25. *The Oxidation of Ferrous Hydroxide.*

By J. E. O. Mayne.

The composition has been examined of the air-dried material produced by addition of alkalis to ferrous sulphate solution. When the pH was low, γ-Fe_2O_3,H_2O was obtained; in more alkaline solutions α-Fe_2O_3,H_2O was formed when the oxidation was fast and a material having a composition intermediate between Fe_3O_4 and γ-Fe_2O_3 when it was slow. The results are explained in terms of the oxidation and hydrolysis of a basic sulphate.

There is confusion in the literature regarding the composition of the material produced by oxidation of ferrous hydroxide. The nature of the product is important, not only from the academic point of view, but also in connection with the theory of the mechanism of the inhibition of the corrosion of iron by alkaline solutions. The following investigation was carried out in order to clarify the position.

It is well known that ferrous hydroxide is a white solid, which becomes green in the presence of a trace of air; if oxidation continues, the green material becomes brown and may darken. Deiss and Schikorr (*Z. anorg. Chem.*, 1928, **172**, 32) examined the reaction and concluded that the green product was a basic ferrous ferrite, $Fe(OH)\cdot O\cdot Fe(OH)_2$. On the other hand, Girard and Chaudron (*Compt. rend.*, 1935, **200**, 127) regarded the green material as hydrated magnetite.

Krause (*Z. anorg. Chem.*, 1928, **174**, 145) investigated the effect of pH on the composition of the fully oxidised precipitate. A constant volume of N-ferrous sulphate solution was mixed with varying quantities of N-sodium hydroxide and the precipitate was filtered off, washed, and dried in air. The total iron and ferrous iron in the precipitate were then determined. When the pH of the filtrate did not exceed 5·2, the precipitate was free from ferrous iron and it was concluded that it consisted of γ-Fe_2O_3,H_2O. As the filtrate became more alkaline the ferrous oxide content of the precipitate increased to the constant value of 10·8% at pH's above 11; it was concluded that under these conditions the material was magnetite. When precipitation was by aqueous ammonia, the ferrous iron content of the precipitate did not increase so rapidly when the pH was raised. Schikorr (*ibid.*, 1930, **191**, 322) considered that any intermediate compounds, *i.e.*, ferrous ferrites, could be oxidised to hydrated ferric oxide and suggested that α-Fe_2O_3,H_2O is formed when the oxidation proceeds directly to the ferric condition, and γ-Fe_2O_3,H_2O when it proceeds *via* an intermediate ferrous ferrite.

These views concerning the final product cannot all be true. An investigation has, therefore, been made of the composition of the green intermediate compound, and its oxidation has been carried out under conditions similar to those described by Schikorr and and by Krause. The ferrous iron content of the final product was determined by analysis, and its structure by means of *X*-rays.

EXPERIMENTAL

The Green Intermediate Product.—Composition. This substance was prepared by mixing 25 ml. of 0·1N-ferrous sulphate with 100 ml. of N-sodium hydroxide in a 500-ml., wide-neck, conical flask; the green precipitate was then dissolved by addition of 10 ml. of 6N-sulphuric acid, and the ferrous iron content determined by titration against 0·1N-potassium dichromate (diphenylamine as indicator). It was found that 6·3% of the iron had been oxidised before titration; the amount increased to 7·7% when the precipitate had been kept for 1 hour, but the precipitate was still green. After a week's exposure the colour had darkened and 84·6% of the iron had been oxidised.

Effect of oxygen. Schikorr (*loc. cit.*, Expt. 3) dissolved 1·2 g. of $FeSO_4,7H_2O$ in 200 ml. of water and added 1·4 ml. of a 10% solution of ammonia, the stoicheiometric quantity, and the mixture had pH 5·6. Oxygen was then passed through the solution for 30 min., and the precipitate was filtered off, washed, dried at 100°, heated for 3 hours at 230°, and tested with a magnet. This experiment has now been repeated, with the following modifications. The precipitate, after being oxidised and washed, was dried at room temperature for 2 days, sheltered from dust by filter-paper. Its structure was then determined by means of *X*-rays, in a 19-cm. powder camera with cobalt radiation and an iron filter. The photographs were compared with those obtained from magnetite (Fe_3O_4), lepidocrocite (γ-Fe_2O_3,H_2O), and goethite (α-Fe_2O_3,H_2O), and proved to be those of γ-Fe_2O_3,H_2O. The precipitate was shown to be free from ferrous iron as follows : 50 ml. of 2N-hydrochloric acid were boiled and cooled in a current of carbon dioxide, a weighed portion of the dried precipitate was added, the mixture gently boiled to effect solution, and the solution cooled with the gas still passing through, and then titrated against 0·05N-potassium dichromate (barium diphenylaminesulphonate as indicator) : there was a nil result.

The experiment was then repeated, the ammonia solution being replaced by 11·5 ml. of 2·5N-sodium hydroxide, so that the alkalinity of the solution was 0·1N after completion of precipitation. The dried precipitate was found to be free from ferrous ions and had the structure of α-Fe_2O_3,H_2O.

Effect of air. A similar procedure was used, except that oxygen was not bubbled through the suspension; the precipitate was allowed to settle for an hour before being filtered off, washed, and air-dried; under such conditions oxidation commenced as soon as the precipitate was formed and continued during filtration. This procedure was used by Krause (*loc. cit.*).

Varying quantities of ammonia and sodium hydroxide were used as precipitants and the pH of the filtrate was measured by means of a glass electrode. The results obtained are shown in the Table.

pH of filtrate	Fe^{++}, %, precipitate	Composition of precipitate from X-ray powder photographs	
		Major constituent	Minor constituent
	Precipitant:	Ammonium hydroxide.	
5·0	1·9	$\gamma\text{-}Fe_2O_3,H_2O$	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$
5·6	2·4	$\gamma\text{-}Fe_2O_3,H_2O$	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$
9·0	4·1	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	$\gamma\text{-}Fe_2O_3,H_2O$
	Precipitant:	Sodium hydroxide.	
4·2	1·8	$\gamma\text{-}Fe_2O_3,H_2O$	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$
5·0	3·9	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	$\gamma\text{-}Fe_2O_3,H_2O$
6·5	6·4	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	$\gamma\text{-}Fe_2O_3,H_2O$
9·3	9·3	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	—
10·6	9·1	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	—
10·6	8·1	Fe_3O_4 or $\gamma\text{-}Fe_2O_3$	—

In the last experiment the precipitate was allowed to settle for 24 hours before being filtered off.

DISCUSSION

Addition of excess of sodium hydroxide solution to a solution of ferrous sulphate yielded a green precipitate, which contained only 6·3% of ferric iron; so it follows that the precipitate cannot have the composition ascribed to it by previous workers. Schikorr oxidised it with a current of oxygen, but it has now been found that under these conditions either $\alpha\text{-}Fe_2O_3,H_2O$ or $\gamma\text{-}Fe_2O_3,H_2O$ is formed according to the pH at which oxidation occurs; consequently, it is difficult to accept the view that $\gamma\text{-}Fe_2O_3,H_2O$ is always formed when the oxidation proceeds *via* the green intermediate compound.

When the precipitate was allowed to oxidise slowly in air at relatively low pH values it consisted mainly of $\gamma\text{-}Fe_2O_3,H_2O$, together with a small quantity of material having the cubic structure of either Fe_3O_4 or $\gamma\text{-}Fe_2O_3$. Hagg (*Z. phys. Chem.*, 1935, *B*, **29**, 95) has shown that when Fe_3O_4 is oxidised at a low temperature to $\gamma\text{-}Fe_2O_3$, the spinel structure is retained; this process is accompanied by a continuous but slight diminution of the lattice constant, so the product of oxidation should be regarded as a phase of variable composition. The dried precipitate contained 1·8% of ferrous iron; it was concluded that it contained a small quantity of either magnetite or a material having a composition intermediate between Fe_3O_4 and $\gamma\text{-}Fe_2O_3$. It should be noted that Krause (*loc. cit.*) detected ferrous ions in material prepared in this way, but he attributed their presence to an error in his method of analysis.

As the pH of the filtrate rose, the $\gamma\text{-}Fe_2O_3,H_2O$ content of the dried precipitate diminished. This change was less complete when ammonia was used as the precipitant, thus confirming Krause's observation. When the pH of the filtrate exceeded 9, the precipitate showed the cubic structure of either Fe_3O_4 or $\gamma\text{-}Fe_2O_3$; from the ferrous iron content of the product, 9·2%, it can be calculated that the precipitate corresponded to a product in which a 70—75% conversion of Fe_3O_4 into $\gamma\text{-}Fe_2O_3$ had occurred. Moreover, this value is in reasonable agreement with that (8·3%) calculated from the FeO content found by Krause. There is, however, a general indication that the figures for ferrous iron obtained in this investigation are all slightly higher than those obtained by Krause, but as he did not publish full experimental details of his method, the difference cannot be resolved.

The conclusions to be drawn from this investigation are that when ferrous hydroxide is oxidised in the pH range 4—5 $\gamma\text{-}Fe_2O_3,H_2O$ is formed, irrespective of the rate of oxidation; in alkaline solutions either $\alpha\text{-}Fe_2O_3,H_2O$ or a material having a composition intermediate between Fe_3O_4 and $\gamma\text{-}Fe_2O_3$ is produced according as oxidation is fast or slow.

It is possible that the $\gamma\text{-}Fe_2O_3,H_2O$ arises from the hydrolysis of a basic salt; Arden's work (*J.*, 1950, 882) suggests that a basic sulphate is first precipitated when sodium hydroxide is run into a solution of ferrous sulphate, in the presence of air or ferric ions. In alkaline solutions the basic compound will be hydrolysed and the resulting product, which probably contains both ferrous and ferric iron, may be oxidised to either $\alpha\text{-}Fe_2O_3,H_2O$ or magnetite and then to $\gamma\text{-}Fe_2O_3$ according to the rate of oxidation. Deiss and Schikorr (*loc. cit.*) have suggested that when oxidation is slow, the hydrated ferric oxide first formed may interact with the remaining ferrous hydroxide to form magnetite. This explanation agrees with the views of Forrest, Roethelli, and Brown (*Ind. Eng. Chem.*, 1931, **23**, 650) and of Girard and Chaudron (*loc. cit.*) on the formation of magnetite, and the mechanism may well be operative.

These results have an important bearing on the theory of the inhibition of the corrosion of iron by alkaline solutions. It was shown (*J.*, 1950, 3229) that the film formed on iron by sodium hydroxide solution, in the presence of air, was mainly composed of material having the cubic structure of γ-Fe_2O_3. It is now clear that such a film could be formed by oxidation of ferrous hydroxide; this possibility will be discussed in a later paper.

This investigation formed part of a programme of research carried out for the British Iron and Steel Research Association by the group of investigators associated with Dr. U. R. Evans. The author is indebted to that Association and to Dr. U. R. Evans for their support and interest, without which the work could not have been performed. He also thanks Mr. D. E. Davies for taking and interpreting the *X*-ray photographs, Dr. F. A. Bannister for the supply of a sample of lepidocrocite, and Drs. J. N. Agar and F. Wormwell for helpful criticism.

DEPARTMENT OF METALLURGY, UNIVERSITY OF CAMBRIDGE. [*Received, July 23rd*, 1952.]