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Some aspects of the reactivity of olivine and serpentine towards different chlorinating gas mixtures

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Abstract

The reactivities of olivine and serpentine towards mixture of chlorine in air, nitrogen and carbon monoxide were studied in non-isothermal conditions up to 1000°C. The samples were also chlorinated in a horizontal reactor over 2 h between 500° and 1000°C, under oxidizing and reducing atmospheres. The chlorination products were examined by XRD and SEM.

The iron-bearing compounds contained in the natural olivine and serpentine samples can be eliminated through chlorination or oxychlorination of these solids at temperatures lower than 900°C. Carbochlorination of olivine and serpentine is incomplete even at 1000°C for a reaction time of 2 h. Pure magnesium chloride can be recovered by cooling the gas phase at ca. 500°C.

Keywords: Chlorination; Olivine; Reactivity; Serpentine; TGA

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1. Introduction and literature review

The chlorination of magnesium silicates can be considered an alternative for the extraction of pure magnesium compounds. The literature is relatively poor in this field. This paper describes preliminary result on this procedure. It is part of a larger programme devoted to the study of chlorine technology [1–3].

Ishii et al. [4] studied the chlorination of FeO, Fe_2O_3, SiO_2, MgO as well as olivine, protoenstatite and talc between 25° and 1000°C using differential thermal and thermogravimetric analysis (DTA and TGA). According to these authors, the reactivity of MgO towards chlorine is negligible at 640°C in the absence of carbon. In its presence, however, an exothermic peak was observed at 500°C corresponding to the formation of $MgCl_2$. This peak shifts to lower temperatures with increasing amounts of carbon. An endothermic peak was observed at ca. 700°C and attributed to the fusion of $MgCl_2$. The initial reaction rate was rapid. However, as the reaction progressed, its rate decreased and, finally, stopped at ca. 55% of MgO chlorination. The authors suggest

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that $MgCl_2$ formed on the surface of the MgO particles acts as a barrier for further progress of the reaction. They also indicated that chlorination of olivine was only possible in the presence of carbon and suggested that two types of magnesium coexist in this solid, both having different reactivities towards chlorine. Protoenstatite and talc gave exothermic peaks at 950° and 750°C, respectively. Eqs. (1) and (2) describe, respectively, the interaction of olivine and protoenstatite with Cl_2+C corresponding to these exothermic peaks, while the chlorination of talc proceeded together with its decomposition following Eq. (3).

$$Mg_2SiO_4 + C + Cl_2 \rightarrow MgSiO_3 + MgCl_2 + CO \qquad (1)$$

$$4MgSiO_3 + C + Cl_2 \rightarrow 3MgSiO_3 + MgCl_2 + SiO_2 + CO \qquad (2)$$

$$Mg_3(Si_2O_5)_2(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O \qquad (3)$$

2. Thermodynamic study

Natural olivine and serpentine samples contain iron impurities. The standard free energy changes (ΔG^0) of chlorination of MgO, FeO, Mg_2SiO_4, $MgSiO_3$ and SiO_2 by chlorine (Eqs. (4)–(10)) and by Cl_2+CO (Eqs. (11)–(17)) are calculated using the data listed in Refs. [5,6]. Figs. 1 and 2 show the change in standard free energy as a function of temperature, for the chlorination and carbochlorination of each reaction. Only the chlorination of FeO by chlorine is thermodynamically favorable over the whole temperature range under examination. On the other hand, ΔG^0 of MgO chlorination is slightly positive at temperatures >500°C, while the chlorination of SiO_2 is thermodynamically unfavorable up to 1000°C. However, in the presence of a reducing atmosphere, all the carbochlorination reactions are thermodynamically favorable in the temperature range investigated.

$$2MgO + 2Cl_2 \rightarrow 2MgCl_2 + O_2 \qquad (4)$$

$$2FeO + 3Cl_2 \rightarrow 2FeCl_3 + O_2 \qquad (5)$$

$$2Mg_2SiO_4 + 2Cl_2 \rightarrow 2MgSiO_3 + 2MgCl_2 + O_2 \qquad (6)$$

$$Mg_2SiO_4 + 4Cl_2 \rightarrow 2MgCl_2 + SiCl_4 + 2O_2 \qquad (7)$$

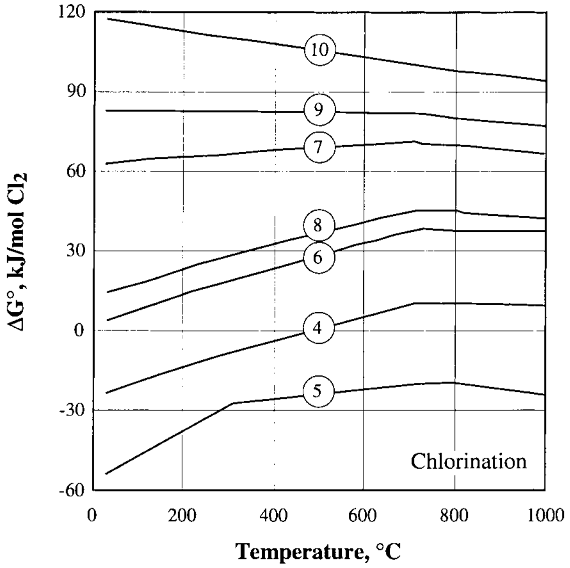

Fig. 1. Standard free-energy change of chlorination reactions as a function of temperature [5,6].

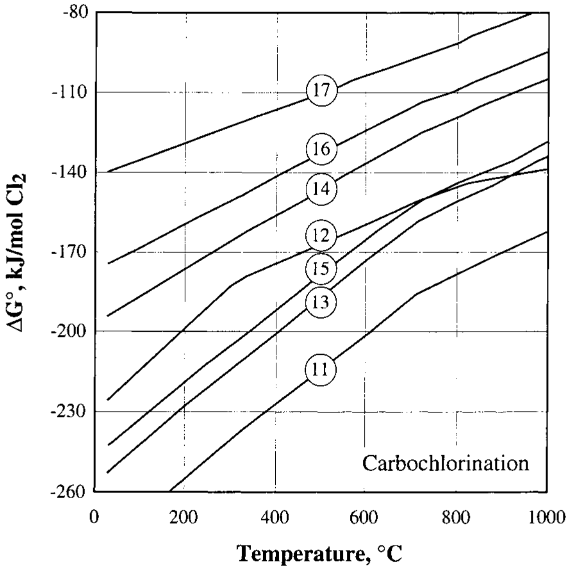

Fig. 2. Standard free-energy change of carbochlorination reactions as a function of temperature [5,6].

$$2MgSiO_3 + 2Cl_2 \rightarrow 2MgCl_2 + 2SiO_2 + O_2 \qquad (8)$$

$$2MgSiO_3 + 6Cl_2 \rightarrow 2MgCl_2 + 2SiCl_4 + 3O_2 \qquad (9)$$

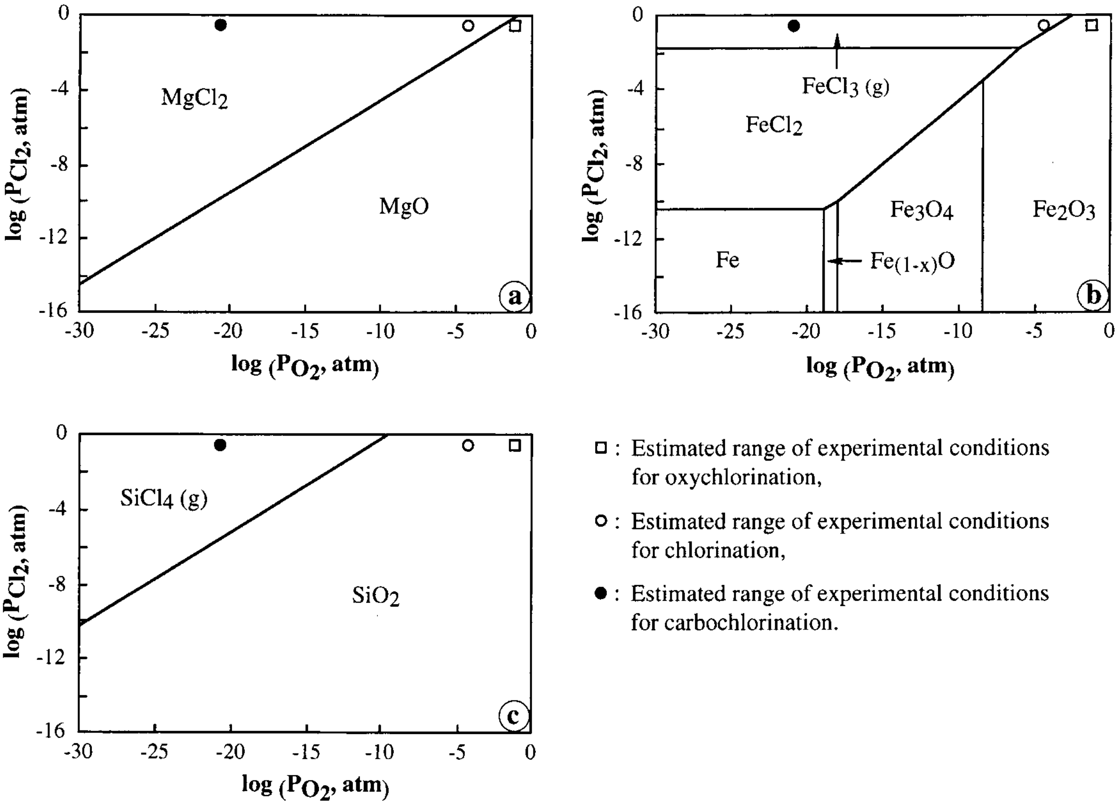

Fig. 3. Phase stability diagram of (a) Mg–O–Cl, (b) Fe–O–Cl and (c) Si–O–Cl systems at 800°C [5].

$$SiO_2 + 2Cl_2 \rightarrow SiCl_4 + O_2 \quad (10)$$

$$MgO + Cl_2 + CO \rightarrow MgCl_2 + CO_2 \quad (11)$$

$$2FeO + 3Cl_2 + 2CO \rightarrow 2FeCl_3 + 2CO_2 \quad (12)$$

$$Mg_2SiO_4 + Cl_2 + CO \rightarrow MgSiO_3 + MgCl_2 + CO_2 \quad (13)$$

$$Mg_2SiO_4 + 4Cl_2 + 4CO \rightarrow 2MgCl_2 + SiCl_4 + 4CO_2 \quad (14)$$

$$MgSiO_3 + Cl_2 + CO \rightarrow MgCl_2 + SiO_2 + CO_2 \quad (15)$$

$$MgSiO_3 + 3Cl_2 + 3CO \rightarrow MgCl_2 + SiCl_4 + 3CO_2 \quad (16)$$

$$SiO_2 + 2Cl_2 + 2CO \rightarrow SiCl_4 + 2CO_2 \quad (17)$$

Fig. 3 shows the phase-stability diagrams for the (Mg,Fe,Si)–O–Cl systems at 800°C. These diagrams were determined using the data listed in Ref. [6]. The estimated experimental partial pressures of Cl_2 and O_2 are indicated in these diagrams for the different chlorination atmospheres. According to these diagrams, oxides of the three elements will react with chlorine in the presence of CO at 800°C, whereas with the Cl_2+N_2 gas mixture, only iron oxide and MgO could be chlorinated. The thermodynamic probability of chlorination of all the oxides decreases as the oxygen partial pressure increases.

3. Materials and experimental procedure

Natural olivine and serpentine were used for this investigation. X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses of samples were summarized in Fig. 4. The main phases identified in these samples are Mg_2SiO_4 and $Mg_3Si_2O_5(OH)_4$,

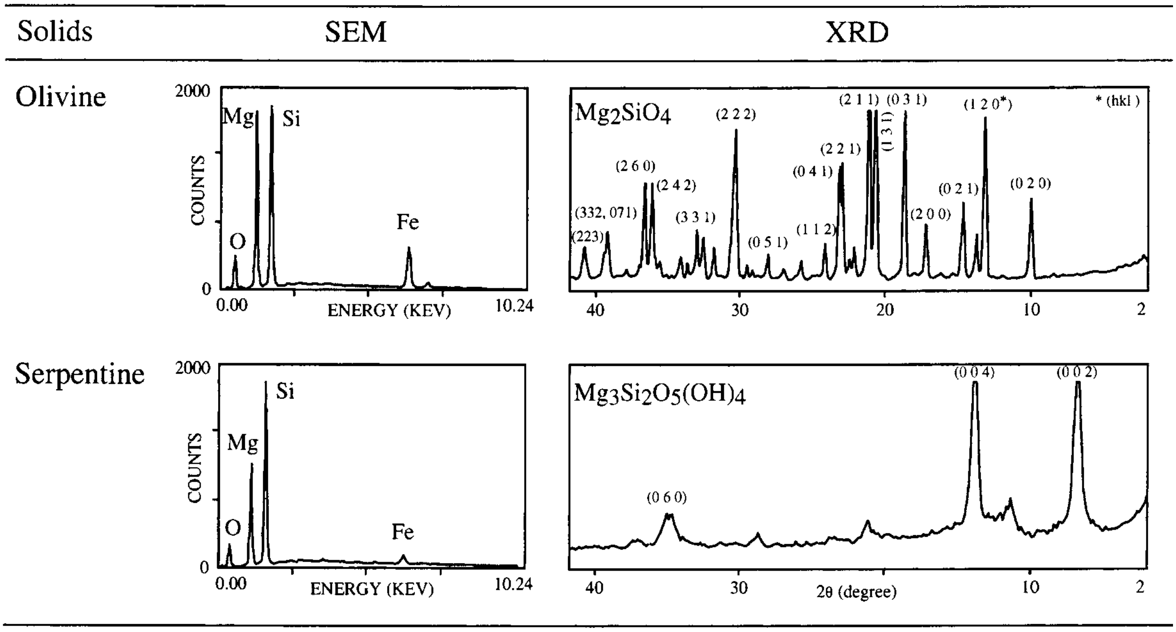

Fig. 4. Results of SEM and XRD analyses of samples investigated.

respectively. However, SEM analysis indicated the presence of iron compounds in these solids. Thermogravimetric (TG) chlorination tests were carried out on 100 mg of sample, using the experimental procedure described previously [1]. The furnace was heated at the rate of ca. 25°C min^{-1}.

The oxy- and carbochlorination tests with these samples were carried out in a horizontal experimental set described elsewhere [1]. This set was composed of a gas metering unit, followed by a gas purification one and an automatically controlled electrical furnace. The outlet gas mixture was cooled to condense and recover volatile chlorides. The exhaust gases were purified before releasing in the atmosphere. The reaction products were subjected to SEM and XRD analysis to identify the phases present.

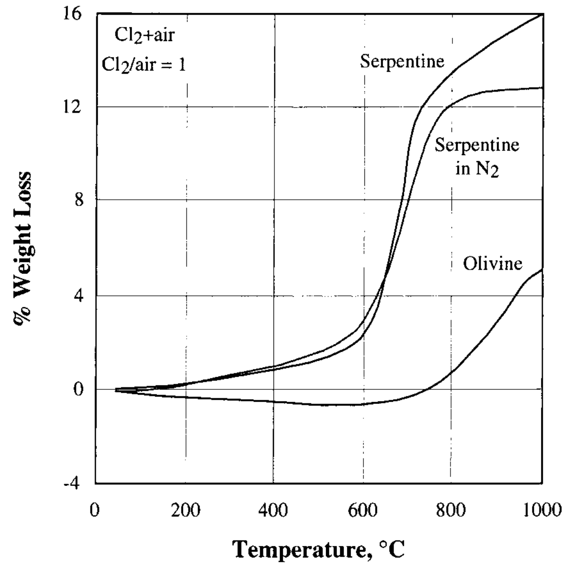

Fig. 5. Thermogravimetic analysis of magnesium compounds in Cl_2+air.

4. Results and discussion

4.1. Non-isothermal TG measurements

4.1.1. Oxychlorination

Fig. 5 shows the percent weight loss of olivine and serpentine samples with temperature during treatments in Cl_2+air gas mixtures. The reaction of olivine with this gas mixture started with a slight weight increase due to chlorine adsorption on to the sample surface. The Mg_2SiO_4 weight loss started at a temperature >750°C. Its reaction rate is low and its weight loss is <5% even at temperatures approaching 1000°C. This weight loss was due to the chlorination of the iron impurities and the volatilization of the ferric chloride produced.

At temperatures <500°C, the serpentine weight loss is ca. 1%. This weight change can be attributed to adsorbed water. At temperatures >500°C, the weight loss is ca. 16%. However, treatment of $Mg_3Si_2O_5(OH)_4$ in nitrogen, using the same experimental conditions, leads to a weight loss of ca. 13%, which is equal to the calculated weight loss from Eq. (18). This is due to the thermal decomposition of the serpentine and subsequent volatilization of H_2O, as described by the following equation.

$$Mg_3Si_2O_5(OH)_4 \rightarrow Mg_2SiO_4 + MgSiO_3 + 2H_2O \qquad (18)$$

Consequently, the weight loss of $Mg_3Si_2O_5(OH)_4$, ca. 3%, may be attributed to the chlorination of the iron-bearing compounds and the volatilization of $FeCl_3$. XRD of the reaction products shows the presence of Mg_2SiO_4 and $MgSiO_3$. $MgSiO_3$ is thermodynamically stable in Cl_2 as indicated by reactions (8) and (9) (Fig. 1).

4.1.2. Chlorination

TG chlorination weight changes for Mg_2SiO_4 and $Mg_3Si_2O_5(OH)_4$ in the Cl_2+N_2 atmosphere are shown in Fig. 6. The changes for olivine indicate that the reactivity of olivine to chlorination is low. This is in good agreement with the thermodynamic considerations (Fig. 1). Only the iron-bearing compounds were chlorinated up to 1000°C. The behavior of serpentine in Cl_2+N_2 is almost identical to that in Cl_2+air. However, the weight loss is slightly higher than that corresponding to the thermal decomposition of this solid.

4.1.3. Carbochlorination

As expected from the thermodynamic calculations, carbochlorination of these solids is more favorable than their chlorination with Cl_2+N_2 or Cl_2+air. Fig. 7 traces the % weight loss with temperature for the chlorination of magnesium-bearing compounds. The olivine begins to react with Cl_2+CO at ca. 600°C. The weight increases with temperature up to 900°C. The stabilization of weight loss, beyond this temperature, is due to the overlapping of the sample's rates of carbochlorination and that of $MgCl_2$ volatilization.

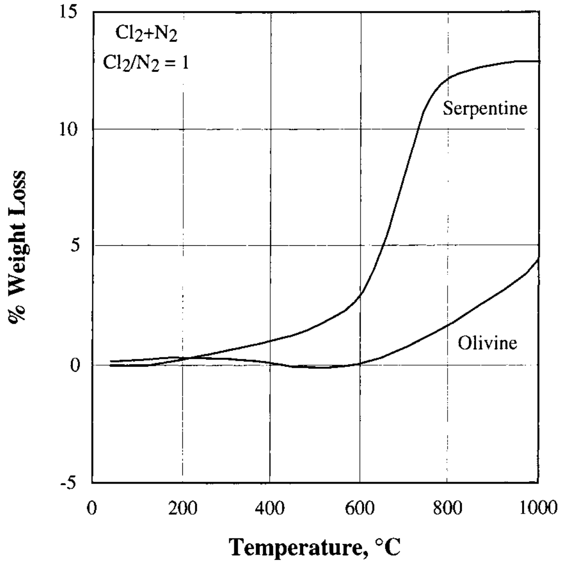

Fig. 6. Thermogravimetic analysis of magnesium compounds in Cl_2+N_2.

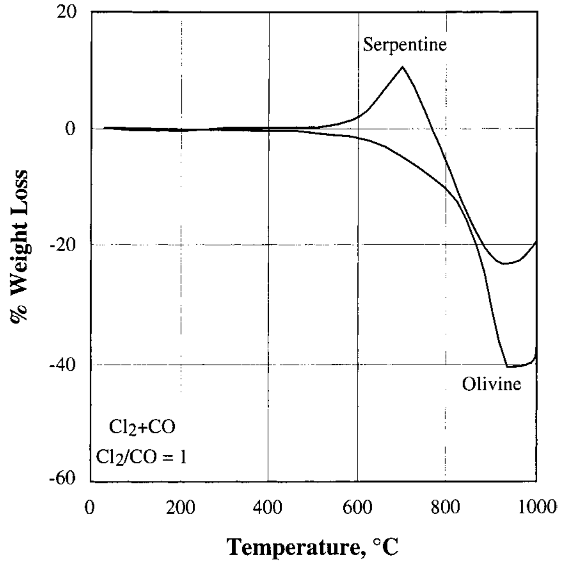

Fig. 7. Thermogravimetic analysis of magnesium compounds in Cl_2+CO.

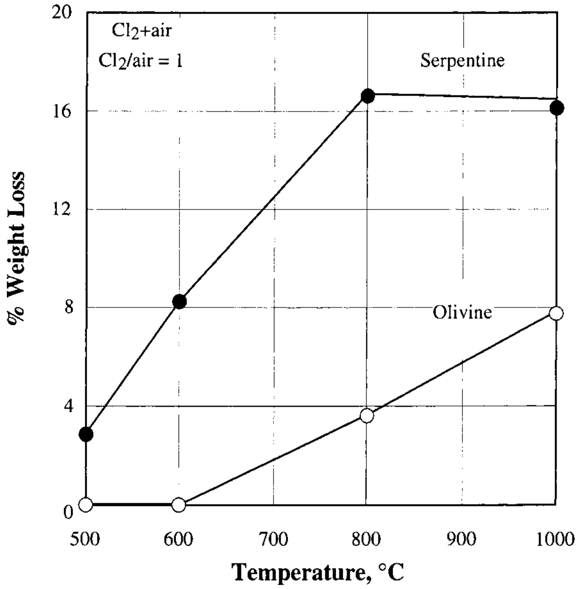

Fig. 8. Oxychlorination of magnesium silicates in a horizontal set during 2 h.

The curve of serpentine carbochlorination first exhibits a weight loss from 500° to 700°C, attributed to its thermal decomposition. At temperatures >700°C, the weight increase is due to the formation of $MgCl_2$. Further weight loss above 900°C is due to the volatilization of magnesium chloride. One may underline that boiling point of $MgCl_2$ is 1412°C [7].

4.2. *Isothermal treatment in the horizontal experimental set*

4.2.1. *Oxychlorination*

Following the preliminary experimentation on the chlorination behavior of these samples in non-isothermal conditions, a series of experiments were performed under isothermal conditions in the temperature range of 500° and 1000°C for two hours using ca. 3 g. Fig. 8 shows the % weight loss from the samples as a function of temperature.

The reactivity of olivine towards Cl_2+air is low even for a reaction time of 2 h. The observed weight loss of ca. 8% at 1000°C corresponds to the chlorination of iron oxide contained in the sample and, probably, to partial chlorination of this sample. Analysis of residue shows the presence of Mg_2SiO_4 (Table 1) as the only stable phase in all residues obtained by the oxychlorination of olivine. The reaction of serpentine with the oxychlorinating gas mixture started after its thermal decomposition according to Eq. (18). Again, the chlorination rate of serpentine is low even at 1000°C. As is shown in Table 1, the XRD analysis confirms the decomposition of serpentine at temperatures >600°C and the formation of Mg_2SiO_4 and $MgSiO_3$. The absence of magnesium chloride in the reaction product, if formed, can be justified by its volatilization because of the important linear velocity of the gas mixture (ca. 50 cm/min).

4.2.2. *Carbochlorination*

Fig. 9 shows the % weight loss of olivine and serpentine samples during their carbochlorination between 500° and 1000°C. The olivine sample reacts with the gas mixture at 500°C leading to a weight increase. Between 600° and 700°C, the weight loss remains constant. This observation agrees with that of Ishii et al. [4] concerning the presence of two types of magnesium present in the olivine, having different reactivities to the chlorination. Table 2 confirms the presence of Mg_2SiO_4 and $MgSiO_3$. For temperatures >800°C, the volatilization of $MgCl_2$ leads to a decrease in the weight. As indicated by the XRD results listed in Table 2, the phases detected in the chlorination residue are Mg_2SiO_4 and $MgCl_2$ at 500° and 600°C. $MgSiO_3$ was identified at temperatures $\geq$800°C and confirms the reaction described by Eq. (13). The carbochlorination of olivine is incomplete even at 1000°C. This is because of the formation

Table 1
XRD analysis of the oxychlorination residues

Solid	Temperature of treatment, °C			
	500	600	800	1000
Olivine	Mg_2SiO_4	Mg_2SiO_4	Mg_2SiO_4	Mg_2SiO_4
Serpentine	$Mg_3Si_2O_5(OH)_4$	$Mg_3Si_2O_5(OH)_4$	Mg_2SiO_4, $MgSiO_3$	Mg_2SiO_4, $MgSiO_3$

Table 2
XRD analysis of the carbochlorination residues

Solid	Temperature of treatment/ °C			
	500	600	800	1000
Olivine [a]	Mg_2SiO_4, $MgCl_2$	Mg_2SiO_4, $MgCl_2$	Mg_2SiO_4, $MgSiO_3$, $MgCl_2$	$MgCl_2$
Serpentine [a]	$Mg_3Si_2O_5(OH)_4$	$MgCl_2$	Mg_2SiO_4, $MgSiO_3$, $MgCl_2$	Mg_2SiO_4, $MgSiO_3$

[a] $MgCl_2$ is identified as $MgCl_2{\cdot}6H_2O$.

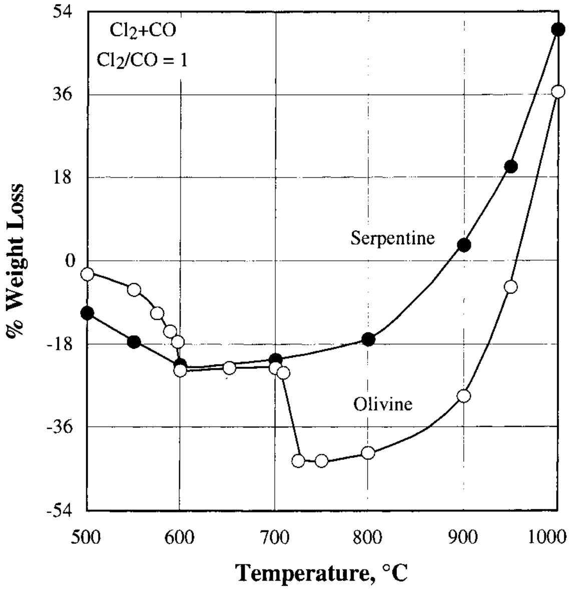

Fig. 9. Carbochlorination of olivine and serpentine in a horizontal set during 2 h.

of a magnesium chloride and amorphous silica layer that acts as a barrier between the rest of olivine and the carbochlorinating gas mixture. This hypothesis is confirmed by the presence of only $MgCl_2$ as revealed by XRD and that of amorphous silica identified by the SEM analysis.

Serpentine reacted with the Cl_2+CO gas mixture at 500°C. The observed weight loss up to 800°C is the algebraic sum of the weight increase due to the chlorination of the iron and magnesium compounds and the weight loss due to the thermal decomposition of the sample (Eq. (18)) and the volatilization of $FeCl_3$ and $MgCl_2$. At higher temperatures, the rate of volatilization of $MgCl_2$ seems to be higher than that of its formation. This is confirmed by the presence of silicates in the residue treated at 1000°C (Table 2).

5. Conclusions

The reactivity of Mg_2SiO_4 and $Mg_3Si_2O_5(OH)_4$ towards oxychlorinating and chlorinating gas mixtures is low. In both cases, only the iron contained in these minerals is chlorinated and volatilzed at temperatures <1000°C. At temperatures >500°C, the serpentine is thermally decomposed. These results show that the elimination of the iron compounds from these solids is possible through their chlorination in the 800–1000°C range.

Chlorination and carbochlorination of serpentine and olivine start at ca. 500°C and remain incomplete at 1000°C. The serpentine is decomposed to Mg_2SiO_4 and $MgSiO_3$ at temperatures <800°C. The iron-bearing compounds were fully chlorinated and volatilzed at temperatures <900°C. The magnesium and iron chlorides are recovered by cooling the outlet gases to ca. 500° and 25°C, respectively. The recovered magnesium chloride is of high purity and identified by XRD as $MgCl_2{\cdot}6H_2O$. Such products can be used as raw material for the fabrication of pure magnesium employed for the production of alloys devoted to the aeronautic sector.

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