

The Point of Zero Charge and the Isoelectric Point of γ -Fe₂O₃ and α -Fe₂O₃

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The difference of the point of zero charge (PZC) and isoelectric point (IEP) values for γ - and α -Fe₂O₃ were measured and are quantitatively explained by the difference in crystal structure. Great care was taken to assure the purity of the samples and that measurements were taken under identical conditions. The PZC and the IEP for the "unhydrated" samples, were the same for each crystal structure, with the values for γ -Fe₂O₃ being more acidic, by 1.1 or 1.2 pH units, than for α -Fe₂O₃. This difference can be quantitatively explained by Parks' equation, in terms of the difference in the coordinations of the Fe³⁺ ions in the two crystal structures.

γ -Fe₂O₃ is a ferrimagnetic inverse-spinel type iron oxide, which is widely used for making magnetic recording tapes. Its surface properties have a large influence on its dispersibility in the paint, and thus on the output and noise characteristics of the tape.¹⁾ Although the PZC and the IEP are important parameters which characterize the surface of the γ -Fe₂O₃, little work has been reported on this subject. Iwasaki et al.²⁾ reported an IEP at pH 6.7 for a sample with a γ -FeOOH phase. Parks' review³⁾ of the work on α -Fe₂O₃ shows a wide scattering of the reported values of IEP and PZC, ranging from 1.9 to 9.04. This can be attributed to variations, in the level of surface impurities, the hydration states, and in the conditions and methods of measurement.

The dependence of the IEP value on the crystal structure was reported for manganese⁴⁾ and aluminum oxides.⁵⁾ Kittaka and Morimoto⁶⁾ reported that the IEP in inverse-spinel type oxides is lower than that in normal-spinel type oxides. They explained this in terms of the coordination between the hydroxyl group and the metal ions at the surface.

The aim of the present work is to measure the inherent PZC and IEP values of acicular γ - and α -Fe₂O₃, and to provide a quantitative explanation for the difference between them. In order to obtain reliable values, care was taken to assure both the purity of the samples and the reproducibility of the measurement conditions. The control of the measurement conditions is especially important in measurements involving the state of hydration of the samples.

Experimental

Samples. The γ -Fe₂O₃ sample was prepared by the dehydration reduction of synthetic acicular α -FeOOH, followed by an oxidation. The α -FeOOH was prepared by the oxidation of the precipitate, formed by adding a NaOH aqueous solution to an iron (II) sulfate aqueous solution. The α -FeOOH was subjected to dehydration reduction at 350 °C under a hydrogen flow for 1 h, and then, oxidized at 250 °C under an air flow for 1 h. The product was confirmed to be spinel latticed γ -Fe₂O₃ by X-ray diffraction and had a magnetization of 73.0 emu g⁻¹ as measured at room temperature by a vibrating sample magnetometer (Princeton Applied Research, Model-155). An electron micrograph of the γ -Fe₂O₃ particles is shown in Fig. 1a. The

specific surface area of the γ -Fe₂O₃ particles was established as 18.6 m² g⁻¹ by the BET method of nitrogen adsorption at liquid nitrogen temperature. The atomic absorption spectrum of the γ -Fe₂O₃ particles revealed no significant metallic ion impurity, although a small amount of sulfate ion was detected. The sulfate ion content was determined from the amount of BaSO₄ precipitate, formed on the addition of BaCl₂ to a HCl solution of the γ -Fe₂O₃ particles, and was found to be 0.96 wt.%.

The α -Fe₂O₃ sample was prepared by heat treating the γ -Fe₂O₃ sample at 550 °C for 2 h in air.⁷⁾ Examination of the sample by X-ray diffraction verified it to be rhombohedral hematite. The α -Fe₂O₃ particles' specific surface area was 16.0 m² g⁻¹, which is a little smaller than that of the parent γ -Fe₂O₃ particles. Electron microscopic observation of α -Fe₂O₃ particles in Fig. 1b indicated that they retained the shape of the γ -Fe₂O₃ particles. The sulfate ion content in these samples was 0.85 wt%.

Cleaning the Samples. The samples were cleaned in 150 g batches using the following procedure. First, a water rinse in which the sample is decanted ten times with 5L of doubly-distilled water. Second, an alkali wash where the sample is decanted 3 times with 5L of KOH solution (pH 9), followed by a second water rinse. Third, the batches were electrodesialized for one week, after which they were then filtered, dried at 100 °C for 24 h in an oven, and then stored in a desiccator.

Potentiometric Titration Method.⁸⁾ Batches of both samples, corresponding to 100 m² of total surface area, were

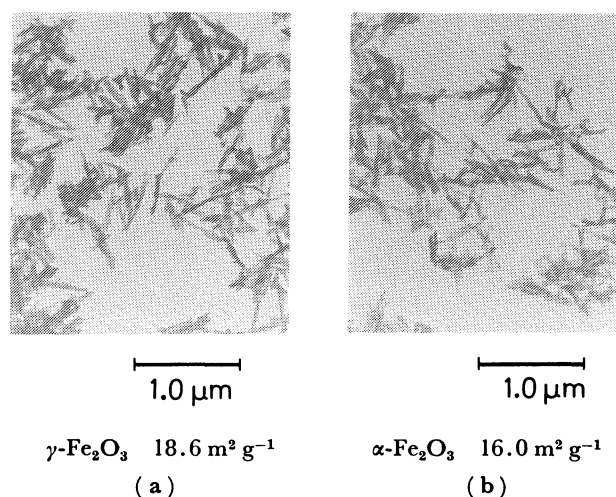


Fig. 1. Electron micrograph of γ -Fe₂O₃ sample (a) and α -Fe₂O₃ sample (b).

dispersed into 150 ml of about 0.01 M[†] KOH solution and adjusted to various values of ionic strength by the addition of KCl. The solution was then titrated potentiometrically. The titration cell was a 500 ml Pyrex flask, with a water jacket through which thermostated water was circulated to maintain the cell temperature at 20 °C. Glass and calomel electrodes, a thermometer, a microburet, and an inlet and outlet for purified nitrogen gas, were inserted into the cell through rubber gaskets. A Teflon stirring rod with Teflon blades, was also inserted into the center of the cell, through a Teflon greaseless seal. The amount of titrant added and the pH of the suspension were recorded by a Recording Auto Titrator (Hiranuma Sangyo Co., Ltd.). The titration was started at about pH 12, and 0.1 ml of the titrant, HCl standard solution, was added at 3 min intervals (because equilibrium was reached in 3 min.) The measurement was repeated 3 times and the pH values differed by less than ± 0.1 pH unit which is equivalent to an adsorption density of $\pm 1.0 \mu\text{C cm}^{-2}$. The measurement was also carried out for solutions of different ionic strength.

Microelectrophoretic Method A lateral quartz cell with plane-parallel walls was used in the microelectrophoretic measurement. The 40 mm long cell had a rectangular cross-section whose inside dimensions were 1.0×10 mm. The electric field strength (E) was about 10 V cm^{-1} . The migration speed (u) of the particles was measured and the ζ -potential was calculated by the following formula by Smoluchowski.⁹⁾

$$\zeta = 4\pi\eta u/\epsilon E,$$

where ϵ is the dielectric constant, and η is the viscosity.

The suspension was prepared by dispersing 5 mg of the sample ultrasonically in 100 ml of aqueous solution, the pH of which was adjusted by KOH and HCl, and the ionic strength of which was adjusted to $4.0 \times 10^{-5} \text{ M}$ by KCl. This suspension was stored in tightly stoppered glass vessel and handled under a nitrogen atmosphere. The pH value of the suspension did not change for 20 h, which is quite adequate for measuring the IEP.

The hydration time hereafter mentioned is the time taken from the preparation of the dispersion to the measurement, that is the time during which the samples were in contact, at room temperature, with the aqueous media.

Results

The $\gamma\text{-Fe}_2\text{O}_3$ sample after washing with water contained 0.56 wt% of sulfate ions, and the $\alpha\text{-Fe}_2\text{O}_3$ sample contained 0.55 wt% of sulfate ions. The $\gamma\text{-Fe}_2\text{O}_3$ sample after electrodialysis contained 0.06 wt% of sulfate ions and the $\alpha\text{-Fe}_2\text{O}_3$ sample contained 0.25 wt%. The higher content of sulfate ions in the $\alpha\text{-Fe}_2\text{O}_3$ sample can be explained by the migration of sulfate ions from the surface into the bulk during the heat treatment. Contamination by potassium ions, possibly introduced during the alkali washing, was found to be less than 5 ppm by the atomic absorption method. The adsorption density of the $\gamma\text{-Fe}_2\text{O}_3$ sample at the three stages of cleaning is plotted

against pH in Fig. 2. The PZC is the pH value when the surface charge density is zero, and was found to be more basic after cleaning. The PZC value of the sample after alkali washing and electrodialysis, was 5.5.

Figure 3 shows the results of the potentiometric titration of the $\alpha\text{-Fe}_2\text{O}_3$ sample. The PZC value of the $\alpha\text{-Fe}_2\text{O}_3$, as with the $\gamma\text{-Fe}_2\text{O}_3$ sample, shifted in the basic direction during cleaning. The PZC value of the $\alpha\text{-Fe}_2\text{O}_3$ sample after alkali washing and electrodialysis was 6.7.

Figures 4 and 5 show the plots of adsorption density versus pH taken at various ionic strengths, for the γ - and $\alpha\text{-Fe}_2\text{O}_3$ respectively. As can be seen for an ionic strength of 1.0 M or less the curves have the same intersection point. Thus, the absence of a shift in the PZC value with variation of ionic strength was ascertained for both samples.

The ζ -potential increased with the hydration time, as shown in Figs. 6 and 7, for the $\gamma\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ samples respectively. Constant ζ -potential values were observed for both the γ - and $\alpha\text{-Fe}_2\text{O}_3$ samples, for hydration times of 15 h and over, with no significant change being observed even after one week's hydration. The ζ -potentials at 0.5 h hydration are plotted

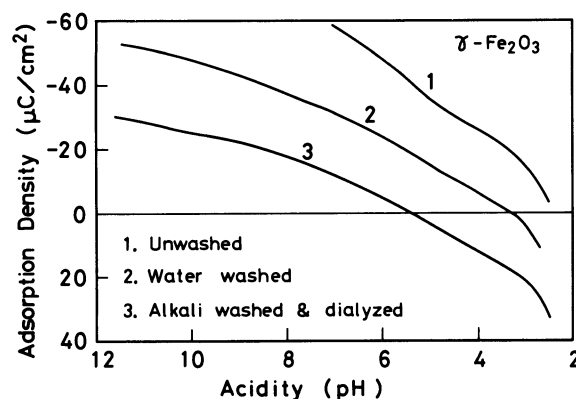


Fig. 2. Surface charge density on $\gamma\text{-Fe}_2\text{O}_3$ as a function of pH: ionic strength, 0.1 M; temperature, 20 °C.

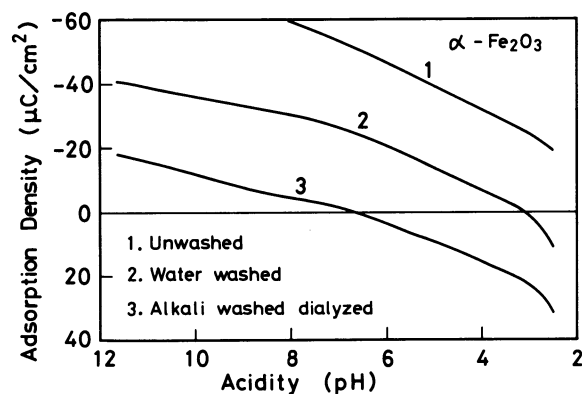


Fig. 3. Surface charge density of $\alpha\text{-Fe}_2\text{O}_3$ as a function of pH: ionic strength, 0.1 M; temperature, 20 °C.

[†] 1 M = 1 mol dm⁻³.

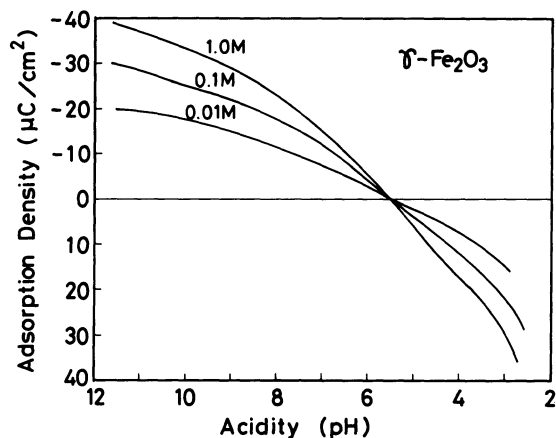


Fig. 4. Surface charge density of γ -Fe₂O₃ as a function of pH: ionic strength, 0.01 M, 0.1 M, 1.0 M; temperature, 20 °C.

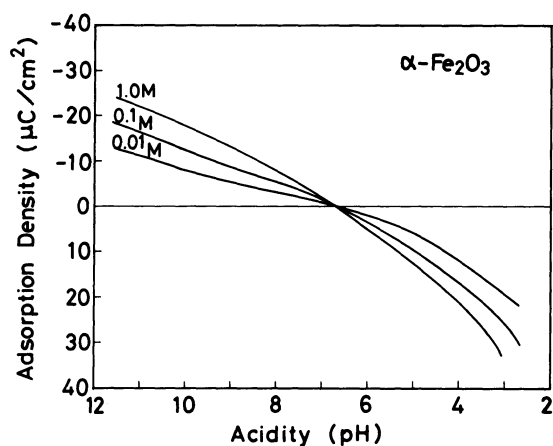


Fig. 5. Surface charge density of α -Fe₂O₃ as a function of pH: ionic strength, 0.01 M, 0.1 M, 1.0 M; temperature, 20 °C.

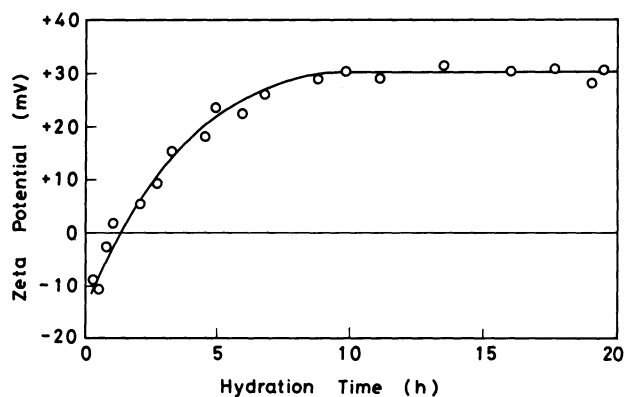


Fig. 6. Zeta potential of γ -Fe₂O₃ at pH 5.70 as a function of the hydration time.

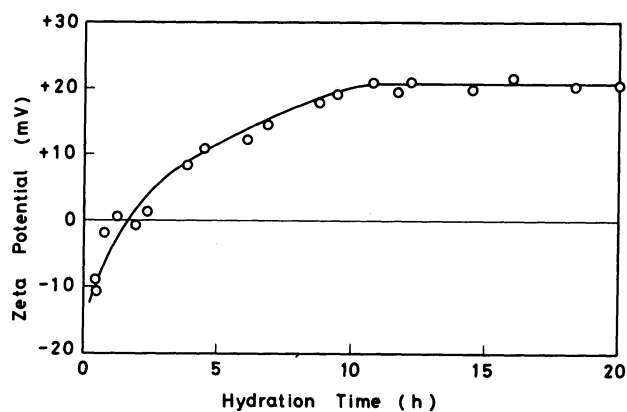


Fig. 7. Zeta potential of α -Fe₂O₃ at pH 7.05 as a function of the hydration time.

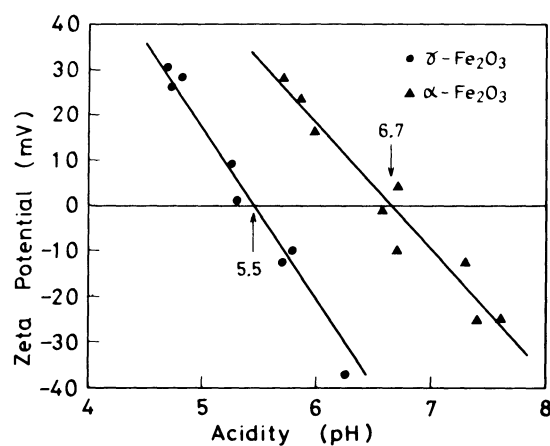


Fig. 8. Zeta potentials of γ -Fe₂O₃ hydrated up to 30 min as a function of pH: ionic strength, 4×10^{-5} M.

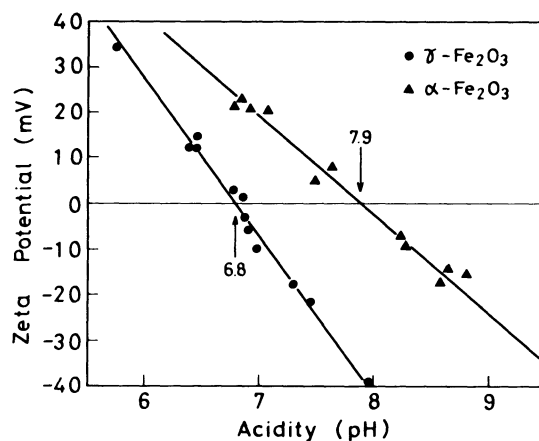


Fig. 9. Zeta potentials of γ - and α -Fe₂O₃ hydrated for 20 h as a function of pH: ionic strength, 4×10^{-5} M.

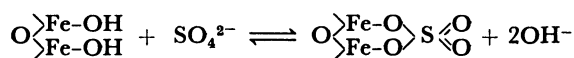
against the pH in Fig. 8. The zero point of the ζ -potential of the γ -Fe₂O₃ sample, that is its IEP, is 5.5 ± 0.2 and that of the α -Fe₂O₃ sample is 6.7 ± 0.2 . These values, for the low hydration state, agree with the PZC values measured by potentiometric titration.

The ζ -potential of the γ - and α -Fe₂O₃ sample after 20 h hydration are plotted in Fig. 9. After 20 h hydration, the IEP of the γ -Fe₂O₃ sample was 6.8 ± 0.2 , and that of the α -Fe₂O₃ sample was 7.9 ± 0.2 . The IEPs of the γ - and α -Fe₂O₃ samples move in the basic direction by 1.3 and 1.2 pH units, respectively.

Discussion

Effect of Sulfate Ions. The PZC of the γ - and α -Fe₂O₃ samples shifts to higher values as the sulfate ion content decreases. These results correspond to those reviewed by Parks on α -Fe₂O₃.³⁾

The adsorption equilibrium of sulfate ions on iron oxide is represented as follows,



Parfitt and Smart¹⁰⁾ showed that this adsorption occurs at pH values less than 8. Therefore, the desorption of sulfate ions from the surface is not negligible around the pH values corresponding to the IEP and PZC of the iron oxides. The desorption of sulfate ions causes the adsorption of hydroxide ions, which results in a lowering of the pH of the suspension and thus shifts the PZC value in the acidic direction.

The PZCs obtained by potentiometric titration of the γ - and α -Fe₂O₃ samples after alkali washing and electrodialysis, coincide with the IEPs measured by the electrophoretic method for the short hydration time of 0.5 h. This suggests that the influence of the specific adsorption of ions on the particles' surface has been eliminated.

Effect of Hydration. The value of the PZC and IEP of γ -Fe₂O₃ hydrated for 0.5 h is 5.5, and the value for α -Fe₂O₃ hydrated for 0.5 h is 6.7. This value of 6.7 for α -Fe₂O₃ is nearly equal to the values reported, on natural hematite and ignited α -Fe₂O₃ by Johansen and Buchanan¹¹⁾ and Iwasaki et al.¹²⁾

The value of the IEPs of γ - and α -Fe₂O₃ increases with increasing hydration time. The IEP of hydrated γ -Fe₂O₃ is 6.8, and that of hydrated α -Fe₂O₃ is 7.9. The value of 6.8, for the hydrated γ -Fe₂O₃, is in good agreement with the value of 6.7 obtained by Iwasaki et al.²⁾ for γ -Fe₂O₃, containing a small amount of lepidocrocite. The IEP value of 7.9 for hydrated α -Fe₂O₃ agrees well with the 8.0 value obtained by Johansen and Buchanan.¹¹⁾

The IEPs of γ - and α -Fe₂O₃ increased by 1.3 and 1.2 pH units respectively on hydration. Parks³⁾ calculated that there was an average of 2.1 pH units difference, between the IEPs of the hydrated and

unhydrated oxides. Johansen and Buchanan¹¹⁾ reported a decrease of 1.5 pH units in the IEP after dehydration.

The difference between the value of the IEPs of γ - and α -Fe₂O₃ was 1.2 pH units for the unhydrated samples and 1.1 pH units for the hydrated sample.

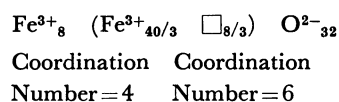
The reason why the IEPs of the oxides shift to the basic direction has been considered in terms of the formation of a hydrated layer³⁾ and the interacting forces between adjacent hydroxyl groups¹³⁾ at the particle surface. Ahmed and Maksimov^{14,15)} also reported the shift of PZC on hydration, and pointed out that the hydration is remarkable, when the amount of metal ions dissolved in the aqueous media, is of the order of the surface concentration of ions.

In this measurement, hydration caused a large increase in the IEP, whereas the PZC was nearly constant for at least a number of days. This discrepancy may be due to the fact that the concentration of the suspensions used in the microelectrophoretic method was smaller by a factor of 10^3 from the concentration used in the potentiometric titration method.

Effect of Crystal Structure. The difference in IEPs of the γ - and α -Fe₂O₃ samples can be considered to be due to the difference in their crystal structures, because the shapes of the particles, their specific surface areas and the cleaning and hydration operations applied to both of the samples were the same.

The crystal structures of γ - and α -Fe₂O₃ are the same as those of γ - and α -Al₂O₃, respectively. In both oxides, the γ -type has an inverse-spinel crystal structure, and the α -type has a corundum crystal structure.¹⁶⁾ Kozumina et al.⁵⁾ measured the IEP's of γ - and α -Al₂O₃, prepared by calcination of a gibbsite sample and obtained IEP values of 7.4 to 8.6 for the γ -Al₂O₃ and of 9.1 to 9.2 for the α -Al₂O₃ using the streaming potential method. The average difference in IEP between γ - and α -Al₂O₃, therefore, is 1.1 to 1.2 pH units, which is similar to the average difference in the IEP values between γ - and α -Fe₂O₃.

The unit lattice of γ -Fe₂O₃ is expressed by the following formula:



In the above formula a vacant lattice point is indicated by $\square$ at the position of the coordination number 6, i.e. 6 oxygen ions adjacent to the Fe³⁺ ion. Fe³⁺ ions having coordination numbers of 4 and 6 are present in the ratio of 3:5. On the other hand, α -Fe₂O₃ is a corundum-type oxide, in which all of the Fe³⁺ ions have a coordination number of 6.

The average IEP is more acidic by 2.6 pH units for four-coordinated ions than for six-coordinated metallic ions.³⁾ Thus, the difference in the IEPs between the γ -Fe₂O₃ and α -Fe₂O₃ is calculated to be $2.6 \times 3 / (3+5) =$

1.0, assuming that the additivity rule holds.¹⁷ Accordingly, the IEP of γ -Fe₂O₃ is about 1.0 pH units lower than that of α -Fe₂O₃. The lower IEP values of γ -Fe₂O₃ and the IEP differences of 1.2 and 1.1 for the hydrated and unhydrated samples respectively, coincide well with the above calculation.

Conclusion

1) The PZC and IEP of the unhydrated γ -Fe₂O₃ were 5.5 and the IEP of the hydrated γ -Fe₂O₃ was 6.8.

2) The PZC and IEP of γ -Fe₂O₃ were more acidic by 1.1 and 1.2 pH units than those of α -Fe₂O₃ for the hydrated and unhydrated stages respectively.

3) These differences were explained quantitatively in terms of the crystal structure.

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