

Carbochlorination kinetics of tantalum and niobium pentoxides^(•)

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Abstract The carbochlorination kinetics of pure Nb₂O₅ and Ta₂O₅ by gas mixture (Cl₂ + CO + N₂) between 380 and 1,000 °C is studied. A calculation of the standard free energy of the carbochlorination reactions is made. A diagram of the phases stability is drawn. The influence of the gas flow, temperature and the partial pressure of Cl₂ and CO at temperatures below 650 °C on the reaction rate is studied. The apparent activation energy is approximately 75 and 110 kJ/mol for Nb₂O₅ and Ta₂O₅, respectively. At temperatures above 650 °C the Arrhenius diagram presents an anomaly which may be attributed to the decomposition of the COCl₂ formed *in situ*. The apparent reaction order of the carbochlorination of these oxides against Cl₂+CO is approximately 2. The carbochlorination rates of these oxides are much greater than those of chlorination by Cl₂ + N₂. The carbochlorination kinetics of tin furnace slag leaching concentrates containing tantalum and niobium compounds are also studied and compared with the carbochlorination kinetics of the pure oxides.

Keywords: **Carbochlorination. Tantalum pentoxide. Niobium pentoxide. Tin furnace slag.**

Cinética de carbochloruración de los pentóxidos de tantalio y de niobio

Resumen En este trabajo se estudia la cinética de carbochloruración del Nb₂O₅ y del Ta₂O₅ por la mezcla de gases (Cl₂ + CO + N₂) entre 380 y 1000 °C. Se hace un cálculo de la energía libre estandar de carbochloruración y se dibujan los diagramas de equilibrio de fases. Se estudia la influencia del flujo de gas, la temperatura y la presión parcial de Cl₂ y CO a temperaturas por debajo de 650 °C sobre la velocidad de reacción. La energía de activación es aproximadamente 75 y 110 kJ/mol para el Nb₂O₅ y el Ta₂O₅, respectivamente. A temperaturas por encima de 650 °C, el diagrama de Arrhenius presenta una anomalía que puede ser atribuida a la descomposición del COCl₂ formado *in situ*. El orden aparente de reacción de la carbochloruración de estos óxidos frente a Cl₂ + CO es aproximadamente 2. La velocidad de carbochloruración de estos óxidos es mucho más grande que la que se conseguía con una mezcla de Cl₂ y N₂. Se ha comparado la cinética de carbochloruración de los compuestos de niobio y tantalio contenidos en los concentrados de lixiviación de las escorias de hornos de estaño con la cinética de carbochloruración de los óxidos puros.

Palabras clave: **Carbochloruración. Pentóxido de tantalio. Pentóxido de niobio. Escorias de horno de estaño.**

1. INTRODUCTION

The tantalum and niobium metals have applications in advanced technologies such as electronics,

superconductivity and in the aerospace industry. They are used as alloying elements in superalloys and even in high definition television, etc (1 y 2).

Current methods of tantalum and niobium extraction, from minerallurgical concentrates or from tin furnace slags, are often polluting or costly (3 y 4). These reasons have led several teams to research different possibilities for recovering these elements. The line considered by our team consists of the selective leaching of slags followed by the carbochlorination of the concentrate obtained (5). Complementing data from the literature (6 y 7), the aim of the study presented below has been to better understand the mechanisms susceptible to

(•) Trabajo recibido el día 17 de febrero de 1999 y aceptado en su forma final el 8 de julio de 1999.

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controlling the carbochlorination reactions of pure Ta₂O₅ and Nb₂O₅ and in this way improve their extraction from leaching concentrates.

2. EXPERIMENTAL METHOD

The carbochlorination kinetics of Nb₂O₅ and Ta₂O₅ have been studied by thermogravimetric analysis using a CAHN thermobalance, model C 1000, with a sensitivity of 0.01 mg. The tests were carried out using a 100 mg sample in the interval of temperatures from 20 to 1000 °C. The tests finalized when the sample ceased to lose weight.

For these tests samples were taken of pure tantalum and niobium oxides in powder form, whose characteristics are shown in Table I.

These oxides have been used without any prior treatment.

When tin furnace slags are leached two concentrates are obtained, one with a high content of tantalum and niobium compounds, which we call rich concentrate, CR, and another with a lesser content which we call poor concentrate CP. Table II shows the chemical composition of these concentrates.

3. RESULTS AND DISCUSSION

3.1. Thermodynamic study

The main carbochlorination reactions of the tantalum and niobium oxides are given by equations [1] to [6]:

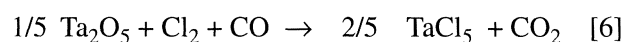
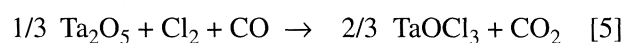
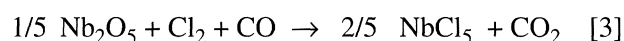
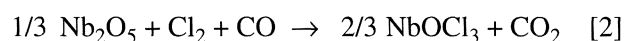


TABLE II.— Chemical composition of the tin furnace slags and of the leaching concentrates

TABLA II.— Composición química de las escorias de horno de estaño y de los concentrados de lixiviación

Oxide, %	Nb ₂ O ₅	Ta ₂ O ₅	SiO ₂	CaO	FeO	Al ₂ O ₃	SnO ₂	MnO	K ₂ O	TiO ₂
Brut.+	5.2	7.5	41.9	11.6	3.3	11.2	0.7	3.7	1.4	1.3
CP*	7.7	15.6	43.3	9.8	2.5	5.2	0.9	2.3	0.8	1.2
CR**	28.0	31.1	10.0	0.6	0.2	0.6	0.2	0.0	0.4	1.4

+ Tin furnace slags.

* Poor concentrate CP.

** Rich concentrate CR.

TABLE I.— Some characteristics of the pure Ta₂O₅ and Nb₂O₅ powders

TABLA I.— Algunas características de los polvos Ta₂O₅ y Nb₂O₅ en estado puro

Oxides, %	Nb ₂ O ₅ , >99.4	Ta ₂ O ₅ , >99
JCPDS* file	27-1003	25-922

* JCPDS = Joint Committee for Powder Diffraction Standard.

All the thermodynamic data presented in this article are calculated from the HSC database (8). Figure 1 shows the standard free energy evolution of the carbochlorination reactions of tantalum and niobium oxides between 0 and 1,000 °C. All the reactions considered are thermodynamically possible.

Figure 2 shows the stability diagram of the compounds in the Ta-O-Cl and Nb-O-Cl systems at

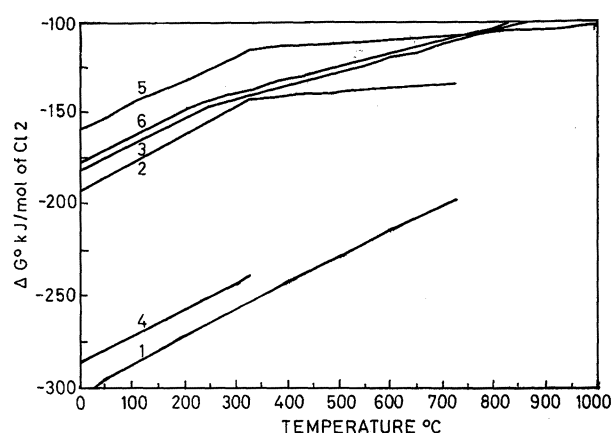


FIG. 1.— Free energy of carbochlorination of Nb₂O₅ and Ta₂O₅ as a function of temperature.

FIG. 1.— Energía libre de carbochloruración del Nb₂O₅ y del Ta₂O₅ en función de la temperatura.

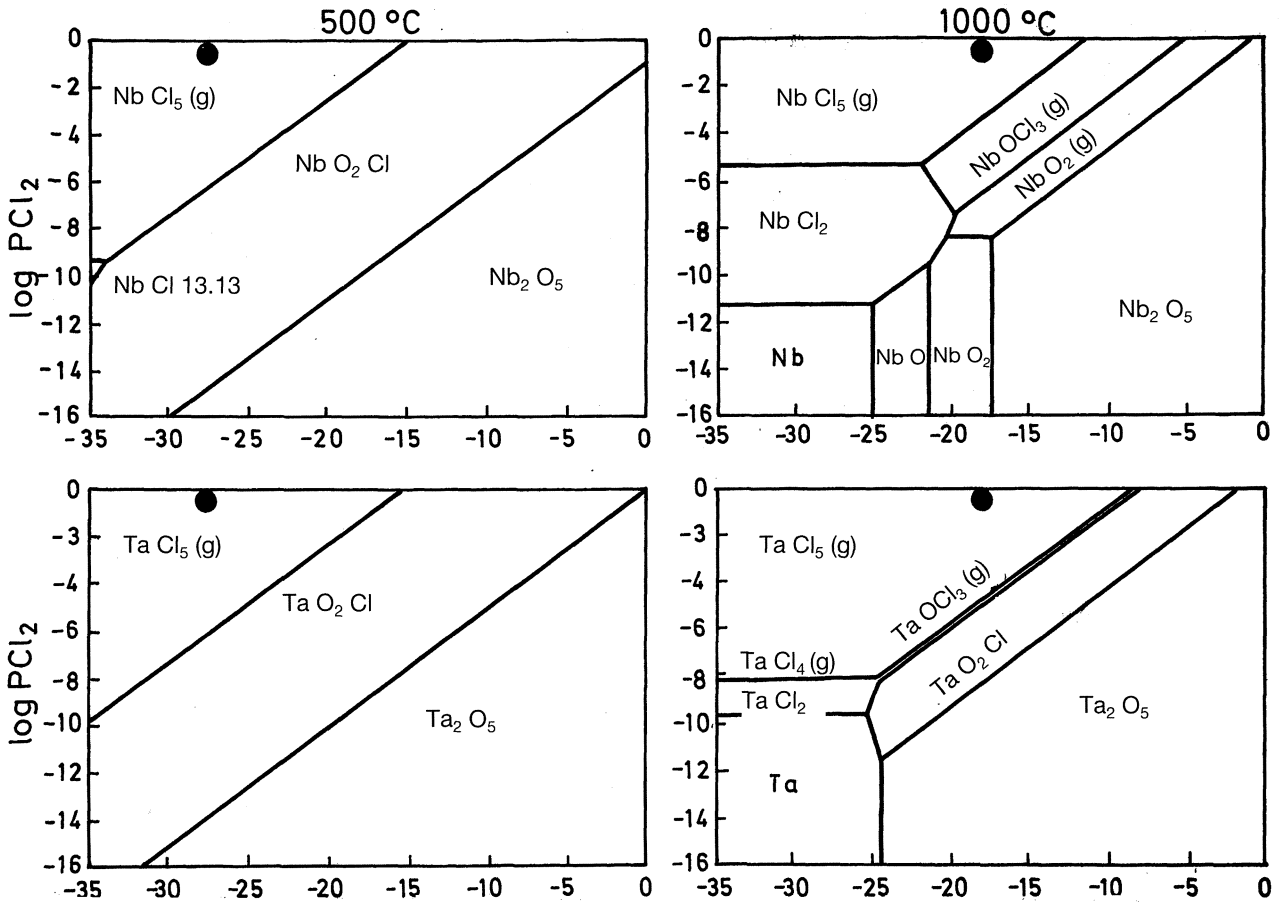


FIG. 2.— Phase diagram of (Mo, Nb, Ta and V)-O-Cl at 500 and 1,000 °C.

FIG. 2.— Diagrama de fases del (Mo, Nb, Ta y V)-O-Cl a 500 y 1.000 °C.

500 and 1,000 °C. The experimental carbochlorination conditions, shown by black dots, indicate that the most probable carbochlorination products are NbCl_5 for Nb_2O_5 and TaCl_5 for Ta_2O_5 .

3.2. Influence of heating and of the gas flow

As can be seen in figure 3, Nb_2O_5 and Ta_2O_5 start to react with $\text{Cl}_2 + \text{CO} + \text{N}_2$ at around 400 and 500 °C, respectively. It should be noted that the carbochlorination kinetics of Ta_2O_5 are similar to those of Nb_2O_5 .

Figure 4 shows the influence of the flow of $\text{Cl}_2 + \text{CO} + \text{N}_2$ on the carbochlorination rate of Nb_2O_5 and Ta_2O_5 . An increase in the chlorination rate is seen in the tests as the flow of chlorinating mixture increases, much more pronounced in the case of tantalum oxide than for niobium oxide. This tendency is maintained until the test reaches a flow of 30 L/h, after which the chlorination rate does not increase whatever the increase in the flow. The effects of the transfer of mass may be reduced to a minimum, using this flow, which corresponds to a speed of gases with respect to the sample of 0.35

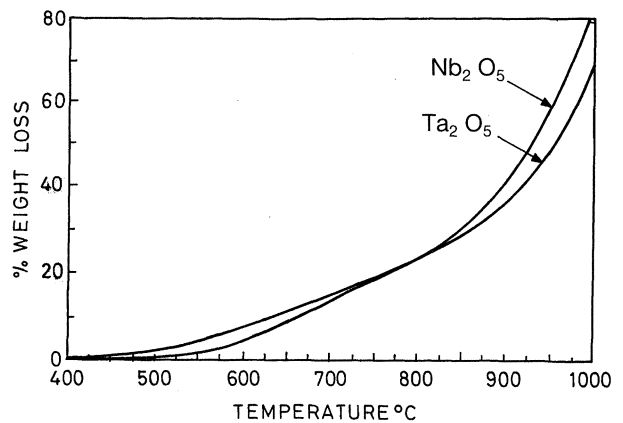


FIG. 3.— Carbochlorination of Nb_2O_5 and Ta_2O_5 as a function of temperature.

FIG. 3.— Carbochloruración de Nb_2O_5 y Ta_2O_5 en función de la temperatura.

cm/s. The use of this flow makes it possible to determine the intrinsic parameters of the carbochlorination of Nb_2O_5 and Ta_2O_5 , and to eliminate the effects of the transfer of matter between the gas mixture and the solids.

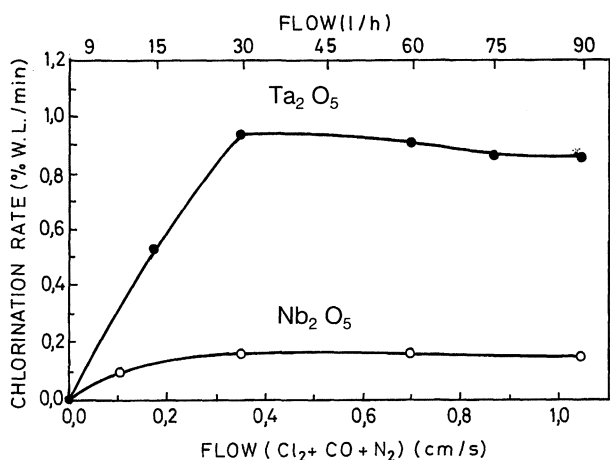


FIG. 4.— Influence of the flow on the carbochlorination rate of Nb₂O₅ and Ta₂O₅.

FIG. 4.— Influencia del caudal sobre la velocidad de carbochloruración del Nb₂O₅ y Ta₂O₅.

3.3. Influence of the partial pressure of the reagents

Figure 5 represents the logarithm of the carbochlorination rate of Nb₂O₅ and Ta₂O₅ (LnR), as a function of the partial pressure of the gas mixture (Cl₂ + CO). In both cases the apparent order of reaction is equal or close to 2. This value generally indicates the existence of a bimolecular reaction between the gaseous reagents themselves. For the present case the following reaction [7] may be considered:

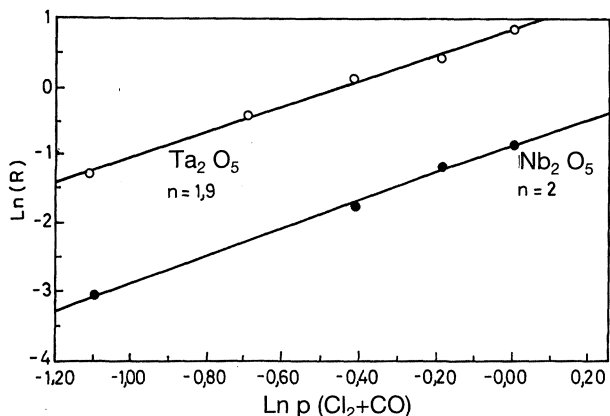
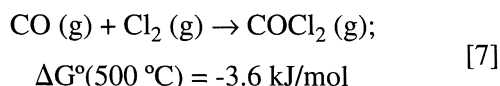


FIG. 5.— Effect of $p_{(\text{Cl}_2+\text{CO})}$ on the carbochlorination rate of Nb₂O₅ and Ta₂O₅.

FIG. 5.— Efecto de $p_{(\text{Cl}_2+\text{CO})}$ sobre la velocidad de carbochloruración del Nb₂O₅ y Ta₂O₅.

3.4. Influence of the $p_{\text{Cl}_2}/p_{\text{CO}}$ relation

Figure 6 shows that the maximum carbochlorination rate of Nb₂O₅ and Ta₂O₅ is obtained when $p_{\text{Cl}_2}/p_{\text{CO}} = 1$. This result confirms that the carbochlorination mechanism of Nb₂O₅ and Ta₂O₅ is equimolar with regard to Cl₂ and CO. On the other hand, it has been seen that neither of these two oxides is reduced by CO at temperatures lower than 420 and 600 °C, respectively. However, their chlorination will only commence in the presence of a small quantity of CO.

3.5. Effect of temperature

Two series of carbochlorination isotherms have been realized for Nb₂O₅ and Ta₂O₅ between 380 and 1,000 °C (Fig. 7). On the basis of this data the corresponding Arrhenius diagram has been obtained (Fig. 8), which indicates that the apparent activation energies are 74 and 78 kJ/mol for the carbochlorination of Nb₂O₅, between 380 and 600 °C and between 800 and 1,000 °C, respectively. The best correlations obtained in these two temperature intervals have been with the function $k_t = 1 - (1-X)^{1/3}$ (Fig. 9). This relation describes the complete gasification in a porous sphere, when the mechanism is controlled by the diffusion in the pores. This may be equally adequate, in the case of a non-porous sphere, with a chemically controlled gasification mechanism (9). In the case of Nb₂O₅, bearing in mind the values of the apparent activation energies, the first hypothesis seems the most appropriate.

The Arrhenius diagram represented in figure 8 indicates that the apparent activation energies for

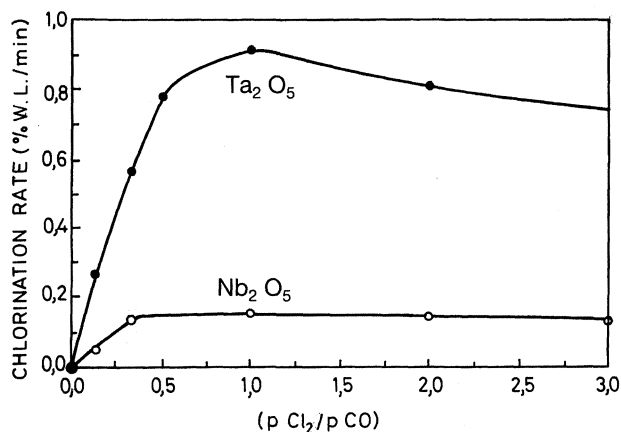


FIG. 6.— Effect of the Cl₂/CO ratio on the carbochlorination rate of Nb₂O₅ and Ta₂O₅.

FIG. 6.— Efecto de la relación Cl₂/CO sobre la velocidad de carbochloruración del Nb₂O₅ y Ta₂O₅.

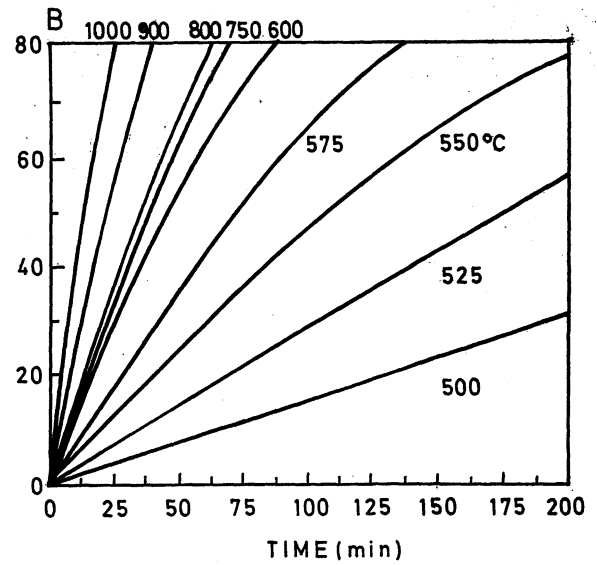
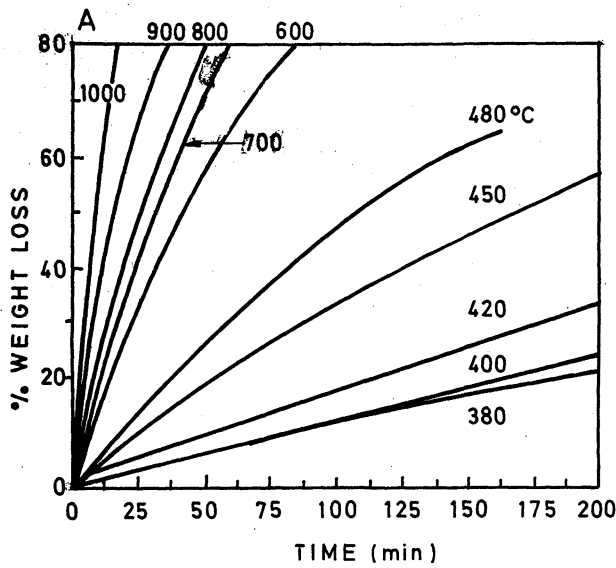


FIG. 7.— Carbochlorination isotherms for Nb₂O₅ (A) and Ta₂O₅ (B).

FIG. 7.— Isotermas de carbochloruración para Nb₂O₅ (A) y Ta₂O₅ (B).

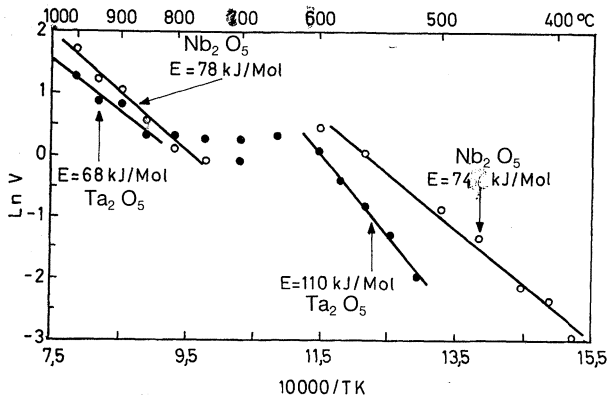


FIG. 8.— Arrhenius diagram of the carbochlorination of Nb₂O₅ and Ta₂O₅.

FIG. 8.— Diagrama de Arrhenius de la carbochloruración del Nb₂O₅ y Ta₂O₅.

Ta₂O₅ are 110 and 68 kJ/mol between 500 and 600 °C and between 850 and 1,000 °C, respectively. In both cases the best correlations have been obtained with the relation $k_t = 1 - (1 - X)^{1/2}$. This function is susceptible to representing the complete gasification of a porous cylinder in agreement with a mechanism affected by the diffusion in the pores (9). Bearing in mind the values of the apparent activation energies, it seems that between 500 and 600 °C the carbochlorination of Ta₂O₅ is controlled by the chemical reaction, while between 850 and 1,000 °C, the diffusion in the pores interferes with the chemical reaction.

Figure 8 also shows the existence of an important anomaly in the speed between 600 and 800 °C. This minimum of speed has also been

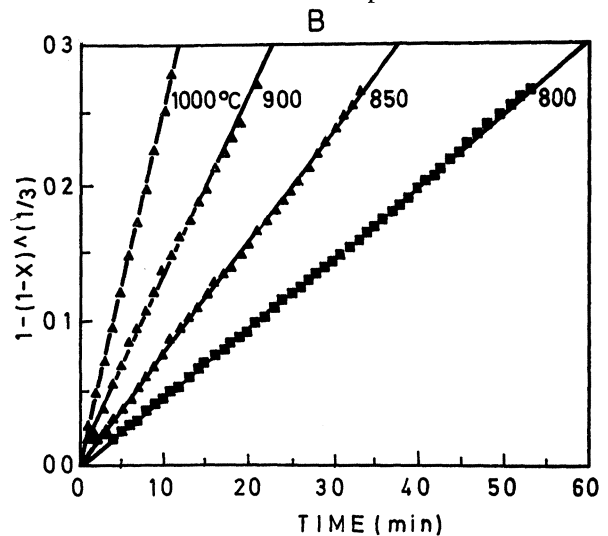
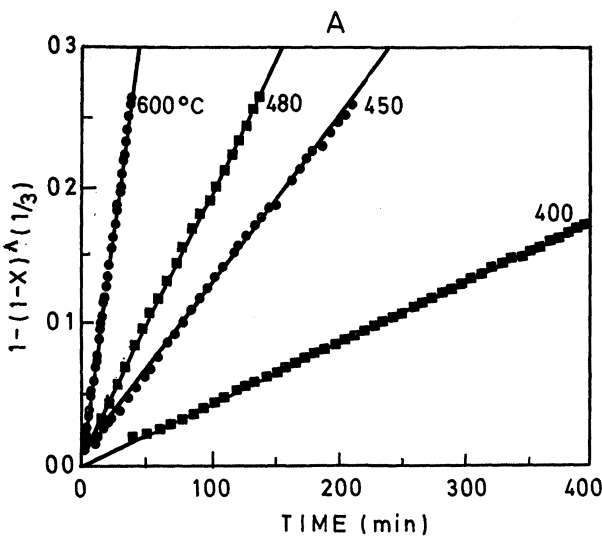


FIG. 9.— Function $1 - (1 - X)^{1/3}$ against time for the carbochlorination of Nb₂O₅ at $T < 600$ (A) and $T > 800$ °C (B).

FIG. 9.— Función $1 - (1 - X)^{1/3}$ frente al tiempo para la carbochloruración del Nb₂O₅ a $T < 600$ (A) y a $T > 800$ °C (B).

detected during the carbochlorination of oxides such as Al_2O_3 , ZrO_2 , Nb_2O_5 and V_2O_5 (10-13) by the $\text{Cl}_2 + \text{CO}$ mixture. This phenomenon is attributed to the presence of COCl_2 in this chlorinating mixture. Indeed, this compound may be synthesized *in situ* and be the predominant chlorinating agent at $T < 600$ °C. Its progressive decomposition as a function of the temperature (Fig. 10) probably gives rise to another carbochlorination mechanism at $T > 800$ °C.

Table III shows the rates R of carbochlorination by $\text{Cl}_2 + \text{CO} + \text{N}_2$ and chlorination by $\text{Cl}_2 + \text{N}_2$ (14) of Nb_2O_5 and Ta_2O_5 , respectively, as a function of the temperature. These values vary between 164 and 8.2, diminishing as the temperature increases. The production of chlorinated compounds of tantalum and niobium will be more efficient by carbochlorination than by chlorination, above all at low temperatures.

3.6. Leaching concentrates

Carbochlorination isotherms have also been carried out on poor CP and rich CR leaching concentrates, containing approximately 23.3 and 60 % ($\text{Nb} + \text{Ta}$) $_2\text{O}_5$, respectively. The Arrhenius diagram in figure 11 indicates that the carbochlorination kinetics of the rich concentrate are faster than those of the poor concentrate. On the other hand, comparison with figure 8 indicates that the carbochlorination rate of the rich concentrate is of the same order as that of pure Nb_2O_5 and Ta_2O_5 , while that of the poor concentrate is clearly lower.

At temperatures < 600 °C, the apparent activation energy of the carbochlorination of the poor concentrate and the rich concentrate are 115.5 and 103 kJ/mol, respectively. In this interval of

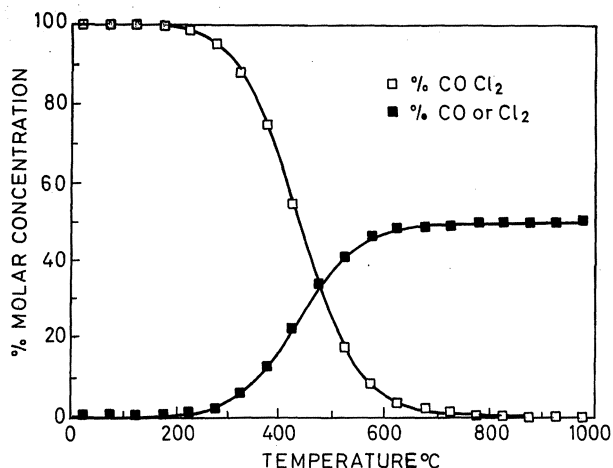


FIG. 10.— Dissociation of COCl_2 as a function of the temperature.

FIG. 10.— Disociación del COCl_2 en función de la temperatura.

TABLE III.— Evolution of the rates R of carbochlorination and chlorination of Nb_2O_5 and Ta_2O_5 , as a function of temperature

TABLA III.— Evolución de las relaciones R de carbochloruración y cloruración del Nb_2O_5 y Ta_2O_5 en función de la temperatura.

T , °C	R	
	Nb_2O_5	Ta_2O_5
679	164.0	—
780	17.3	—
903	8.6	121.5
1,060	8.2	13.5

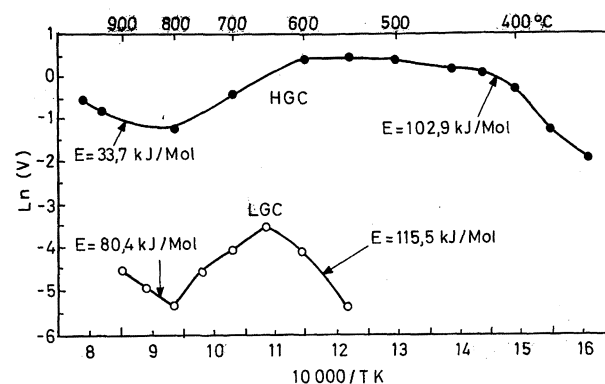


FIG. 11.— Arrhenius diagram of the carbochlorination of the poor and rich concentrates.

FIG. 11.— Diagrama de Arrhenius de la carbochloruración de los concentrados pobre y rico.

temperatures the carbochlorination process of these solids seems to be controlled by the chemical reaction.

Between 600 and 800 °C, an anomaly is observed similar to that found for pure Nb_2O_5 and Ta_2O_5 . The presence of COCl_2 in the gaseous mixture seems to be the origin of this phenomenon. The formation of calcium chlorides and/or solid and liquid manganese in the poor concentrate may contribute to causing this minimum in the rate.

At temperatures above 800 °C, it is likely that the diffusion in the pores affects the carbochlorination mechanism of these two concentrates.

4. CONCLUSIONS

— At temperatures below 600 °C, the apparent energies of the carbochlorination of Nb_2O_5 and Ta_2O_5 are 74 and 110 kJ/mol, respectively. The

controlling mechanism seems to be the diffusion in the pores, in the first case, and the chemical reaction in the second.

- An anomaly in the rate is observed in the Arrhenius diagram of the carbochlorination of Nb₂O₅ and Ta₂O₅ between 600 and 800 °C, probably due to the dissociation of the COCl₂.
- Between 850 °C and 1,000 °C the apparent activation energy is 78 kJ/mol for Nb₂O₅ and 68 kJ/mol for Ta₂O₅. The reaction rates of the two oxides are probably controlled by the chemical reaction affected by the diffusion in the pores.
- Above 600 °C the apparent order of the carbochlorination of Nb₂O₅ and Ta₂O₅ against p_(Cl₂+CO) is approximately 2.
- The maximum carbochlorination rate of Nb₂O₅ and Ta₂O₅ is obtained with a p_{Cl₂}/p_{CO} ratio of approximately 1.
- The carbochlorination kinetics of the poor concentrate is slower than those of the rich concentrate, due to the formation of a layer of diffusion of solid and/or liquid chlorides (Ca, Mn, etc.)

Acknowledgements

The authors would like to thank P. Blazy, C. Houzé, R. Solozabal, J.C. Múgica (INASMET, San Sebastián) and Ruiz-Ayucar, E. (CENIM). They also express their thanks to A. Bonazezi, M. Djona, S. Ivanaj, N. Kanari, N. Menad and N. Mirghafari N. (LEM-GPE), for discussion and suggestions, S. Dominiak, Université de Metz, J.M. Claude and A. Kohler of l'Université de Nancy for analysis of the samples by SEM, and F. Lhote (CNRS-CRPG) for XRD analyses.

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