

Reactions of wüstite and hematite with different chlorinating agents

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Abstract

Chlorination of wüstite ($\text{Fe}_{(1-x)}\text{O}$) and hematite (Fe_2O_3) with $\text{Cl}_2 + \text{CO}$ and $\text{Cl}_2 + \text{N}_2$ 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 carbochlorinating gas mixture. The separate treatment of the two oxides under isothermal conditions in $\text{Cl}_2 + \text{CO}$ for 2 h led to their full 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. 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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1. Introduction

The Clarke of iron is 56 300 that represents about 5% of the Earth's crust. Consequently, iron oxides are major compounds of ores of several valuable metals such as ilmenite, chromite, bauxite, etc. They are also the main constituents of the solid wastes and slag generated by the metallurgical processing of these ores. The selective extraction of valuable metals from these materials could be achieved using chlorination techniques provided a good understanding of the beha-

avior 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 [1]. The most common chlorinating agents were Cl_2 , $\text{CO} + \text{Cl}_2$, COCl_2 , CCl_4 and HCl . These experiments were mostly carried out using thermogravimetric analysis (TGA).

The main observations regarding the chlorination of wüstite are summarized in Table 1. 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

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Table 1
Summary of the researches concerning the chlorination of wüstite

Chlorinating agent	Temperature range ^a (°C)	Observations	Reference
CO + Cl ₂	27–727	Effect of CO at temperatures higher than 577°C	[2]
CO + Cl ₂	27–927	Formation of FeCl ₂ , FeCl ₃ , FeOCl, Fe ₃ O ₄ , and Fe ₂ O ₃ . Carbon monoxide effect observed at temperatures higher than 577°C	[3]
COCl ₂	27–727	Formation of the intermediate phases: FeCl ₂ , Fe ₃ O ₄ , and Fe ₂ O ₃	[2]
COCl ₂	27–927	Formation of FeCl ₂ , Fe ₃ O ₄ , and Fe ₂ O ₃	[3]
CCl ₄	27–927	Formation of FeCl ₂ , Fe ₃ O ₄ , and Fe ₂ O ₃	[3]
CCl ₄	27–927	Formation of FeCl ₂ , Fe ₃ O ₄ , and Fe ₂ O ₃	[4]
Cl ₂	25–800	Reaction occurred at low temperature. Formation of FeCl ₃ and Fe ₃ O ₄	[5]
Cl ₂	25–800	Rapid chlorination producing FeCl ₃ and Fe ₃ O ₄	[6]
Cl ₂	690–780	$E_a^b = 140$ kJ/mol	[7]
Cl ₂	27–927	Formation of FeCl ₂ , FeCl ₃ , FeOCl, Fe ₃ O ₄ , and Fe ₂ O 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 , $E_a \approx 111$ kJ/mol between 700°C and 800°C	[8]

^a When treatment temperature starts from room one, non-isothermal conditions were also used.

^b Apparent activation energy.

the other hand, Fe₃O₄ and Fe₂O₃ 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 2 gives some results concerning the chlorination of hematite using various chlorinating agents. Researchers agreed that, whilst using the same chlorinating agents, 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 to 190 kJ/mol depending on the chlorinating agent used and on the temperature range explored (Table 2).

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

2. Materials and experimental procedure

Hematite used in this study had a purity higher than 99.9% of Fe₂O₃ and supplied by Merck. 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 Fig. 1. The phases identified in the wüstite

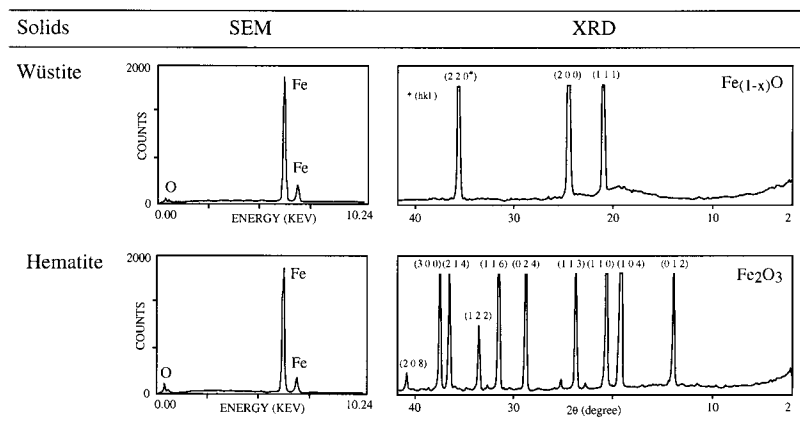


Fig. 1. Results of SEM and XRD analyses of used samples.

Table 2
Summary of the researches concerning the chlorination of hematite

Chlorinating agent	Temperature range ^a (°C)	Observations	Reference
C + Cl ₂	25–800	Formation of FeCl ₂ which volatilized as FeCl ₃	[5]
CO + Cl ₂	27–727	Reaction started at $T > 577^\circ\text{C}$ with formation of Fe ₂ Cl ₆	[2]
CO + Cl ₂	27–927	$E_a^b = 84$ kJ/mol between 327°C and 527°C	[3]
COCl ₂	27–727	Reaction started at $T > 427^\circ\text{C}$ with formation of Fe ₂ Cl ₆	[2]
COCl ₂	27–927	$E_a = 88$ kJ/mol between 237°C and 297°C	[3]
		$E_a = 60$ kJ/mol between 297°C and 447°C	
CCl ₄	27–927	$E_a = 125$ kJ/mol between 397°C and 597°C, $n_{\text{CCl}_4}^c = 0.5$ 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, $n_{\text{Cl}_2} = 0.85$	[9]
Cl ₂	25–900	$E_a \approx 96$ kJ/mol between 700°C and 900°C	[6]
Cl ₂	597–777	$E_a = 188$ –191 kJ/mol between 597°C and 777°C	[7]
	>777	$E_a = 100$ kJ/mol at $T > 777^\circ\text{C}$	
Cl ₂	27–927	$E_a = 188$ kJ/mol between 597°C and 777°C	[3]
		$E_a = 100$ kJ/mol between 777°C and 807°C	
Cl ₂	800–1200	$E_a = 167$ kJ/mol, $n_{\text{Cl}_2} = 1$	[10]
Cl ₂ + O ₂	700–900	$n_{\text{Cl}_2} = 2.75$	[9]
Cl ₂ + O ₂	25–900	Oxygen had little effect from 0% to 40% in the gas mixture	[6]
HCl	25–900	Formation of FeOCl and its decomposition between 300°C and 400°C	[6]
HCl	800–1000	$E_a = 34$ kJ/mol, $n_{\text{HCl}} = 1$	[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]

^a When treatment temperature starts from room one, non-isothermal conditions were also used.

^b Apparent activation energy.

^c Apparent reaction order.

sample and that of hematite ore 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 [1]. While 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.

3. Thermodynamic considerations

The phase stability diagram of the system Fe–O–Cl [12] is given in Fig. 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 Cl₂.

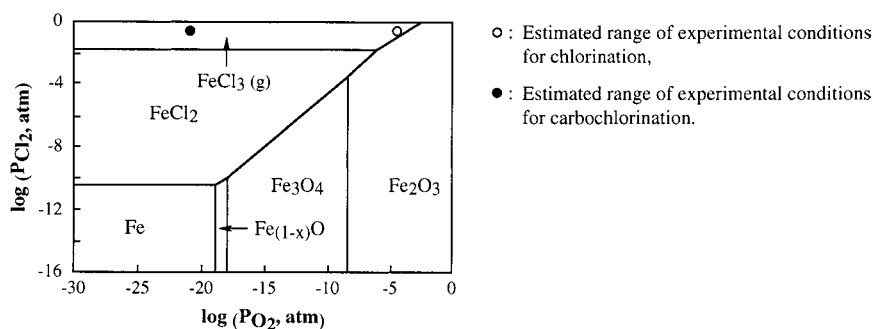


Fig. 2. Phase stability diagram of Fe–O–Cl system at 800°C [12].

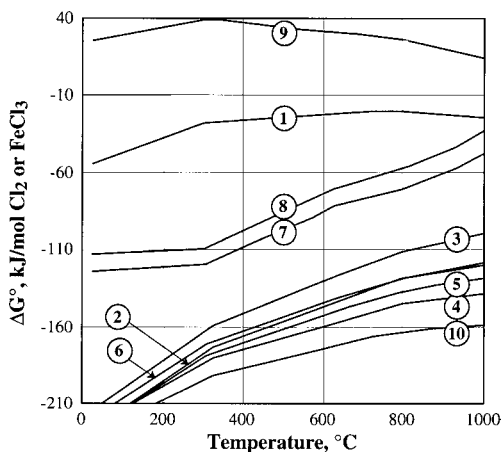


Fig. 3. Evolution of standard free energy changes as function of temperature for the reactions of wüstite and hematite with different chlorinating agents [12,13].

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)–(10)) is traced in Fig. 3. Data listed in [12,13] were used for these calculations. Only FeCl_3 was considered as thermodynamically stable chloride product of the reactions of $\text{Fe}_{(1-x)}\text{O}$ and Fe_2O_3 with Cl_2 and $\text{Cl}_2 + \text{CO}$. Eqs. (7) and (8) were envisaged to describe the interactions of $\text{Fe}_{(1-x)}\text{O}$ with FeCl_3 . The reactions generating FeOCl formation were not considered because FeOCl is expected to be decomposed at temperatures higher than 200°C [14].

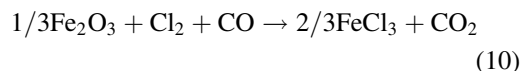
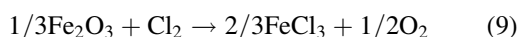
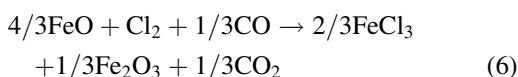
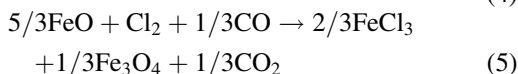
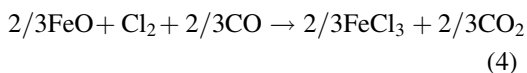
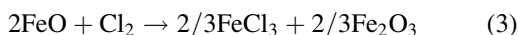


Fig. 3 clearly shows that all envisaged reactions, except that described by Eq. (9), are thermodynamically feasible in the whole temperature range investigated. From the thermodynamic point of view, it is important to note that ferric chloride can react with wüstite producing higher oxides of iron and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

4. Results

4.1. TGA of $\text{Fe}_{(1-x)}\text{O}$ and Fe_2O_3 using $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ mixtures

The samples of wüstite and hematite were treated in $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ 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/min). The Cl_2/N_2 and Cl_2/CO molar ratios were equal to 1. Fig. 4 illustrates the evolution of the percentage weight loss '%WL' of the wüstite as a function of temperature during its treatment using the two gas mixtures described above. Wüstite started to react with both gas mixtures at temperatures lower than 250°C . This is translated by a weight gain of about 20% at 320°C . At higher temperatures, only weight losses were observed up to 500°C . One may underline that the curves relative to the chlorination of wüstite using $\text{Cl}_2 + \text{N}_2$ and

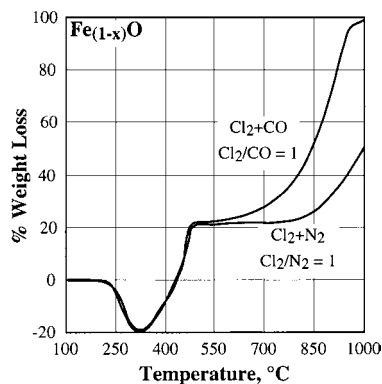


Fig. 4. Thermogravimetric analysis of wüstite treatment in $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ gas mixtures.

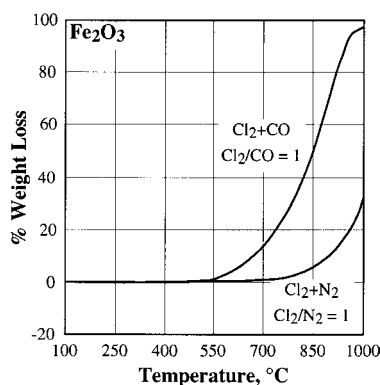


Fig. 5. Thermogravimetric analysis of hematite treatment in $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ gas mixtures.

$\text{Cl}_2 + \text{CO}$, are almost identical 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 Eqs. (3) and (6), respectively. The effect of CO on the chlorination of wüstite at temperatures lower than 550°C is negligible and consistent with observations reported by [2,3] (Table 1).

A plateau of %WL of wüstite sample in $\text{Cl}_2 + \text{N}_2$ was observed in the temperature range $500\text{--}700^\circ\text{C}$. Beyond this temperature range, the %WL increased with temperature and about 50% of sample had

reacted at 1000°C . In the case of carbochlorination, the %weight loss of the sample increased starting from 550°C . Almost full reaction of wüstite with $\text{Cl}_2 + \text{CO}$ was achieved at temperatures approaching 1000°C .

The results concerning the treatment of hematite using the same conditions as wüstite are given in Fig. 5. Hematite reacted with $\text{Cl}_2 + \text{N}_2$ starting from about 700°C and 30% of sample had reacted at 1000°C . While in the case of its carbochlorination, the reaction started at 550°C and almost total reaction was achieved at 1000°C . At temperatures higher than 500°C , the curves of Figs. 4 and 5 are similar and may be considered as an indirect confirmation of the formation of Fe_2O_3 during the treatment of wüstite at low temperature despite the presence of carbon monoxide.

4.2. Isothermal carbochlorination of $\text{Fe}_{(1-x)}\text{O}$ and Fe_2O_3

As mentioned earlier, TGA were performed in non-isothermal conditions with a high heating rate of the furnace ($25^\circ\text{C}/\text{min}$). To avoid this disadvantage, series of isothermal carbochlorination tests of wüstite and hematite were performed between 350°C and 550°C . A carbochlorination gas mixture of $\text{Cl}_2 + \text{CO}$ ($\text{Cl}_2/\text{CO} = 1$) was used and the reaction time was fixed to 2 h. Fig. 6(a) shows the obtained curves. The similarity of two sample isotherms is clear at temperatures higher than 425°C . XRD analyses indicated that the

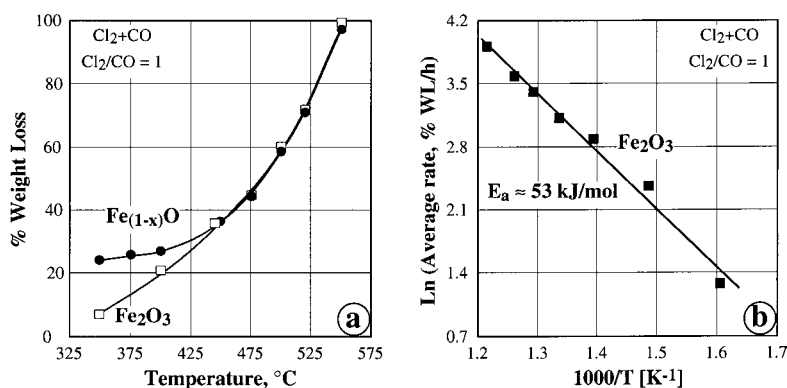


Fig. 6. Isothermal treatment of wüstite and hematite in $\text{Cl}_2 + \text{CO}$ (a) and Arrhenius plot of hematite carbochlorination between 350°C and 550°C (b).

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 Fe_2O_3 . As the weight losses at 550°C were about 100% for $\text{Fe}_{(1-x)}\text{O}$ and Fe_2O_3 , the final gaseous product was obviously FeCl_3 because the ferrous chloride is solid at this temperature [14].

An attempt was made to estimate the effect of temperature on the carbochlorination of Fe_2O_3 by establishing the Arrhenius diagram. The average reaction rate of Fe_2O_3 carbochlorination as function of temperature is plotted in Fig. 6(b). An apparent activation energy of about 53 kJ/mol was deduced for the hematite carbochlorination between 350°C and 550°C.

4.3. Reaction of $\text{Fe}_{(1-x)}\text{O}$ with FeCl_3

As mentioned earlier, the reactions of wüstite with ferric chloride (Eqs. (7) and (8)) were thermodyna-

mically favorable. On the other hand, the gaseous product of the reaction of wüstite with chlorine is ferric chloride. To investigate an eventual interaction of $\text{Fe}_{(1-x)}\text{O}$ with FeCl_3 a series of TG non-isothermal tests were performed up to 1000°C.

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

The reaction of wüstite with $\text{Cl}_2 + \text{N}_2$ and $\text{Cl}_2 + \text{CO}$ (curves 2 and 3, Fig. 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 phase in both residues. Ferric chloride started to volatilize at temperatures higher than 200°C in N_2 or CO and about 80% of the sample were volati-

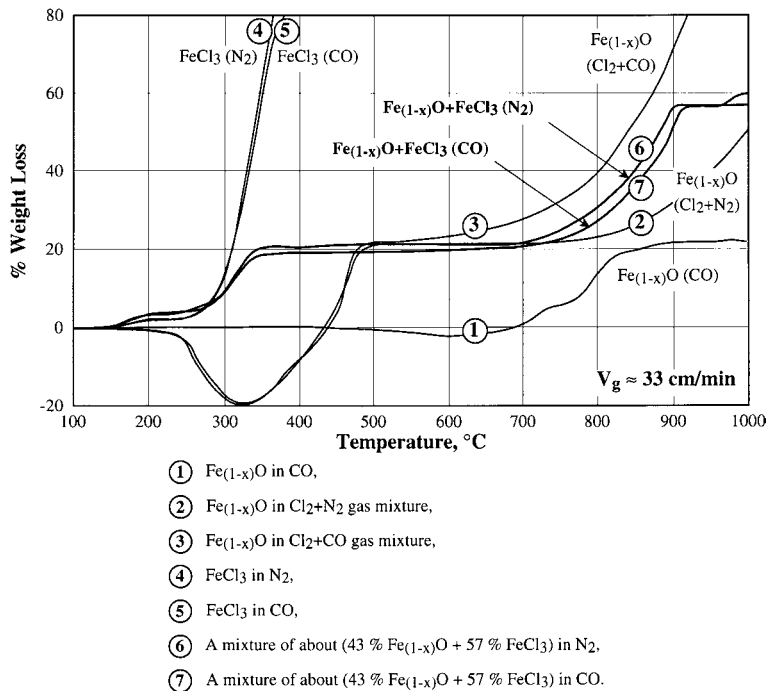
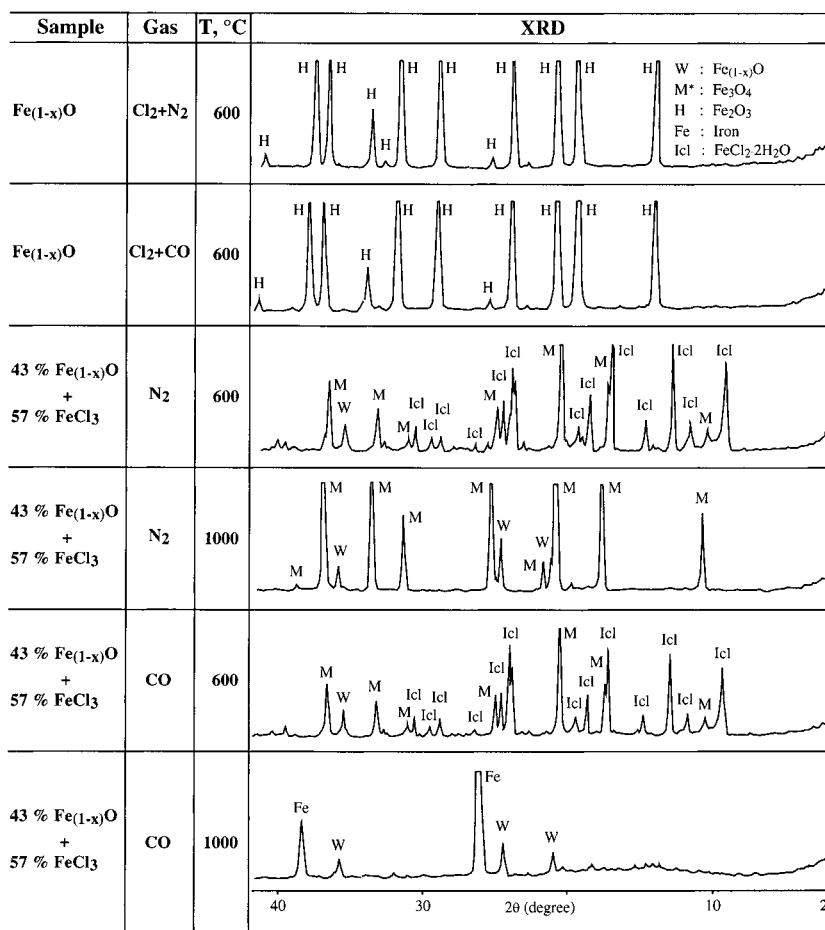


Fig. 7. TGA of wüstite and FeCl_3 using different conditions.



* Peaks of Fe₃O₄ overlapped with those of γ-Fe₂O₃

Fig. 8. XRD analyses of residues of wüstite treatment using different conditions.

lized at temperatures lower than 400°C (curves 4 and 5, Fig. 7).

About 20% 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, Fig. 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 Fig. 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 Fig. 7 and XRD result of Fig. 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 700–900°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 Fig. 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.

5. 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 $\text{Cl}_2 + \text{N}_2$ gas mixture up to about 700°C. Its carbochlorination began at about 550°C and total reaction was achieved at temperatures approaching 1000°C.

Full carbochlorination of wüstite and hematite producing gaseous ferric chloride was possible at 550°C and a reaction time of 2 h. 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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