propagation and are responsible for the extended planar arrangement of $Fe(OOH, H_2O)_6$ octahedra in the protoferrihydrite gel structure. Also, these variations may be accounted for by the differences in bonding of Fe^{3+} ions associated with OH groups located, respectively, at surfaces and deeper in the structure of the gel phase, as pointed out earlier in the IR spectroscopy study by Russel [27] for ferrihydrite.

4. Conclusions

Table II summarizes the data discussed above on structural, morphological and magnetic characteristics of the xerogel as indicated by the different techniques employed. IR spectroscopy, X-ray diffraction, electron optical measurements, magnetometry and Mössbauer resonance studies on brown ferric oxide hydrate xerogel prepared by room-temperature neutralization of ferric chloride

TABLE II Structural, morphological and magnetic features of the brown ferric oxide hydrate xerogel at room temperature (300 K)

Physical method	Observed features
1. Infrared spectroscopy	Broad absorption band centred around 3450, 1640 and 580 cm^{-1}.
2. Powder X-ray diffraction	Two broad reflections with *d*-spacings of 0.256 and 0.149 nm.
3. Selected-area electron diffraction	Two sharp rings with *d*-spacings of 0.257 and 0.152 nm.
4. Electron microscopy	Small discrete subunit particles of 7 to 10 nm and their aggregates.
5. Magnetic measurements	Field-dependent magnetization, χ_g (magnetic susceptibility per gram) $\sim 220 \times 10^{-6}\,\text{emu g}^{-1}$.
6. Mössbauer resonance	A two line spectrum with a shift δ/Fe of 0.37 mm sec^{-1} and splitting ΔE_Q of 0.64 mm sec^{-1}. Resolved spectrum yields two Lorentzian doublets with $\delta_1 = 0.36\,\text{mm sec}^{-1}$, $\Delta E_{Q_1} = 0.95\,\text{mm sec}^{-1}$ and $\delta_2 = 0.38\,\text{mm sec}^{-1}$, $\Delta E_{Q_2} = 0.50\,\text{mm sec}^{-1}$, respectively.

solution by sodium hydroxide at pH ~ 7 and oven drying in air at 600° C for 24 h showed that protoferrihydrite is the only phase formed in the gel. This consists of a hexagonal close packed oxygen ion component similar to that of a haematite. The morphology and microstructure of the gel is characterized by the presence of hexagonal subunit particles of 7 to 10 nm and their coherent agglomerates, both possessing the same basic structure as that present in protoferrihydrite. The gel particles are superparamagnetic and have an incompletely compensated antiferromagnetic structure, in keeping with the pseudohexagonal structure of the protoferrihydrite. Fitting of the Mössbauer spectrum of the gel resulted in two doublet patterns with similar isomer shifts but different quadrupole splittings. The difference in quadrupole splittings arises from a distribution in the site symmetry of the iron ions in the gel. The doublets with smaller and larger quadrupole splittings are observed to be caused by the different extents of asymmetric contributions for q_{Lattice} from the surfaces in the layered structure of the gel, owing to the different degrees of aggregation and chain formation by the primary particles of protoferrihydrite.

Acknowledgements

The authors thank Professor Nam Prakash, Senior Physicist, Nuclear Research Laboratory, IARI, New Delhi, India for his continued interest and encouragement. We express our gratitude to CSIR, New Delhi, for granting financial support to this work.

References

1. H. B. WEISER and W. O. MILLIGAN, in "Advances in Colloid Science", Vol. I, edited by E. O. Kramer, E. F. Bartet and S. S. Kistler (Interscience, New York, 1942) p. 227.
2. *Idem, J. Phys. Chem.* **44** (1940) 1081.
3. R. C. MACKENZIE and G. BERGGREN, in "Differentiatial Thermal Analysis", Vol. I, edited by R. C. Mackenzie (Academic Press, London, 1970) p. 277.
4. R. C. MACKENZIE and R. C. MELDAU, *Mineral. Mag.* **33** (1959) 153.
5. M. KOBAYASHI and M. UDA, *J. Non Crystalline Solids* **29** (1978) 419.
6. M. MAGINI, *J. Inorg. Nucl. Chem.* **39** (1977) 409.
7. A. A VAN DER GIESSEN, *Philips Res. Rep. Supl.* **12** (1968.
8. *Idem, J. Inorg. Nucl. Chem.* **28** (1966) 2155.
9. S. OKAMOTO, H. SEKIZAWA and S. I. OKAMOTO, in Proceedings 7th International Conference on the Reactivity of Solids, edited by J. S. Anderson, M. W. Roberts and F. S. Stone (Chapman and Hall, London, 1972) p. 341.
10. K. M. TOWE and W. F. BRADLEY, *J. Coll. Interface Sci.* **24** (1967) 384.
11. F. V. CHUKHROV, B. B. ZVYGIN, A. I. GORSHKOV, L. P. ERMILOVA and E. S. RUDNITSKAYA, *Izvestia. AN SSSR Ser. geol.* **1** (1971) 3.
12. F. V. CHUKHROV, B. B. ZVYAGIN, L. P. ERMILOVA and A. I. GORSHKOV, in Proceedings International Clay Conference, Madrid, edited by J. M. Serratsova (Sociedad Espanola de Arcillas and Association Internationale pour L'Etude des Argilles, 1972) p. 397.
13. M. H. HEY and P. G. EMBREY, *Mineral. Mag.* **39** (1974) 903.
14. M. FLEISCHER, C. Y. CHAO and A. KATO, *Amer. Mineral.* **60** (1975) 485.
15. T. A. JACKSON and W. D. KELLER, *Amer. J. Sci.* **269** (1970) 446.
16. U. SCHWERTMANN and W. R. FISCHER, *Geoderma* **10** (1973) 237.

17. U. SCHWERTMANN, D. G. SCHULZE and E. MURAD, *Soil Sci. Soc. Am. J.* **46** (1982).
18. E. MURAD and U. SCHWERTMANN, *Amer. Mineral.* **65** (1980) 1044.
19. A. C. VAJPEI, PhD thesis, University of Roorkee, Roorkee, India (1978).
20. I. P. SARASWAT, A. C. VAJPEI, V. K. GARG, V. K. SHARMA and NAM PRAKASH, *J. Coll. Interface Sci.* **73** (1980) 373.
21. I. P. SARASWAT, A. C. VAJPEI, V. K. GARG, *Indian J. Chem.* **15A** (1977) 493.
22. Y. I. RYSKIN, in "The IR spectra of Minerals", edited by V. C. Farmer (Mineralogical Society, London, 1974) p. 137.
23. R. A. NYQUIST and R. O. KAGEL, "Infrared Spectra of Inorganic Compounds" (Academic Press, New York, 1971).
24. C. N. R. RAO, 'Chemical Applications of Infrared Spectroscopy" (Academic Press, New York, 1963).
25. F. F. BENTLEY, L. D. SMITHSON and A. L. ROZECK, "Infrared Spectra and Characteristic Frequencies 700–300 cm^{-1}" (Interscience, New York, 1968).
26. K. KAUFFMAN and F. HAZEL, *J. Inorg. Nucl. Chem.* **37** (1975) 1139.
27. J. D. RUSSEL, *Clay Minerals* **14** (1979) 109.
28. G. MATZEN and P. POIX, *J. Mater. Sci.* **17** (1982) 701.
29. C. W. CHILDS and J. H. JOHNSTON, *Aust. J. Soil. Res.* **18** (1980) 245.

Received 17 October 1983
and accepted 13 January 1984