Hydrothermal stability of hematite and magnetite

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Abstract. Hydrothermal phase stability studies were carried out in the systems (a) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$, (b) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2$, (c) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2\text{-H}_2$ and (d) $\text{Fe}_2\text{O}_3\text{-HNO}_3$. In the pure system $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$, only $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 are the stable solids, with the phase boundary nearly pressure independent around 700°C . The introduction of CO_2 into the system catalyses the stability of $\alpha\text{-FeOOH}$ in the system at low temperatures. The presence of H_2 in the system produces traces of Fe_3O_4 at temperatures as low as 230°C and at around 500°C , Fe_3O_4 is the only stable phase. The stabilisation of Fe_3O_4 is suppressed even up to 850°C , when NO_3^- ion is present in the fluid phase.

Keywords. Hydrothermal stability ; Fe_2O_3 ; magnetite; goethite; phase diagram.

1. Introduction

Studies on the hydrothermal stability of hematite and magnetite are important because the reaction of water and iron, particularly in the presence of oxidising or reducing fluids will help in determining the life-time and safe operating conditions for steam boilers, turbines, heat exchangers in nuclear reactors and hydrothermal autoclaves (Kolb *et al* 1973). Thus phase equilibria studies in the pure $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system, as well as the stability of hematite and magnetite in the presence of different oxidising and reducing agents are important for providing information on aqueous corrosion of steel autoclaves, turbines, etc. (Ikornikova 1960). It is generally agreed (Ikornikova 1960; Tomlinson 1973; Mann 1973) that with pure water (under high temperatures and pressures) passivation of steel takes place due to the formation of dense layer of magnetite. The present authors have investigated the stability of hematite and magnetite in the following systems : (a) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$, (b) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2$, (c) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}$, (d) $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2\text{-H}_2$ and (e) $\text{Fe}_2\text{O}_3\text{-HNO}_3$. The results of $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}$ system and part of the $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system were reported by the authors earlier (Viswanathiah *et al* 1980). In the $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}$ system ($\text{Fe}_2\text{O}_3\text{-HCOOH}$) the magnetite was reported to crystallise at temperature as low as 200°C . With further studies in the $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system the phase diagram has been constructed, which is presented in the present paper, along with the discussion on the other systems mentioned above.

2. Experimental

Iron hydroxide gel (amorphous to x-rays) prepared by hydrolysing ferric chloride solution with aqueous ammonia was used as the starting material. The dried gel (at 110° C) on analysis gave 21% of H₂O and 79% of Fe₂O₃. The following materials were used to introduce CO₂, H₂ and NO₃ in the fluid phase of the different systems.

(a) Fe₂O₃-H₂O-CO₂ system : Ferric hydroxide gel (70 mg) mixed with freshly prepared silver oxalate (100 mg), along with 3-4 drops of distilled water, has been taken as the starting material. Silver oxalate decomposes at about 150° C, to give silver and carbon dioxide.

(b) Fe₂O₃-H₂O-CO₂-H₂ system : Iron hydroxide gel (80-100 mg) oxalic acid dihydrate (H₂C₂O₄·2H₂O) (20-30 mg) have been used as the source CO₂ and H₂ along with H₂O. The expected decomposition is

$$\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O} \xrightarrow{200^\circ \text{C}} \text{CO}_2 + \text{CO} + 3\text{H}_2\text{O}$$

thus producing a partial pressure of in steam

CO₂ (X_{CO₂}) value of 0.5, in the fluid phase.

(c) Fe₂O₃-HNO₃ system : Concentrated nitric acid (4-5 drops) is taken along with about 100 mg of the iron hydroxide gel.

The charges in all the above systems and also for the pure Fe₂O₃-H₂O systems were taken in platinum ampoules (L : 5 cm, I.D. : 5 mm, O.D. : 5.2 mm) and sealed by arc welding. Leaks in the ampoule were checked through extended heating as well as by recording the weight before and after the experiment. The experiments were done using test-tube-type stellite cold seal reactors with Tempress unit HR-IB-4. The vessels after the run were quenched with air blast before venting out the pressure. The Fe₂O₃-H₂O system was studied in the temperature range of 100-850° C in the pressure range of 60-1300 atm. The other systems were studied at low pressures of 200-500 atm. and at selected ranges of temperatures. All the experiments were for a duration 90-100 hr. The products were identified with the x-ray powder photographs (114 mm CZ camera, COK_α-radiation.)

3. Results and discussion

3.1. Fe₂O₃-H₂O system

Although a limited number of experiments conducted in this system were reported earlier (Viswanathiah *et al* 1980), further studies on this system with over twenty runs, enabled the authors to construct a phase diagram (figure 1). The results of the new experiments along with the reported ones are tabulated in table 1. It is interesting to note that the α-Fe₂O₃ is stable up to temperatures as low as 100° C and the boundary between α-Fe₂O₃ and Fe₃O₄ lies around 700° C. The goethite phase (α-FeOOH) which is reported to be stable by Schmalz (1956) upto 130° C is not detected in the present experiment. The α-Fe₂O₃ should thermodynamically be in equilibrium with H₂O up to 1050° C (Wagman *et al* 1945; Laudise 1962; Norton 1955; Eugster 1959). But in the present case it is stable only up to 700° C and beyond this Fe₃O₄ is the stable phase. The stabilization of Fe₃O₄ at lower temperatures was attributed by Laudise *et al* (1961) to slow diffusion of hydrogen.

Figure 1. Phase diagram for $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system. $\circ$: $\alpha\text{-Fe}_2\text{O}_3$, $\bullet$: Fe_3O_4 .

3.2. $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2$ system

The experimental conditions and results in this system are given in table 1. Only three experiments have been carried out to check if CO_2 in the system would catalyse the formation of goethite ($\alpha\text{-FeOOH}$) or lepidocrocite ($\beta\text{-FeOOH}$) since these phases are not detected in pure $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system. Experiments from 100° C to 500° C showed that goethite does stabilize at 100° C but above 130° C, $\alpha\text{-Fe}_2\text{O}_3$ is the stable phase. The upper stability limit of $\alpha\text{-Fe}_2\text{O}_3$ is not determined in this system.

3.3. $\text{Fe}_2\text{O}_3\text{-H}_2\text{O-CO}_2\text{-H}_2$ system

Only three runs have been carried out in this system to check the stability of hematite and magnetite. Oxalic acid dihydrate is the source of H_2O , CO_2 as well as H_2 . It is interesting to note that the hydrogen liberated in the system does not quickly diffuse out through the platinum ampoule and instead it reduces $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 . In fact at 550° C and above magnetite is the only stable phase. Although the duration of the run in the present case is only of 60 hr, it is not certain whether the extended runs for several days would still retain enough H_2 in the ampoule and Fe_3O_4 would get stabilised.

3.4. $\text{Fe}_2\text{O}_3\text{-HNO}_3$ system

This system was investigated to understand the stability of iron oxide in an oxidizing atmosphere in the presence of NO_3 ions in the fluid phase. As expected, Fe_3O_4 formation is suppressed and even at 850° C $\alpha\text{-Fe}_2\text{O}_3$ is the only stable phase.

4. Conclusion

The authors hope that the present results have given a fairly good picture of the hydrothermal chemistry of iron oxides in the presence of different oxidising and reducing ions in the fluid phase and its implications on the boilers, turbine and other steel autoclaves using such fluids are obvious. The fact that goethite is not stable in pure $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ system and that the same appears in the system $\text{Fe}_2\text{O}_3\text{H}_2\text{O-CO}_2$ indicate that the formation of an oxyhydroxide phase requires a catalyser in the system and here CO_2 has served to stabilise goethite.

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