

Acceleration Effect of a High Speed Rotating Generator on the Transformation of Iron(III) Oxide Hydroxides in Aqueous Media

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Hydrodynamic effects produced by a high speed rotating (Ultra-Turrax) generator accelerate the transformation of γ -FeOOH to α -FeOOH in aqueous media and cause an increase in the proportion of α -FeOOH in the products of amorphous iron(III) gel ageing.

It is well known¹ that γ -FeOOH (lepidocrocite) is transformed to γ -Fe₂O₃ when heated in air at 200—300 °C. A recent report² described mechanical dehydration of γ -FeOOH at substantially lower temperatures to yield α -Fe₂O₃. Grinding in cyclohexane under analogous conditions, on the other hand, results in the formation of γ -Fe₂O₃.³

When heated in water at 160—180 °C, γ -FeOOH is transformed into a mixture of α -FeOOH and α -Fe₂O₃. Boiling in distilled water causes no phase transformation of γ -FeOOH even when continued for 50 h.⁴ The amorphous iron(III) gel Fe₂O₃·*n*H₂O, when boiled in water for several hours, is

transformed to a mixture of α -FeOOH and α -Fe₂O₃; the phase composition of the products and the transformation rate depend on the conditions for preparation of the starting gel.⁵

It has been discovered that the transformation of unstable iron(III) hydroxides in aqueous media can be accelerated by the mechanical action of a high speed rotating (Ultra-Turrax) generator. The action of this equipment consists of shear and impact effects, a cavitation occurring in the generator, and an extremely effective turbulence rate acting on the media handled.

The generator used in this work was an Ultra-Turrax T-45

Table 1. Effect of stirring with an Ultra-Turrax generator on the transformation of hydrated iron(III) oxides in an aqueous medium at 97°C.

| Starting compound | Reaction time/h | Use of generator | Phase composition of products (%) | | | |
|---|-----------------|------------------|---|-----------------------|-----------------------|--------------------------------|
| | | | Am. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ | $\gamma\text{-FeOOH}$ | $\alpha\text{-FeOOH}$ | $\alpha\text{-Fe}_2\text{O}_3$ |
| $\gamma\text{-FeOOH}$ | 10 | — | 0 | 100 | 0 | 0 |
| $\gamma\text{-FeOOH}$ | 1.5 | + | 0 | 85 | 15 | 0 |
| $\gamma\text{-FeOOH}$ | 2.5 | + | 0 | 75 | 25 | 0 |
| $\gamma\text{-FeOOH}$ | 5.5 | + | 0 | 50 | 50 | 0 |
| $\gamma\text{-FeOOH}$ | 7 | + | 0 | 5 | 95 | 0 |
| $\gamma\text{-FeOOH}$ | 10 | + | 0 | 0 | 100 | 0 |
| Am. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ | 10 | — | 18 | 0 | 26 | 55 |
| Am. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ | 4 | + | 51 | 0 | 24 | 24 |
| Am. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ | 6.75 | + | 40 | 0 | 30 | 30 |
| Am. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ | 10 | + | 23 | 0 | 37 | 40 |

(Janke ü Kunkel GmbH), and the transformation was carried out at 97°C and 10 000 rev. min⁻¹ (calculated frequency of mechanical impulses in the liquid, 18 kHz).

$\gamma\text{-FeOOH}$ was prepared by oxidation of an aqueous solution of FeSO_4 with oxygen from the air, following a previously described procedure.⁶ The $\gamma\text{-FeOOH}$ so obtained was free from any contamination by other crystalline or amorphous modifications. The specific surface area as determined by the thermal desorption method of Nelsen and Eggertsen was 110 m²/g. Amorphous iron(III) gel was prepared by precipitating an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ with ammonia at pH 10 and 25°C. The precipitate was filtered off and washed with distilled water. Part of the product was dried at room temperature and the remainder was suspended in distilled water. The precipitate was amorphous by X-ray analysis, and its specific surface area was 160 m²/g.

Table 1 presents the results obtained for the transformations of $\gamma\text{-FeOOH}$ and the amorphous $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Clearly, the transformation of $\gamma\text{-FeOOH}$ to the stable modification $\alpha\text{-FeOOH}$ is substantially accelerated when the Ultra-Turrax generator is used. In 10 h, the reaction at 97°C occurred practically quantitatively, while in a comparative experiment under the same conditions except for the use of the generator, no $\alpha\text{-FeOOH}$ was detected in the products by any identification method (X-ray powder diffraction; i.r. and Mössbauer spectroscopy).

The development of goethite particles in the course of the transformation was followed by recording electron micrographs. A continuous growth of the particle size was observed, up to $0.4 \times 0.1 \mu\text{m}$ found for the final product.

Table 1 also includes results for the transformation of the amorphous $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Comparison of the experiments performed with and without the use of the Ultra-Turrax generator at the same temperature and Fe_2O_3 content of the suspension shows that the overall transformation rate, as measured by the rate of disappearance of the amorphous $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, is not significantly affected by stirring. There is, however, a substantial difference in the phase composition of the products. The samples obtained in the experiment with the generator contain a substantially larger amount of goethite. Once again, the goethite particle size grows in the course of the transformation, but there is no observable change in the size of the isotropic particles of the iron(III) gel or haematite.

The transformation $\gamma\text{-FeOOH} \rightarrow \alpha\text{-FeOOH}$ in water is mostly assumed to occur by a mechanism involving dissolution of the unstable $\gamma\text{-FeOOH}$ and crystallization of the more stable $\alpha\text{-FeOOH}$ from the solution.^{6,7} An analogous mechanism has also been proposed for the formation of goethite from aged amorphous iron(III) gel.⁸ The formation of $\alpha\text{-Fe}_2\text{O}_3$ from amorphous $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ in aqueous media has been assumed to occur by different variants of the mechanism of crystallization in the solid phase or at the liquid–solid interface (oriented crystallization of primary amorphous particles on $\alpha\text{-Fe}_2\text{O}_3$ nuclei).^{8,9} Thus, a possible explanation for the effect of the Ultra-Turrax generator in the system investigated is in terms of acceleration of primarily those processes which occur by the dissolution crystallization mechanism.

Both the present and previously published results^{2,3} clearly indicate that the transformation of iron(III) oxide hydroxides is among processes that are extremely sensitive to various mechanical influences. Besides these, however, an acceleration may be expected for processes which occur by a dissolution mechanism.

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