ACTA CHEMICA SCANDINAVICA 22 (1968) 1487–1490

Hydrothermal Preparation of Goethite and Haematite from Amorphous Iron(III) Hydroxide

A. NØRLUND CHRISTENSEN

Department of Inorganic Chemistry, University of Aarhus, Aarhus C, Denmark

The hydrothermal preparation of goethite (α-FeOOH) and haematite (α-Fe_2O_3) from amorphous iron(III) hydroxide was studied at various pH values in the temperature range from 100°C to 200°C; the pressure was the vapour presssure of the hydrothermal solvent. In the pH range from 8.0 to 10.0 goethite and haematite were formed. The amount of goethite in the product increases with increasing pH. In the pH range from 0.8 to 2.6 the reaction product was haematite only, and in the pH range from 10.5 to 10.8 goethite was the only component in the product.

The gels prepared by adding ammonium hydroxide rapidly to ferric chloride solutions were shown by Mackenzie and Meldau[1] to consist of amorphous material and crystalline goethite (α-FeOOH). The precipitation was interrupted when pH of the solution in one instance was 5 and in another when pH was 10. The freshly precipitated gels were aged at room temperature over periods of 60 and 155 days. Goethite was found to be the only crystalline component in all the samples investigated. Schwertmann[2] kept gels of ferric hydroxide at room temperature for 4 ½ years. The pH of the solutions in which the ferric hydroxide was kept had values from 5 to 12. After this period of ageing the samples with pH higher than 10 contained goethite only as crystalline compound, and the samples with pH lower than 10 contained goethite and haematite (α-Fe_2O_3).

Schwertmann[3] reported the ageing of ferric hydroxide gels by treatment with solution of potassium hydroxide at 100°C to yield goethite and haematite. By using solutions in the concentration range 0.001 to 0.03 M KOH the reaction products were mixtures of haematite and goethite, with goethite as the minor component. Solutions of 0.1 M KOH and higher concentrations gave products where goethite was the main component.

The hydrothermal preparation of goethite and haematite from amorphous ferric hydroxide gels, and the investigation of the goethite haematite transformation in hydrothermal systems have not been studied in great detail. Smith and Kidd[4] investigated the goethite haematite transformation in 0.1 M

NaOH solutions and reported the decomposition temperature of goethite in that solvent to be 165°±5°C almost independent of the pressure. In pure water they reported the decomposition temperature of goethite to be 125°±15°C. Gheith [5] found that the decomposition temperature of goethite in pure water was 130°±5°C, Klingsberg and Roy [6] reported goethite to be transformed to haematite at 150°C and a pressure of 1020 atm, and Schmalz [7] reported the transformation to take place at 170°C and at a pressure of 895 atm. Ni, Gol'dman, Bunchuk, Kuchanskaya, Tsyss and Ponomarev [8] precipitated a solution of ferric perchlorate with concentrated ammonia at 80°C. The precipitation was interrupted at pH=7, and the ferric hydroxide formed was subjected to autoclave treatment at 280°C for 1.5 to 60 min at a Na_2O concentration of 200 to 500 g/l. Haematite was formed, and its shape and size depended on the concentration of the hydrothermal solvent and on the length of treatment. Hydrothermal precipitation of goethite and haematite from ferric nitrate solutions was reported by Robins.[8] The results of the hydrothermal investigation was presented in a temperature-pH-diagram indicating the transformation between goethite and haematite to be strongly pH dependent.

Solid-solid transformations in hydrothermal systems are often dependent upon the composition of the hydrothermal solvent. It was thus demonstrated that the formation ranges of indium oxide hydroxide and of cubic indium oxide are dependent upon the solvent used.[10,11] The present investigation was undertaken in order to examine the dependence of the formation of goethite and haematite of pH when the two compounds are prepared from amorphous iron(III) hydroxide gels in the hydrothermal temperature range from 100°C to 200°C.

EXPERIMENTAL

A solution of 0.1 M ferric nitrate was used in all the experiments. 10 ml of the ferric nitrate solution was titrated with 4 M or with 1 M solutions of ammonia. During the slow and dropwise titration the solution was thoroughly stirred with a magnetic stirrer and the pH of the solution was measured with a Radiometer model PHM22 potentiometer using a glass- and a calomel-electrode. The titration was interrupted at the pH values given in Table 1. The precipitated ferric hydroxide with the mother liquid was transferred to a thick-walled pyrex ampoule. The sealed ampoule was heated for 48 h in a thermostated oven. The temperature (see Table 1) could be kept within 3°C. After the hydrothermal experiment the pH of the mother liquid was measured, the crystalline reaction product was thoroughly washed with water, dried at 100°C, and the X-ray powder pattern of the product was obtained with a Guinier-de Wolff camera. From visually estimated intensities of haematite and goethite lines on the film, the approximate content of goethite in the product was evaluated. The results are given in Table 1.

DISCUSSION

In the temperature and pressure range investigated the experiments show that both goethite and haematite were formed in the pH range from 8.0 to 10.0, that pure haematite was formed in the pH range from 0.8 to 2.6, and that pure goethite was formed in the pH range from 10.5 to 10.8. The pH ranges stated refer to the values measured in the solvent after the hydro-

Table 1. Experimental conditions for the preparation of goethite and haematite from amorphous iron(III) hydroxide.

Expt. No.	pH of mother liquid before	pH of mother liquid after	Temp. °C	mmole Fe^{3+}	mmole NH_3	Product
1	5.0	2.5	104			
2	5.0	2.4	112			
3	5.0	2.3	118			
4	5.0	2.4	126			Haematite
5	5.0	2.6	146			
6	5.0	2.4	154			
7	5.0	2.4	172			
8	5.0	2.5	180			
9	8.0	8.1	104			
10	8.0	8.2	112			
11	8.0	8.2	118			
12	8.0	8.0	126			Haematite with
13	8.0	8.1	146			approx. 20 % goethite
14	8.0	8.0	154			
15	8.0	8.1	172			
16	8.0	8.2	180			
17	9.0	9.0	110			
18	9.0	8.9	124			
19	9.0	8.8	132			
20	9.0	8.8	140			Haematite with
21	9.0	9.2	150			approx. 50 % goethite
22	9.0	9.2	160			
23	9.0	9.1	170			
24	9.0	9.0	189			
25	9.7	9.7	110			
26	9.7	9.5	124			
27	9.7	9.5	132			
28	9.7	9.5	140			Goethite with approx.
29	9.7	9.7	150			20 % haematite
30	9.7	10.0	160			
31	9.7	9.9	170			
32	9.7	9.8	189			
33	10.5	10.8	104			
34	10.5	10.8	112			
35	10.5	10.7	126			
36	10.5	10.8	146			
37	10.5	10.5	154			Goethite
38	10.5	10.6	172			
39	10.5	10.7	180			
40	10.5	10.6	202			
41	5.1	2.5	151	0.495	1.413	
42	4.7	2.4	151	0.495	1.401	
43	3.8	2.3	151	0.495	1.395	Haematite
44	3.7	2.3	151	0.495	1.390	
45	2.9	2.1	151	0.495	1.368	
46	1.7	0.8	151	0.495	0	

thermal experiment. The amount of goethite in the reaction products increases with increasing pH. The haematite content of the products is apparently not dependent upon temperature. Thus it is concluded that the hydrothermal formation of goethite and haematite from amorphous iron(III) hydroxide is strongly pH dependent. Neutral to weakly alkaline hydrothermal solutions in contact with minerals are likely to deposit iron as goethite and haematite, and the amount of goethite is likely to increase with increasing pH. It was suggested by Smith and Kidd,[4] that the goethite haematite relation of a deposit could be used in geological thermometry. In low pressure ranges, as used in this investigation, the goethite haematite ratios of the products are likely to be temperature independent.

It was observed that the pH of the mother liquid is decreased by the hydrothermal treatment when the precipitation of ferric hydroxide is interrupted at pH values lower than 5 and that the pH of the mother liquid is practically unchanged when the suspension has a pH at 8 or higher values before the hydrothermal experiment. The precipitation of ferric hydroxide is not quantitative when the precipitation is interrupted at pH=5 (Table 1, experiment 41 to 46), and the decrease in pH is explained by hydrolysis, resulting in complete precipitation of the iron.

REFERENCES

1. Mackenzie, R. C. and Meldau, R. *Mineral. Mag.* **32** (1959) 153.
2. Schwertmann, U. *Z. Pflanzenernaehr. Dueng. Bodenk.* **108** (1965) 37.
3. Schwertmann, U. *Z. anorg. Chem.* **298** (1959) 23.
4. Smith, F. G. and Kidd, D. J. *Am. Mineralogist* **34** (1949) 403.
5. Gheith, M. A. *Congr. Geol. Intern., Compt. Rend. 19th Session, Algiers,* No. **10** (1952) 79, from *Chem. Abstr.* **48** (1954) 7504 h.
6. Klingsberg, C. and Roy, R. *Am. Mineralogist* **44** (1959) 819.
7. Schmalz, R. F. *Bull. Geol. Soc. Am.* **69** (1958) 1639.
8. Robins, R. G. *J. Inorg. Nucl. Chem.* **29** (1967) 431.
9. Ni, L. P., Gol'dman, M. M., Bunchuk, L. V., Kuchanskaya, O. F., Tsyss, N. N. and Ponomarev, V. D. *Tr. Inst. Met. i Obogashch. Akad. Nauk Kaz. SSR* **12** (1965) 9, from *Chem. Abstr.* **63** (1967) 9413 d.
10. Liebertz, J. *Ber. Bunsenges. phys. Chem.* **70** (1966) 1051.
11. Christensen, A. N., Broch, N. C., von Heidenstam, O. and Nilsson, Å. *Acta Chem. Scand.* **21** (1967) 1046.

Received January 4, 1968.