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Reactions of Wüstite and Hematite with Different Chlorinating Agents

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Chlorination of wüstite ($\text{Fe}_{(1-x)}\text{O}$) and hematite (Fe_2O_3) with Cl_2+CO and Cl_2+N_2 was studied by thermogravimetric analysis using non isothermal conditions up to about 1000 °C. The wüstite started to react with the carbochlorinating gas mixtures at low temperatures producing FeCl_3 and Fe_2O_3 as final reaction products. The presence of carbon monoxide, during non isothermal tests, enhanced the chlorination of wüstite at temperatures higher than 550 °C when the produced hematite started to react with Cl_2+CO . The separate treatment of the two oxides under isothermal conditions in Cl_2+CO for two hours led to their total reaction at about 550 °C. An apparent activation energy of about 53 kJ/mol was obtained for the carbochlorination of hematite between 350 °C and 550 °C.

Reaction of wüstite with FeCl_3 was also studied by thermogravimetric analysis using non isothermal conditions. It was observed that the higher oxides of iron and ferrous chloride were the main reaction products at 600 °C, even in the presence of carbon monoxide.

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I. INTRODUCTION

Iron oxides are the major compounds of several valuable metal bearing ores such as ilmenite, chromite, bauxite, etc. They are also the main constituents of the solid wastes and slags generated by metallurgical oxidation operations. The selective extraction of valuable metals from these materials could be achieved using chlorination techniques provided a good understanding of the behavior and reactivity of iron oxides towards different chlorinating agents. For this reason, several investigations concerning the Fe-Cl-O system were carried out, focusing on both the thermodynamic and kinetic aspects.

Details concerning the reaction of iron oxides with different chlorinating agents were described in Reference [1]. The most usual chlorinating agents were Cl_2 , $\text{CO}+\text{Cl}_2$, COCl_2 , CCl_4 and HCl . The experiments were mostly carried out using thermogravimetric analysis 'TGA'.

The main observations regarding to the chlorination of wüstite were summarized in Table I. It was reported that wüstite starts to react with the chlorinating gas at low temperatures generating several intermediate phases such as FeCl_2 , FeCl_3 , FeOCl , Fe_3O_4 , and Fe_2O_3 . On the other hand, the higher oxides of iron (Fe_3O_4 and Fe_2O_3) were generated even during the chlorination of wüstite in the presence of a reducing atmosphere. However, no studies were devoted to the reaction of wüstite with ferric chloride.

Table I. Summary of the Researches Concerning the Chlorination of Wüstite.

| Chlorinating Agent | Temperature Range*, °C | Observations | R** |
|--------------------------|------------------------|---|-----|
| $\text{CO}+\text{Cl}_2$ | 27-727 | Effect of CO at temperatures higher than 577 °C. | [2] |
| $\text{CO}+\text{Cl}_2$ | 27-927 | Formation of FeCl_2 , FeCl_3 , FeOCl , Fe_3O_4 , and Fe_2O_3 . Carbon monoxide effect observed at temperatures higher than 577 °C. | [3] |
| COCl_2 | 27-727 | Formation of the intermediate phases : FeCl_2 , Fe_3O_4 , and Fe_2O_3 . | [2] |
| COCl_2 | 27-927 | Formation of FeCl_2 , Fe_3O_4 , and Fe_2O_3 . | [3] |
| CCl_4 | 27-927 | Formation of FeCl_2 , Fe_3O_4 , and Fe_2O_3 . | [3] |
| CCl_4 | 27-927 | Formation of FeCl_2 , Fe_3O_4 , and Fe_2O_3 . | [4] |
| Cl_2 | 25-800 | Reaction occurred at low temperature. Formation of FeCl_3 and Fe_3O_4 . | [5] |
| Cl_2 | 25-800 | Rapid chlorination producing FeCl_3 and Fe_3O_4 . | [6] |
| Cl_2 | 690-780 | $E_a^\bullet = 140 \text{ kJ/mol}$. | [7] |
| Cl_2 | 27-927 | Formation of FeCl_2 , FeCl_3 , FeOCl , Fe_3O_4 , and Fe_2O_3 . | [8] |
| Cl_2+O_2 | 25-800 | Oxygen had little from 0 to 40 %. | [6] |
| HCl | 25-800 | Formation of FeCl_2 . | [6] |
| HCl | 25-850 | Formation of FeCl_2 , $E_a \approx 111 \text{ kJ/mol}$ between 700 °C and 800 °C. | [8] |

* When treatment temperature starts from room one, non isothermal conditions were also used.

** Reference number.

• Apparent activation energy.

Table II gives some results concerning the chlorination of hematite using various chlorinating agents. The researchers agreed that, whilst using the same chlorinating reagents, the chlorination of hematite starts at higher temperatures than that of wüstite. The final reaction product was found to be FeCl₃. The values of the apparent activation energy of hematite chlorination varied from about 6 kJ/mol to 190 kJ/mol depending on the chlorinating agent used and on the temperature range explored (Table II).

The present paper focuses on the chlorination and carbochlorination of wüstite and hematite. Both, TG analysis and boat experiments were used. An attempt was made to study the interaction of Fe_(1-x)O with FeCl₃.

Table II. Summary of the Researches Concerning the Chlorination of Hematite.

| Chlorinating Agent | Temperature Range*, °C | Observations | R** |
|---------------------------------|------------------------|---|------|
| C+Cl ₂ | 25-800 | Formation of FeCl ₂ which volatilized as FeCl ₃ . | [5] |
| CO+Cl ₂ | 27-727 | Reaction started at T > 577 °C with formation of Fe ₂ Cl ₆ . | [2] |
| CO+Cl ₂ | 27-927 | E _a [•] = 84 kJ/mol between 327 °C and 527 °C. | [3] |
| COCl ₂ | 27-727 | Reaction started at T > 427 °C with formation of Fe ₂ Cl ₆ . | [2] |
| COCl ₂ | 27-927 | E _a = 88 kJ/mol between 237 °C and 297 °C, E _a = 60 kJ/mol between 297 °C and 447 °C. | [3] |
| CCl ₄ | 27-927 | E _a = 125 kJ/mol between 397 °C and 597 °C, n ⁺ CCl ₄ = 0.5 at 527 °C. | [4] |
| CCl ₄ | 27-927 | E _a = 130 kJ/mol between 452 °C and 552 °C. | [3] |
| Cl ₂ | 25-800 | Reaction started at 700 °C generating FeCl ₃ and O ₂ . | [5] |
| Cl ₂ | 700-900 | E _a = 136.8 kJ/mol, nCl ₂ = 0.85. | [9] |
| Cl ₂ | 25-900 | E _a ≈ 96 kJ/mol between 700 °C and 900 °C. | [6] |
| Cl ₂ | 597 to > 777 | E _a = 188 - 191 kJ/mol between 597 °C and 777 °C, E _a = 100 kJ/mol at T > 777 °C. | [7] |
| Cl ₂ | 27-927 | E _a = 188 kJ/mol between 597 °C and 777 °C, E _a = 100 kJ/mol between 777 °C and 807 °C. | [3] |
| Cl ₂ | 800-1200 | E _a = 167 kJ/mol, nCl ₂ = 1. | [10] |
| Cl ₂ +O ₂ | 700-900 | nCl ₂ = 2.75. | [9] |
| Cl ₂ +O ₂ | 25-900 | Oxygen had little from 0 to 40 %. | [6] |
| HCl | 25-900 | Formation of FeOCl decomposing from 300 °C to 400 °C. | [6] |
| HCl | 800-1000 | E _a = 34 kJ/mol, nHCl = 1. | [9] |
| HCl | 25-750 | Formation of FeOCl, E _a = 5.9 kJ/mol. | [10] |
| FeCl ₃ | 25 to > 500 | Formation of FeOCl at 225 °C, volatilization of FeCl ₃ at 307 °C, and decomposition of FeOCl at 430 °C. | [11] |

* When treatment temperature starts from room one, non isothermal conditions were also used.

** Reference number.

• Apparent activation energy.

+ Apparent reaction order.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

Hematite used in this study had a purity higher than 99 % Fe₂O₃. Wüstite was prepared from hematite by its reduction using a controlled H₂-H₂O atmosphere. The results of scanning electron microscopy 'SEM' and that of X-ray diffraction 'XRD' analyses of these iron oxide samples are given in Figure 1. The phases identified in the wüstite and hematite samples were Fe_(1-x)O and Fe₂O₃, respectively.

The chlorination tests of samples were performed using the TG and horizontal experimental set-up described earlier in Reference [1]. Whilst chlorination was investigated using TG technique, a heating rate of furnace of about 25 °C/min was used. The treatment residues were analyzed by XRD.

III. THERMODYNAMIC CONSIDERATIONS

The phase stability diagram of the system Fe-O-Cl^[12] is given in Figure 2. This diagram shows that at high chlorine partial pressure and low partial pressure of oxygen the most stable phase is ferric chloride. The ferrous chloride becomes a predominant specie only at low partial pressure of chlorine.

The evolution of free standard energy changes (ΔG°) as a function of temperature for the chlorination reactions of wüstite and hematite using different chlorinating agents (Eqs. 1 through 10) is traced in Figure 3. Data listed in Reference [12] and [13] were used for these calculations. Only FeCl₃ was considered as chloride product of the reactions of Fe_(1-x)O and Fe₂O₃ with Cl₂ and Cl₂+CO. Equations 7 and 8 were envisaged to describe the reactions of Fe_(1-x)O with FeCl₃. The reactions generating FeOCl formation were not considered because FeOCl is expected to be decomposed at temperatures higher than 200 °C^[14].

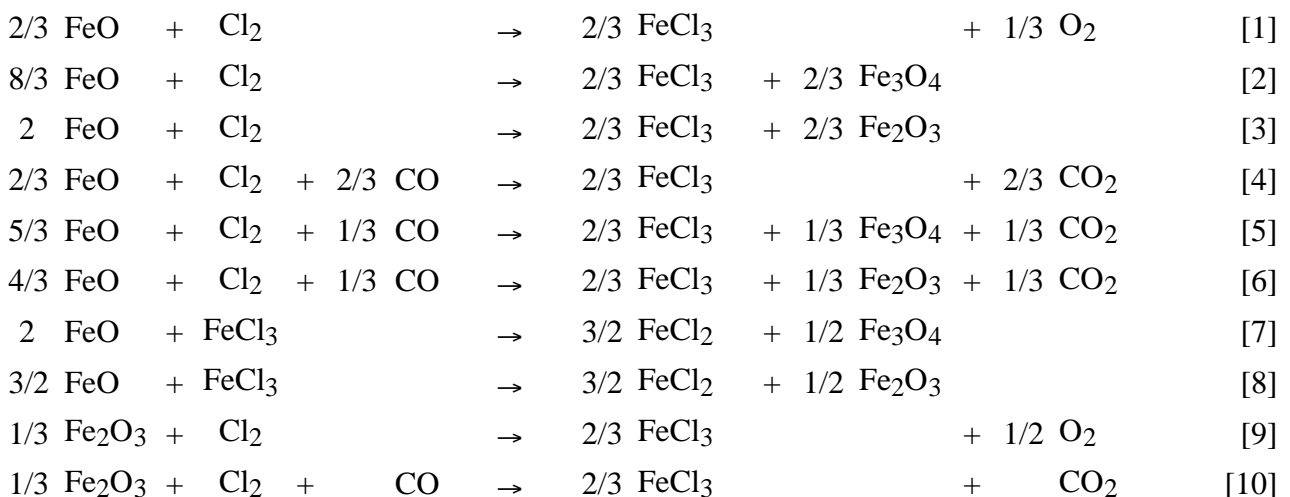


Figure 3 clearly shows that all envisaged reactions, except the one described by Eq. 9, are thermodynamically feasible in the whole temperature range investigated. It is important to note that ferric chloride can react with wüstite, from the thermodynamic point of view, producing higher oxides of iron and ferrous chloride (Eqs. 7 and 8).

IV. RESULTS

A. TG analysis of $Fe_{(1-x)}O$ and Fe_2O_3 using Cl_2+N_2 and Cl_2+CO mixtures

The samples of wüstite and hematite were treated in Cl_2+N_2 and Cl_2+CO gas mixtures from room temperature up to 1000 °C. The total gas flow rate was kept constant and equal to 40 L/h (linear gas velocity ' V_g ' \approx 33 cm/minute). The Cl_2/N_2 and Cl_2/CO molar ratios were equal to 1. Figure 4 illustrates the evolution of the percent weight loss 'pct WL' of the wüstite as a function of temperature during its treatment in the two above-mentioned atmospheres. Wüstite started to react with both chlorinating gas mixtures at temperatures lower than 250 °C resulting in a weight gain of about 20 pct at 320 °C. Above this last temperature, only weight losses were observed up to 500 °C. One may point at the curves relative to the wüstite treatments using Cl_2+N_2 and Cl_2+CO , they almost overlap up to 550 °C. The XRD results of the residues obtained at this temperature shows the presence of Fe_2O_3 in both cases. This observation indicates that the global reactions of wüstite chlorination and carbochlorination up to 550 °C are those described by Eq. 3 and 6, respectively. The weak effect of CO on the chlorination of wüstite at temperatures lower than 550 °C is consistent with observations reported by Reference [2] and [3] (Table I).

A plateau of pct WL of wüstite sample in Cl_2+N_2 was observed in the temperature range from about 500 °C to 700 °C. Beyond this temperature range, the pct WL increased with temperature and about 50 pct of sample had reacted at 1000 °C. In the case of carbochlorination, the raise of pct WL of sample was observed from 550 °C and almost total reaction of wüstite with Cl_2+CO was achieved at temperatures approaching 1000 °C.

The results concerning the treatment of hematite using the same conditions as wüstite are given in Figure 5. Hematite reacted with Cl_2+N_2 starting from about 700 °C and 30 pct of sample had reacted at 1000 °C. While in the case of its carbochlorination, the reaction had already started at 550 °C and almost total reaction was achieved at 1000 °C. The similar trends of wüstite (see Figure 4) and hematite (see Figure 5) pct WL curves at temperature higher than 500 °C is an indirect confirmation of the formation of Fe_2O_3 during the treatment of wüstite at low temperature despite the presence of carbon monoxide.

B. Isothermal carbochlorination of $Fe_{(1-x)}O$ and Fe_2O_3

As mentioned earlier, the TG analyses were performed in non isothermal conditions with a high furnace heating rate (25 °C/min). To avoid this disadvantage, a series of isothermal carbochlorination tests of wüstite and hematite were performed between 350 °C and 550 °C. A carbochlorination gas mixture of Cl_2+CO ($Cl_2/CO = 1$) was used and the reaction time was fixed to be 2 hours. Figure 6 (a) shows the isotherm curves obtained. The similarity of two sample isotherms is clear at temperatures higher than 425 °C. XRD analyses indicated that the residue of wüstite carbochlorination at 350 °C was essentially composed of Fe_2O_3 and Fe_3O_4 while only Fe_2O_3 was identified in the residue obtained at 500 °C. As expected, the carbochlorination residues

of hematite at 350 °C and 500 °C contained only Fe₂O₃. As the weight losses at 550 °C were about 100 pct for Fe_(1-x)O and Fe₂O₃, the final gaseous product was obviously FeCl₃ because the ferrous chloride is solid at this temperature^[14].

An attempt was made to estimate the effect of temperature on the carbochlorination of hematite by establishing the Arrhenius diagram. The average reaction rate of Fe₂O₃ carbochlorination as function of temperature is plotted in Figure 6 (b). An apparent activation energy of about 53 kJ/mol was deduced for the hematite carbochlorination between 350 °C and 550 °C.

C. Reaction of Fe_(1-x)O with FeCl₃

As mentioned earlier, the reactions of wüstite with ferric chloride (Eqs. 7 and 8) were thermodynamically favorable. On the other hand, the gaseous product of the reaction of wüstite with chlorine is ferric chloride. To investigate an eventual interaction of Fe_(1-x)O with FeCl₃ a series of TG non isothermal tests were performed up to 1000 °C.

The experimental conditions and results of these tests are illustrated in Figure 7. Some treatment residues obtained at 600 °C and 1000 °C were analyzed by XRD to identify the crystallized phases. Results of XRD analysis were displayed in Figure 8. Curve 1 of Figure 7 gives the evolution of pct WL of wüstite versus temperature during its treatment in pure CO. A final weight loss of about 22 pct could be attributed to almost complete reduction of wüstite to iron.

The reaction of wüstite with Cl₂+N₂ and Cl₂+CO (curve 2 and 3, Figure 7) started at temperatures lower than 250 °C. The tests were stopped at 600 °C and the XRD analysis results of the obtained residues indicated that hematite was the main phases in both residues. Ferric chloride started to volatilize at temperatures higher than 200 °C in N₂ or CO and about 80 pct of the sample were volatilized at temperatures lower than 400 °C (curve 4 and 5, Figure 7).

About 20 pct of the sample were volatilized at temperatures lower than 350 °C when a mixture of Fe_(1-x)+FeCl₃ was treated under N₂ (curve 6, Figure 7). Then, the weight loss remained constant up to 700 °C. Beyond this temperature, the sample lost some weight up to 900 °C. XRD analysis of residue obtained at 600 °C (see Figure 8) detected the presence of Fe₃O₄ (γ-Fe₂O₃ ?), FeCl₂·2H₂O, and Fe_(1-x)O. The ferrous chloride was identified as FeCl₂·2H₂O due to its hygroscopic nature. In the residue of treatment at 1000 °C, Fe₃O₄ (γ-Fe₂O₃ ?) was the main phase besides non-reacted Fe_(1-x)O. These results compared with the evolution of the vapor pressure of FeCl₂ as function of temperature^[14] suggest that ferric chloride reacted with wüstite according to Eqs. 7 and 8.

The same observations were valid for the treatment of a Fe_(1-x)+FeCl₃ mixture in CO up to 600 °C (curve 7 of Figure 7 and XRD result of Figure 8). Thus, ferric chloride is able to oxidize wüstite even in presence of carbon monoxide. The sample weight loss was also observed in the temperature range of 700 °C to 900 °C, due to the volatilization of ferrous chloride. It seems that

the reduction of iron oxides by CO started when the ferrous chloride was totally volatilized. As shown by curve 7 of Figure 7, another weight loss of sample was observed at temperature higher than 950 °C. The residue obtained at 1000 °C was essentially composed of metallic iron and wüstite.

V. CONCLUSIONS

Chlorination and carbochlorination of wüstite, under non isothermal conditions, started at temperatures lower than 250 °C. Hematite and ferric chloride were the final reaction product. The presence of carbon monoxide had almost no effect during the treatment up to 550 °C.

Hematite seems to be refractory, under non isothermal conditions, to Cl₂+N₂ gas mixture up to about 700 °C. Its carbochlorination began at about 550 °C and total reaction was achieved at temperatures approaching 1000 °C.

Total reaction of wüstite and hematite producing gaseous ferric chloride was possible during their treatment in Cl₂+CO for two hours at 550 °C. An apparent activation energy of about 53 kJ/mol was obtained for the carbochlorination of hematite between 350 °C and 550 °C.

Besides chlorine, ferric chloride can react with wüstite at low temperatures generating higher oxides of iron and ferrous chloride despite the presence of carbon monoxide.

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FIGURE CAPTIONS

Figure 1 : Results of SEM and XRD analyses of used samples.

Figure 2 : Phase stability diagram of Fe-O-Cl system at 800 °C^[12].

Figure 3 : Evolution of standard free energy changes as function of temperature for the reactions of wüstite and hematite with different chlorinating agents^[12, 13].

Figure 4 : Thermogravimetric analysis of wüstite treatment in Cl₂+N₂ and Cl₂+CO gas mixtures.

Figure 5 : Thermogravimetric analysis of hematite treatment in Cl₂+N₂ and Cl₂+CO gas mixtures.

Figure 6 : Isothermal treatment of wüstite and hematite in Cl₂+CO (*a*) and Arrhenius plot of hematite carbochlorination between 350 °C and 550 °C (*b*).

Figure 7 : Thermogravimetric analysis of wüstite and FeCl₃ using different conditions.

Figure 8 : XRD analyses of residues of wüstite treatment using different conditions.

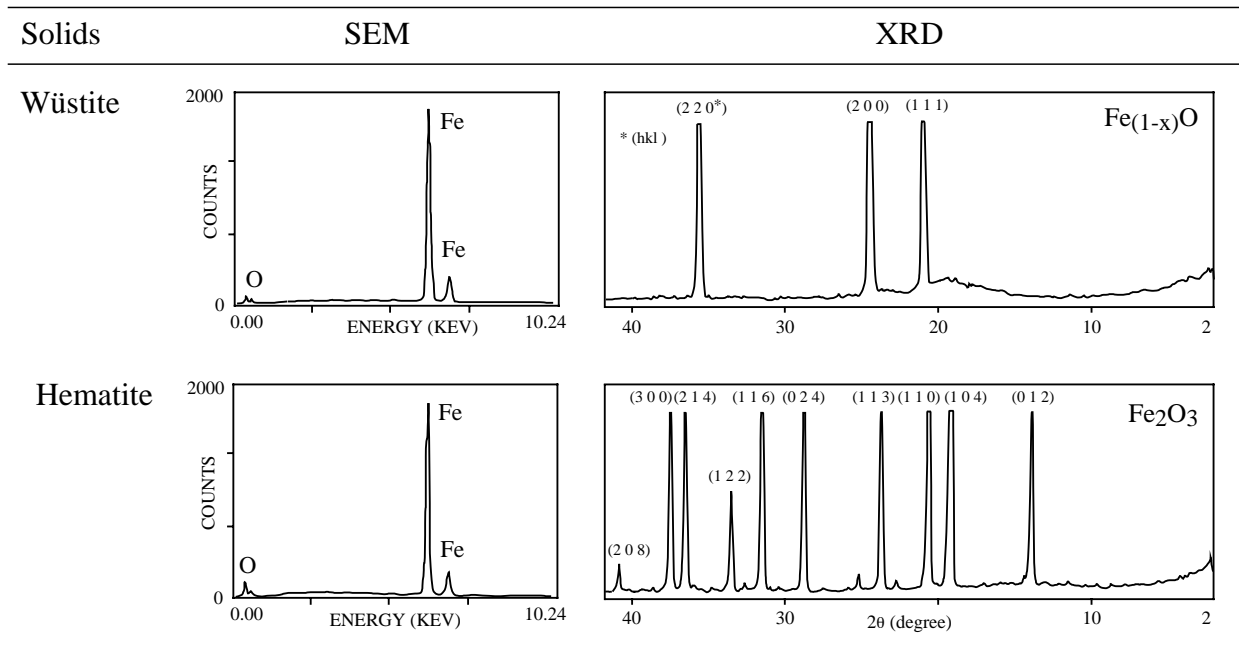


Figure 1 : Results of SEM and XRD analyses of used samples.

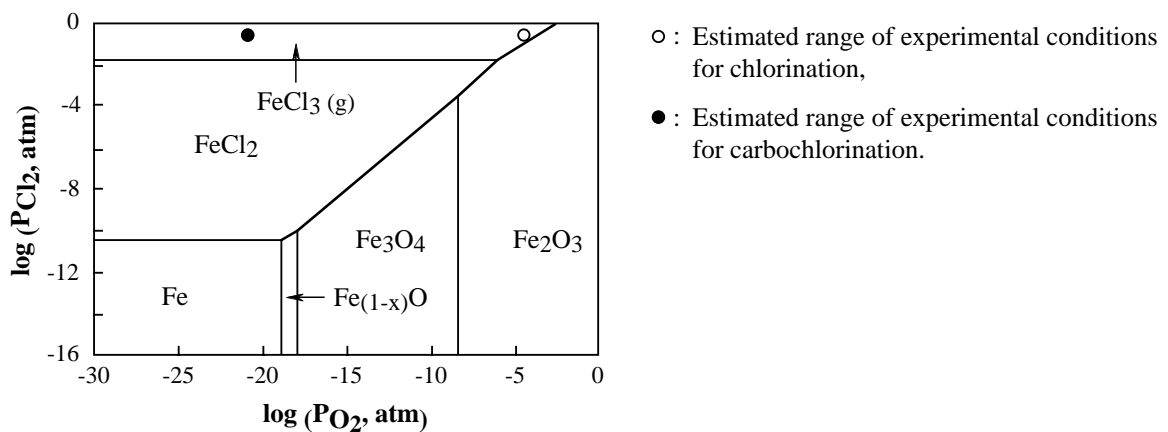


Figure 2 : Phase stability diagram of Fe-O-Cl system at 800 °C[12].

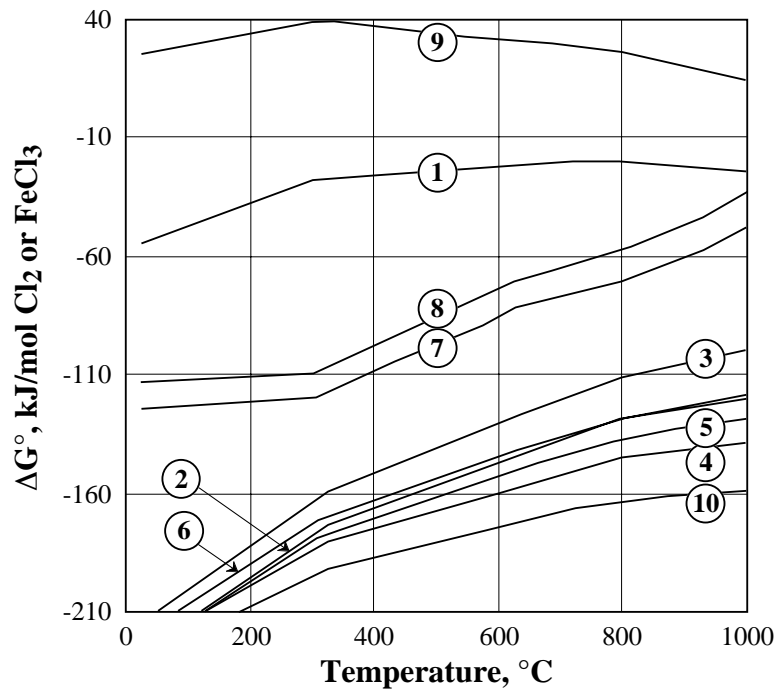


Figure 3 : Evolution of standard free energy changes as function of temperature for the reactions of wüstite and hematite with different chlorinating agents[12, 13].

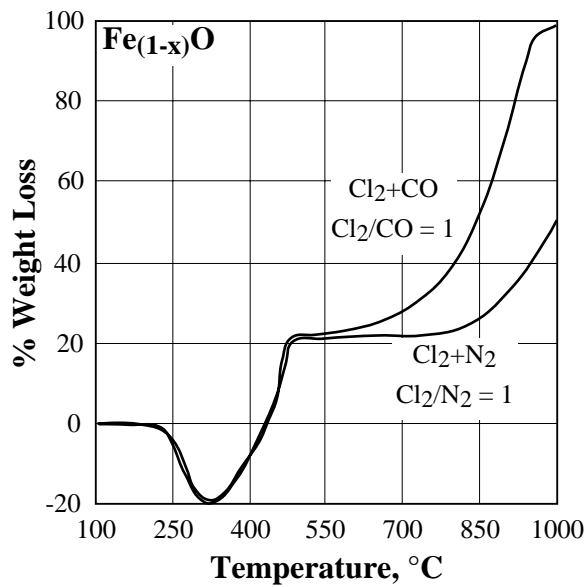


Figure 4 : Thermogravimetric analysis of wüstite treatment in Cl_2+N_2 and Cl_2+CO gas mixtures.

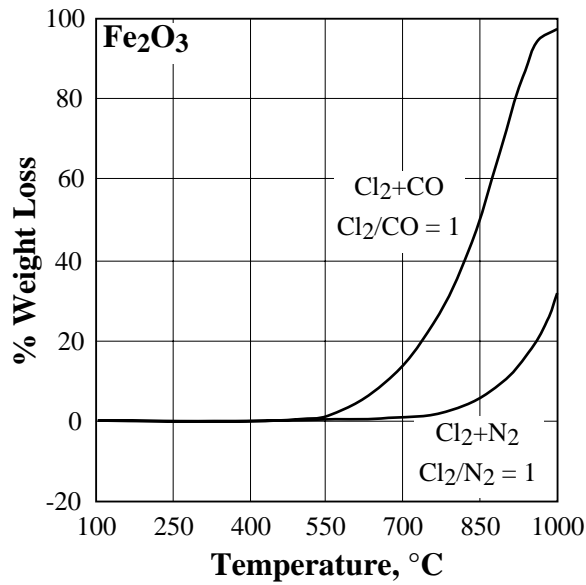


Figure 5 : Thermogravimetric analysis of hematite treatment in $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ gas mixtures.

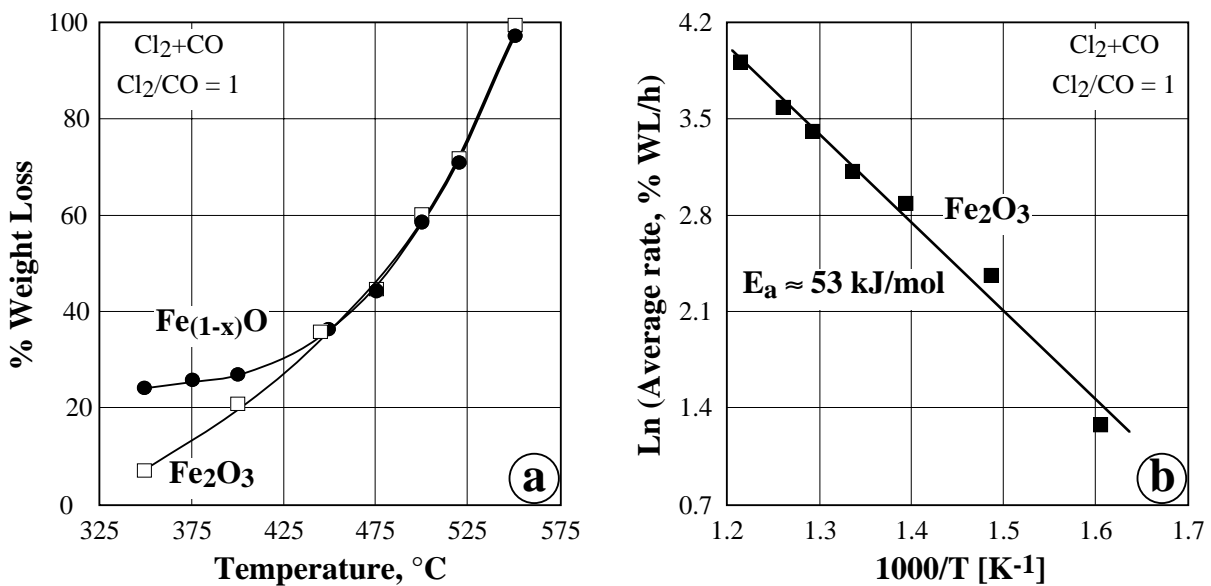
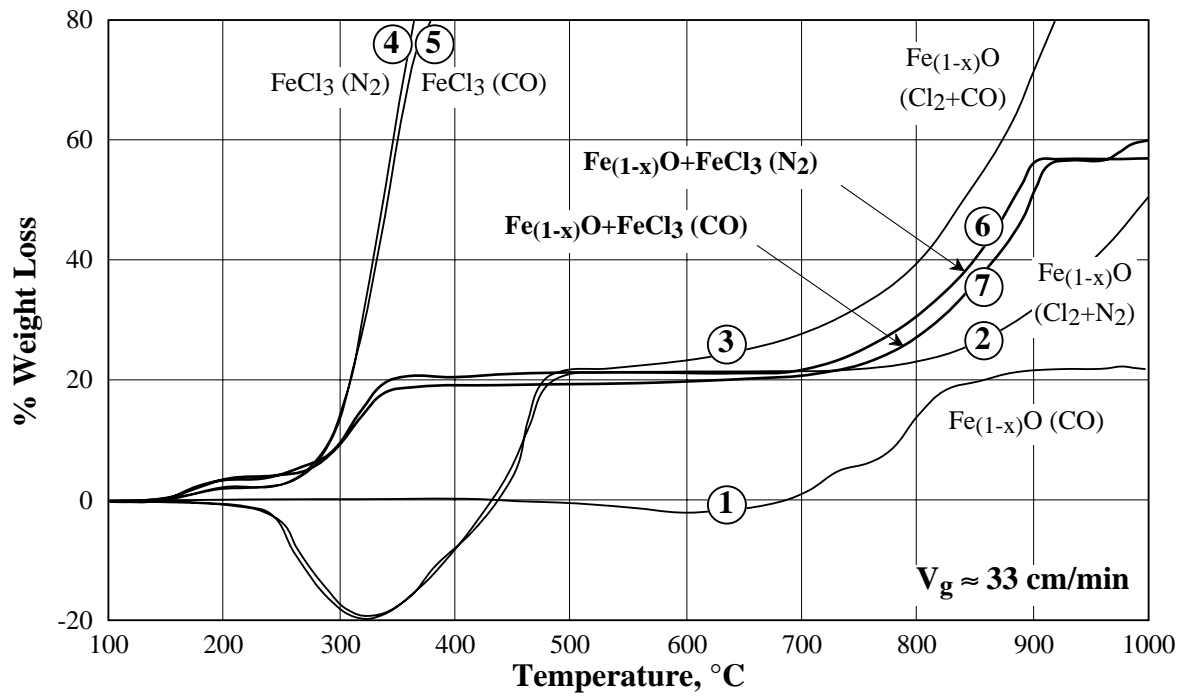
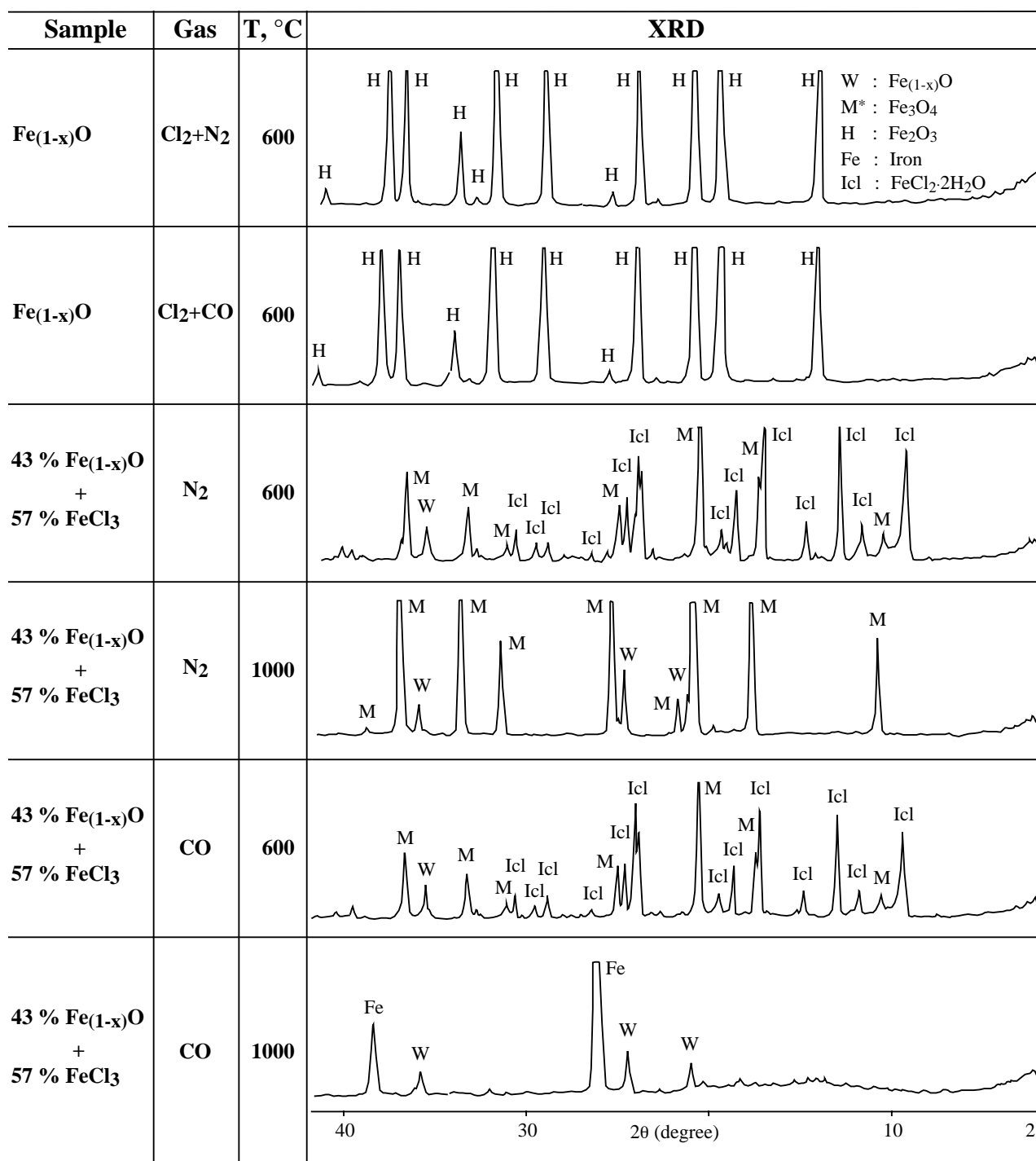


Figure 6 : Isothermal treatment of wüstite and hematite in $\text{Cl}_2 + \text{CO}$ (a) and Arrhenius plot of hematite carbochlorination between 350 °C and 550 °C (b).



- ① $\text{Fe}_{(1-x)}\text{O}$ in CO,
- ② $\text{Fe}_{(1-x)}\text{O}$ in Cl_2+N_2 gas mixture,
- ③ $\text{Fe}_{(1-x)}\text{O}$ in Cl_2+CO gas mixture,
- ④ FeCl_3 in N_2 ,
- ⑤ FeCl_3 in CO,
- ⑥ A mixture of about (43 % $\text{Fe}_{(1-x)}\text{O}$ + 57 % FeCl_3) in N_2 ,
- ⑦ A mixture of about (43 % $\text{Fe}_{(1-x)}\text{O}$ + 57 % FeCl_3) in CO.

Figure 7 : Thermogravimetric analysis of wüstite and FeCl_3 using different conditions.



* Peaks of Fe_3O_4 overlapped with those of $\gamma\text{-Fe}_2\text{O}_3$

Figure 8 : XRD analyses of residues of wüstite treatment using different conditions.