PUC RIO

Dissertação de Mestrado

A thermodynamic study of the Nb_2O_5 chlorination with different chlorine content agents and a kinetics appreciation of the reductive chlorination ($Cl_2 + C$)

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Pontifícia Universidade Católica do Rio de Janeiro
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Departamento de Engenharia Química e de Materiais

Rio de Janeiro, 14 de outubro de 2025

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I dedicate this present study to the

love of my life, Michael ♡∞

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I want to thank God for his divine and infinity LOVE frequency, harmony, wisdom, intelligence, peace and hope that illuminates my thoughts as the sun illuminates the Planet Earth in energy-space-time because ALL that exists comes forth from the LIGHT, and the LIGHT comes forth from the ALL

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Abstract

de Albuquerque Brocchi, Eduardo; (Advisor) Navarro Correia de Siqueira, Rogério (Co Advisor); Teran Ocaña, Stephanie Lizeth. **A thermodynamic study of the Nb_2O_5 chlorination with different chlorine content agents and a kinetics appreciation of the reductive chlorination (Cl_2 + C)**. Rio de Janeiro, 2025. 100p. Dissertação de Mestrado – Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro.

This work present and discuss the possible use of chlorination as an alternative route dedicated to metals extraction, prioritizing a general thermodynamic appreciation related to the behaviour of Nb_2O_5 being submitted to different chlorinating agents, considering the nowadays data available for this type of study. Updated considerations regarding the use of Nb has been emphasized in modern industrial segments. Chlorination has been an important process step in the extraction of some valuable nonferrous metals from their mineral concentrates such as Ti and Zr. Gaseous chlorine is the most important chlorinating agent in industrial terms although some others has been mentioned in the literature as alternatives. Amongst them are the hydrochloric acid, carbon tetrachloride, ferric chloride, and some alkali or alkaline chlorides like KCl, $NaCl$, $CaCl_2$, $MgCl$. The most important feature is the possibility of a high reactivity at lower temperatures which could make them an attractive alternative reagent in an eventual new extraction route for some metals from different sources, including residues. This study aims to evaluate thermodynamically these possibilities by using Nb_2O_5 as a reference oxide. It was clearly observed that carbochlorination ($C + Cl_2$) as well as the use of CCl_4 or C_2Cl_4 are efficient Nb_2O_5's chlorinating agents to form gaseous $NbCl_5$ while the other investigated reagents have no tendency to chlorinate the Nb_2O_5. This work also presents a brief kinetic specific approach focusing on the physical structural transformations of a Nb_2O_5 & C mixture reacting with a top chlorine flow. Three experimental variables, temperature, carbon initial percentage and porosity, were considered to propose a mechanism for the penetration of chlorine into the sample as function of them. The study obtained that for easy initial chlorine penetration the whole system would be chemically controlled while for difficult penetration it will move to diffusion controlled and between these conditions a mixed control takes place.

Keywords

Nb_2O_5 Chlorination; Thermodynamics; Chlorination agents; Kinetics.

Resumo

de Albuquerque Brocchi, Eduardo; (Orientador) Navarro Correia de Siqueira, Rogério (Co Orientador); Teran Ocaña, Stephanie Lizeth. **Um estudo termodinâmico da cloração do Nb_2O_5 com diferentes agentes cloretantes e uma apreciação cinética da cloração com Cl_2 e carbono**. Rio de Janeiro, 2025. 100p. Dissertação de Mestrado – Departamento de Engenharia Química e de Materiais, Pontifícia Universidade Católica do Rio de Janeiro.

Este trabalho apresenta e discute o possível uso da cloração como uma rota alternativa dedicada à extração de metais, priorizando uma apreciação termodinâmica geral relacionada ao comportamento do Nb_2O_5 submetido a diferentes agentes cloretantes, considerando os dados atualmente disponíveis para este tipo de estudo. Considerações atualizadas sobre o uso do Nióbio (Nb) têm sido enfatizadas em segmentos industriais modernos. A cloração tem sido uma etapa importante no processo de extração de alguns metais não ferrosos valiosos a partir de seus concentrados minerais, tais como Titânio (Ti) e Zircônio (Zr). O cloro gasoso é o agente cloretante mais importante em termos industriais, embora alguns outros tenham sido mencionados na literatura como alternativas. Entre eles estão o ácido clorídrico, o tetracloreto de carbono, o cloreto férrico e alguns cloretos alcalinos ou alcalino-terrosos como like KCl, $NaCl$, $CaCl_2$, $MgCl$. A característica mais importante é a possibilidade de uma alta reatividade a temperaturas mais baixas, o que poderia torná-los reagentes alternativos atraentes em uma eventual nova rota de extração para alguns metais de diferentes fontes, incluindo resíduos. Este estudo tem como objetivo avaliar termodinamicamente essas possibilidades usando Nb_2O_5 como óxido de referência. Foi claramente observado que a carbocloração ($C + Cl_2$) assim como o uso de CCl_4 ou C_2Cl_4 são agentes cloretantes eficientes com Nb_2O_5 para formar o $NbCl_5$ gasoso, enquanto os outros reagentes investigados não tendem a clorar o Nb_2O_5. Este trabalho também apresenta uma breve abordagem cinética específica, focando nas transformações estruturais físicas da mistura Nb_2O_5 & C reagindo com um fluxo superior de cloro. Três variáveis experimentais, temperatura, porcentagem inicial de carbono e porosidade, foram consideradas para propor um mecanismo de penetração do cloro na amostra em função delas. O estudo obteve que, para uma penetração inicial fácil do cloro, todo o sistema seria controlado quimicamente, já para uma penetração difícil, o sistema passaria a ser controlado por difusão e entre essas duas condições, o controle misto permanece.

Palavras-Chave

Cloração do Nb_2O_5; Termodinâmica; Agentes cloretantes; Cinética.

SUMMARY

FIGURES' LIST

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1. INTRODUCTION

Mineral processing nowadays faces a big challenge: meeting the growing global demand for materials while protecting our planet. Environmental and social responsibilities were first internationally discussed in the Eco 92 conference, held in Rio de Janeiro in June 1992. Since then, a sustainability development has been an important issue because it is crucial to explore reserves of natural resources through environment friendly processes in order to implement a circular economy. Chlorination may be amongst them as also it has been mentioned in the specialized literature as a process able to recover industrial residues.

Chlorination is an industrial process implemented industrially nowadays for titanium and zirconium oxidized concentrates breakdown due to their reactivity with chlorine, in the presence of a reducing agent, and also to the viable separation of the formed volatile chlorides through their vapour pressures differences. Thus, chlorination process is suitable not only for minerals breakdown but also for the separation or purification of various elements co-occurring in the starting materials such as industrial residuals, making possible the recovery of the content value metals. The formation of chlorides for use in the metallic extraction routes has been attracting different studies for a long time and several articles have appeared in the literature which will be referred in in the section four of this work. Chlorination is directly related to the chlorinating agents which may be gaseous, liquid and solid species.

Gaseous reagents can be chlorine, Cl_2, hydrogen chloride, HCl, and phosgene, $COCl_2$. Elemental chlorine is the most common chlorinating agent. It is produced on large scale by the electrolysis of $NaCl$ solution. Hydrogen chloride is prepared industrially by the reaction of chlorine with hydrogen; it is also a by-product of the organic industry. Phosgene, $COCl_2$, is manufactured by passing chlorine and CO over carbon heated at 125 ºC - 150 ºC.

Liquid reagents may be carbon tetrachloride and sulphur chloride. They are sometimes used in the gaseous state. Carbon tetrachloride, CCl_4, is a non-

flammable liquid, boiling point 76.7 ºC, produced industrially by reacting chlorine with CH_4, as can be observed in reaction 1,

$$2Cl_2 + CH_4 \leftrightarrow CCl_4 + 2H_2 \qquad [r.1]$$

or with carbon disulphide, as can be observed in reaction 2,

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2 \qquad [r.2]$$

Sulphur chloride, S_2Cl_2, is a yellow liquid, boiling point 135.6 ºC, formed together with sulphur dichloride, SCl_2, when chlorine reacts with elemental sulphur or sulphide minerals.

Solid reagents may be sodium, calcium, potassium, magnesium chlorides and other alkaline chlorides, the former being the most tested salt as a chlorinated agent.

As said before the interest in the chlorination process is due to certain properties of the formed metallic chlorides and alternative studies have been reported in the literature, section 3.2 and 3.3, in order to show either the process' diversity or the potential for recovery different value metals which are content in materials such as minerals, slags and general residues.

Amongst these value metals it is possible to mention Niobium (Nb) - grey, refractory, relatively rare - which is an important alloy element for some specific industries (Benson, 2023) as shown in the following chapter. Actually, today lithium-ion batteries (LIBs) are most widely used in portable electronic devices or electric vehicles (EVs) due to their high energy density and excellent rechargeability (Lee *et al*., 2013, Goodenough *et al*., 2010). To this end, niobium oxide is the most promising anode material for LIBs because of its good chemical stability and high stability in various oxidation states $Nb^{5+} - Nb^{+}$ (Barnes *et al*., 2022).

Hydrometallurgical and pyrometallurgical processes are used to recover this metal from their ores following an appropriate serial of steps until the Nb_2O_5 formation (CBMM, de Oliveira, 2022). The next step can be the Nb_2O_5 aluminothermic reduction followed, whenever required, by refining through electrons beans. So, Nb_2O_5, Nb alloy and Nb metallic are produced with different purities.

2. PURPOSES AND METHODOLOGY

2.1 Purposes

Taking into considerations the mentioned points in the previous chapter, the main purposes of this Dissertation are broad since it aims to cover different aspects of the Niobium extractive metallurgy, starting from a general view of this metal natural availability around the world followed by a description of the main Niobium content materials production and their more significant applications. Moreover, this work will also present and discuss the possible use of chlorination as an alternative route dedicated to metals extraction, prioritizing a general thermodynamic appreciation related to the behaviour of Nb_2O_5 being submitted to different chlorinating agents, considering the nowadays data available for this type of study.

Finally, it will also be presented a brief kinetic specific approach focusing on the physical structural transformations of a Nb_2O_5 & C mixture reacting with a top chlorine flow. It is understood that such description can be a relevant contribution to an eventual develop chlorination mathematical modelling in the future. Also, it is a great motivation of this Dissertation to provide a useful didactics approach for the covered theorical subjects such as energy change between states (standard, equilibrium and imposed) and entropy variation for chemical reactions.

2.2 Methodology

2.2.1 Thermodynamic Calculations

In order to evaluate the thermodynamic driving force towards chloride formation due to Nb_2O_5 exposition to an atmosphere containing a mixture of O_2 and Cl_2 , predominance diagrams were constructed in the range between 500 °C and 1500 °C, considering the data-base available in the software *HSC Chemistry, version 10.0.* For these computations, oxides were considered to be stoichiometric (chemical activity equal to one) and the gaseous phase to

behave ideally. This procedure will allow to see all the intermediates possible products formed in this system and the $NbCl_5$ appearance. It is valid to mention that the Species Distribution Diagrams were not covered because the thermodynamics comparative studies were determined to be based on, essentially considering, the $NbCl_5$ formation. The same data-base was also considered in order to construct Ellingham diagrams for Nb_2O_5 chlorination under the presence of graphite in the temperature range between 50 °C and 1000 °C, always considering the formation of $NbCl_5$.

2.2.2 Chlorination Tests

All the chlorination experiments were carried out in the same apparatus, which consisted of a vertical furnace where the crucible was placed inside with the solid sample. The samples were a mixture of spec pure graphite and niobium pentoxide powders elaborated at different percentages and porosities. Kinetic curves were then obtained at experiments under different temperatures. The conversion levels were easily obtained, after the graphite ignition, through the difference between the initial and the final niobium pentoxide weights. Also, in many experiments, the final pellet samples were sliced in two, three or four portions and analysed separately. So, the conversion level could be calculated for different layers of the sample and, consequently, the profile of the total conversion was observed through the sample thickness. Depending on the experimental conditions (temperature, graphite weight fraction and porosity) the chlorine penetration to the inner parts of the sample would vary from a difficult one (high temperature, enough carbon and low porosity) to an easy one (low temperature, low carbon and high porosity). The discussion, appreciation and explanation of these behaviours are the main topics of this work and it will be clearly seen in the section 4.3 of this dissertation:

A Kinetic appreciation and the physical aspect transformations of the reduction chlorination with $Cl_2 + C$. Figure 24 was built with these insights and considering that a good example to observe this phenomenon will be under

an overall 50% Nb_2O_5 conversion for different experimental conditions where it will then be possible to see the specific $\%Nb_2O_5$ reacted in each depth of the sample. Following that, it is proposed a theoretical mechanism for the rate of conversion at each layer of the sample depending on the experimental conditions. Finally, it is presented a figure where the type of reactions is proposed as function of three experimental variables (temperature, %Ci and porosity).

It is important to emphasize that the kinetic discussions are presented as a review of the mechanism proposals available in the work by Brocchi, 1983, called *Reduction Chlorination Reactions of Niobium and Tantalum oxide containing materials*. Also, it is expected to provide a contribution to both the didactics of basic thermodynamics and transport phenomena, the later through a proposal modelling for a gas-solid reaction such as shown in reaction 3.

$$(Nb_2O_5 + C)_{(s)} + Cl_{2(g)} \leftrightarrow NbCl_5 + CO/CO_2 \qquad [r.3]$$

The work mentioned above, Brocchi 1983, was based on more than two hundred runs carried out with samples, both loose powder or pellets with 1.0 cm height, inserted in a bottom perforated crucible with the chlorine flow touching, in most of the runs, only the top of the samples.

3. LITERATURE REVIEW

This study aims to present a group of important and up to date information's related to the two main subjects of this dissertation: niobium and chlorination.

It should be mentioned that with growing demand for certain metals, in order to supply the new technology's needs and some environmental aspects, the development of new extractive processes has again become very important. This tendency is confirmed by looking at the number of patents requirements in this area, which is nowadays very high as can be easily seen on the webpage of European Patent Office www.epo.org of 2023.

Some studies are reported on the hydrometallurgical recovery of niobium from their minerals (Agulyanski, 2004; Ayanda and Adekola, 2011;

Zhu and Cheng, 2011; Nguyen and Lee, 2019), focusing on the chemistry of Nb fluoride-based extraction in view of developing new materials for modern applications. Information on the Nb leaching has been described together with the purification processes that deliver Nb as oxide or as pure metal. Chlorination appears in addition as an alternative and attractive possibility of being part of new extractive routes to obtain particular metals since it is a method already industrially consolidated for extraction of other important metals such as Zr and Ti.

Therefore, based also on these facts, this section will be presented through the following topics.

(3.1) Nb characteristics / Properties and Applications / Availability and Demand;
(3.2) Chlorination of Nb_2O_5 containing materials;
(3.3) General chlorination: different materials and chlorinating agents;

3.1 Nb characteristics / Properties and Applications / Availability and Demand

3.1.1 Nb characteristics

Niobium was discovered by Charles Hatchett (1765-1847), an English chemist, in 1801 (TIC, 2009). Brazil holds the largest reserves of Nb content minerals such as pyrochlore (Shikika *et al*., 2020). This is known as major source for Nb and corresponds to $A_{2-m}B_2O_6(O,OH,F)_{1-n}$, where A is normally Na^+, Ca^{2+}, Ba^{2+} and B is principally Nb^{5+}. These informations remains updated (NIOBIUM, Proceedings of the International Symposium, 1984 & Benson, A. K. 2023).

Niobium (Nb) is element number 33 in the list of abundance in the crust of the Earth; it is less abundant than zinc (Zn), nickel (Ni), copper (Cu) or tungsten (W) but more abundant than cobalt (Co), molybdenum (Mo) or tantalum (Ta). Niobium makes 24 ppm of the crust but only 5ppm of the whole Earth; it is enriched in the mantle and the crust but depleted in the ore. Although, their abundance in the earth's crust is quite low, Nb around 24 ppm

(Makanyire *et al*., 2016; Allain *et al*., 2019). Niobium has a body-centred cubic crystal structure, with melting point 2477 °C and boiling point 4744 °C.

Niobium (Nb) is a metal which have an undisputed technological significance for our modern society, characterized by its high melting point – known as a refractory metal -, great conductivity, good ductility, high strength and exceptional resistance to corrosion (Dolganova *et al*., 2020). Besides that, niobium's growing importance as strategic metal is due to properties such as corrosion resistance, super conductivity, high electrical capacity and biocompatibility (Ayanda and Adekola, 2011).

3.1.2 Nb Properties and Applications

The extraordinary properties of niobium have rendered it a large spectrum of industrial and technological applications. Its significance became evident in the mid-1930s when niobium was first employed to stabilize stainless steel against corrosion. Subsequently, in the late 1950s and early 1960s, niobium's breakthrough role as a micro alloying element (MAE) for steel, typically in the range of 0.05 - 0.15 wt.%, further solidified its importance (Meyer, 2001; Heisterkamp and Carneiro, 2011). The importance of niobium as a MAE is due to its ability to enhance material properties such as high heat and corrosion resistance, increased strength, reduced density, exceptional conductivity, and enhanced biocompatibility. (Dolganova *et al*., 2020; da Silva Lima *et al*., 2022; McCaffrey *et al*., 2023). Its presence is essential in the construction of steel structures, including buildings, pipelines, bridges, offshore platforms, and automotive components, where it is predominantly employed as a MAE (Heisterkamp and Carneiro, 2011; Graedel *et al*., 2022; Bakry *et al*., 2023; McCaffrey *et al*., 2023). For instance, the construction of the Millau Valley in France, where the incorporation of just 0.025 wt.% Nb in steel resulted in a remarkable 60 % reduction in materials (Gibson, 2016). Similarly, the resound Bridge in Sweden utilized steel containing 0.02 wt.% Nb, leading to a 15 % weight reduction and cost savings amounting to 25 million USD (Bakry *et al*., 2023). These examples underscore the impactful role of niobium in enhancing the efficiency and cost-effectiveness of construction projects.

Moreover, Niobium is fundamental in advancing the development of technologies supporting the global energy transition, as it can contribute to this shift from non-renewable to renewable energy usage. The unique properties of Niobium can contribute to the creation of more efficient and sustainable energy solutions, be it through the advancement of next-generation batteries, or the development of powerful nanocrystalline magnetic materials.

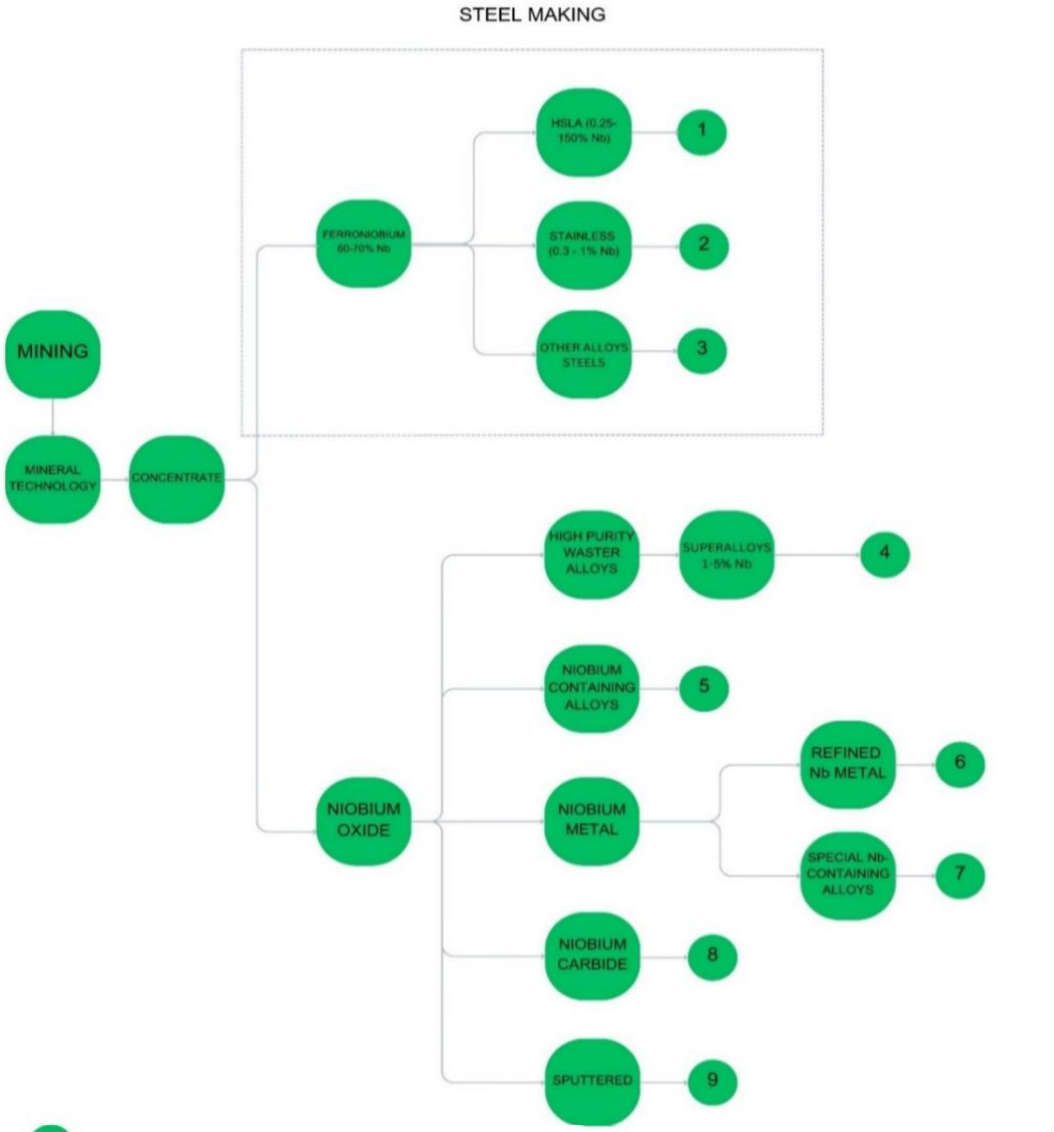
As global transportation demands evolve greater efficiency and safety, the Niobium anode technology is leading the evolution to enable ultra-fast charging and maximize the operational performance of Li on batteries, empowering sectors such as public transportation, logistics, and electrification to achieve their goals more effectively. Niobium is a versatile player when

considering the development of advanced materials revolutionizing the mobility industry. The incorporation of Niobium technology leads to the creation of stronger yet lighter materials, elevating vehicle safety standards and minimizing the impact of accidents (Niobium Tech, 2025).

Furthermore, niobium plays a crucial role in the production of superalloys, holding significant importance in aerospace and power generation technologies. (Heisterkamp and Carneiro, 2011; da Silva Lima *et al*., 2022). Its exceptional conductive properties also find applications in the healthcare industry, such as in MRI machines (Heisterkamp and Carneiro, 2011; McCaffrey *et al*., 2023). Currently, niobium is finding exciting new applications in the energy transition to low-carbon emission solutions, and it is already a key component in wind turbines. Nanocrystalline magnetic materials represent the forefront of innovative soft magnetic alloys designed to control and convert electricity efficiently. They play an important role in components such as common mode chokes (CMCs), filters, transformers & inverters. These components are used in renewable electricity conversion to extend the operating life of wind turbines, whilst ensuring the consistent supply of clean and stable electricity from solar panels. In solar generation, they help to make reliable ultra-compact high-performance EMCs that improve safety and grid stability. Final applications of these critical components include but are not limited to charging stations, on-board chargers and smart meters (Niobium Tech, 2025).

Ongoing research into niobium-based rechargeable batteries holds the potential for further advancements in sustainable energy technologies, and it is being explored for use in solar panels and smart glass that can filter sunlight radiation and control the amount of light and heat entering buildings (European *et al*., 2020; da Silva Lima *et al*., 2022; CBMM 2023, Niobium Tech 2025). In Figure 1 it is presented a selection of those diversified applications of niobium containing materials both as a content element in steels as in different materials. Niobium plays a key role in the development of advanced technologies for batteries, these include fast-charging capabilities, stable delivery of high energy densities, and improved safety for enhanced durability. This makes it an ideal choice for energy storage applications. Niobium's versatility extends to the formulation of new anode materials, enabling

batteries with high power, rapid charging, wider operating temperatures, and exceptional longevity, all while prioritizing safety. By incorporating Niobium as a dopant and coating material, is possible to obtain successfully developed cobalt-reduced or cobalt-free cathodes. These innovative cathodes offer higher performance, improved electronic conductivity, and long-term stability. Niobium also finds application in turbochargers, where small quantities of Niobium addition can improve mechanical and thermal properties, besides increasing margins and productivity by reducing scrap (Niobium Tech 2025).



1. Oil and pipelines; railroad equipment, offshore platforms; bridges; transportation industry.
2. Chemical processing plants.
3. Heat resisting steel(1%Nb): furnace-parts;muffles; tubes; retorts.
4. Gas turbines; rocket parts; heat resistant and combustion equipment; jet engines; petroleum, nuclear and auto industry.
5. Parts in high temperature vacuum furnaces; aerospace applications (rocket parts); nuclear parts.
6. Fusion reactors.
7. Nuclear engineering equipment; space and military industry; superconductors.
8. Machine cutting tools.
9. Optical applications.

Figure 1: A selection of niobium containing materials and their main applications. Source: (Brocchi E. A., Reduction chlorination reactions of Niobium and Tantalum Oxide containing materials, 1983).

Apart from this, Niobium enhanced carbon steels are also paving their way into the hydrogen gas transmission ecosystem, ensuring continued participation in creating a more sustainable future for the world. Figure 2 presents the benefits of Niobium.

Figure 2: Benefits of Niobium. Source: Niobium Tech, 2025.

3.1.3 Nb Availability and Demand

Table 1 outlines the major deposits of Nb ores, as well as the corresponding companies exploiting them. Generally, the concentrate from the pyrochlore flotation is used as ferroniobium feedstock. For this purpose, the concentrate is mixed with iron oxide and aluminium, then these oxides are reduced by an aluminothermic reaction to form a ferroalloy, commonly referred as ferroniobium. In another route Nb_2O_5 is the main product which can also be reduced by aluminothermic reduction to generate Nb metal. A small part of it is purified by electron beam melting for further specific applications such as high-quality alloy.

Three main types of Ta and Nb deposits (Linnen *et al*., 2013; Melcher *et al*., 2017) could be grouped as: (i) carbonatites and associated rocks (pyrochlore: rich in Nb), (ii) alkaline to peralkaline granites and syenites (rich in Ta, Nb and rare earth elements), and (iii) granites and pegmatites of the lithium, caesium and tantalum (LCT) family. More than 150 minerals of Ta and Nb are known to accompany these deposits (Nete, 2009; Theron *et al*., 2011).

Table 1 - *Principal deposits of Nb ores*

Deposit	Mining company	Country	Types of ore	Reserves (Mt)	Mean head grade, (%)	Ore Processing	References
Araxá	CBMM	Brazil	Carbonatite	462	2.48	Alumino thermic reduction, flotation	(Papp, 2008)
Catalão mine	China Molybdenum	Brazil	Carbonatite	42	1.2	Flotation, aluminothermic reduction	(Linnen *et al*., 2013)
Niobec mine	Magris Resources Inc.	Canada	Carbonatite	630	0.42	Flotation, Alumino thermic reduction	(BRGM, 2012)
Aley	Taseko Mines Ltd.Corp	Canada	Carbonatite	84	0.5	Alumino thermic reduction	(Mackay and Mackay and Simandl, 2014)

Table 1: Principal deposits of Nb ores. Source: (Shikika *et al*., Hydrometallurgy, 2020).

However, only two mineral groups (titano-niobates and tantalum-niobates) are considered as economically feasible for extraction of niobium. The titano-niobates group is the largest source of niobium and tantalum. Within this group, a pyrochlore subgroup with predominating niobium presence (40% - 65% Nb_2O_5) in the mineral matrix. Table 2, summarises the most economically important minerals of Nb, and Figure 3 illustrates the global distribution of the ore deposits containing this mineral. (Shikika A., Sethurajan M., Muvundja F., Mugumaodrha M. C., Gaydardzhiev St., 2020).

A separation of these metals from the original ore material – mineral groups – motivates several kind of research since it can be attained throguh

hydrometallurgy (leaching and selective precipitations) or pyrometallurgy (roasting and gaseous separation).

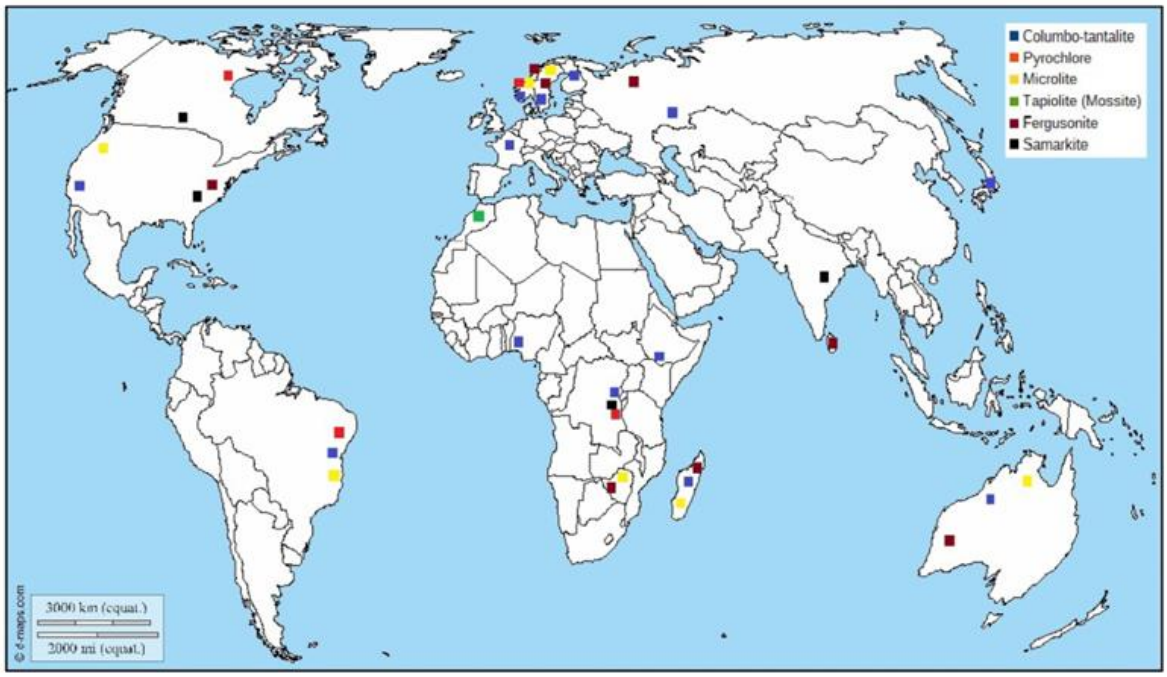


Figure 3: Global distribution of the economically important Nb bearing deposits with the respective main minerals (image developed based on http://www.d maps.com). Source: (Shikika *et al*., 2020).

Table 2 - Overview of the economically important Ta and Nb minerals.

Minerals	Chemical formula	Location	References
Microlite	$(Na, Ca)_2(Ta, Nb)_2$ $(O, OH, F)O_6$	Norway, Sweden, Zimbabwe, U.S.A, Brazil, Australia, Madagascar	(Alfonso *et al*., 2016)
Colombo-tantalite	$(Fe, Mn)(Nb, Ta)_2O_6$	France, Norway, Finland, Russia, Australia, U.S.A, Brazil, DRC, Japan, Madagascar, Ethiopia, Nigeria	(Alfonso *et al*., 2016)
Pyrochlore	$(Na, Ca)_2(Nb, Ta)_2O_6(O, OH$	Brazil, Canada, DRC, Norway	(Papp, 2015; Schulz *et al*., 2017)
Tap iolite MOs site	$Fe\ (Nb, Ta)_2O_6$	Morocco	(Papp, 2015)
Fergusonite	$(Y, Er, Ce, Fe)(Nb, Ta, Ti)O_4$	Norway, Sweden, Russia, Rhodesia, Srilanka, U.S.A, Australia, Madagascar	(Alfonso *et al*., 2016)
Samarskite	$(Y, Er, Ce, Fe, U, Ca, Pb, Th)$ – $(Nb, Ta, Ti, Sn)_2O_6$	U.S.A, Canada, India, DRC	(Papp, 2015; Schulz *et al*., 2017)

Table 2: Overview of the economically important Ta and Nb minerals. Source: (Shikika *et al*., Hydrometallurgy, 2020).

Niobium appears in various minerals and in combination with oxide impurities that impede their metallurgical processing (Ungerer *et al*., 2014). The estimated niobium reserves, primarily located in Brazil, are considerably capable of satisfying future global demand for decades and even centuries (Chaves, 2019; United States Geological Survey (USGS), 2023).

A detailed study of Gómez M. *et al*., 2024 utilizing logistic growth with historical data covers the period from 1940s to 2022. In the same reference it

can also be found the niobium production estimation based on the steel production as the Nb demand is strictly linked to the steel demand due to the enduring role of Nb as crucial alloy element in the steel manufacturing. A forecast prediction for 2030, 2040 and 2050 can be found in the reference Chaves 2019 and USGS 2023. It is valid to mention that niobium has played an important role in the development of our society and its continued importance underscores the need to bring it into focus.

Over the past seven decades, the demand for niobium has significantly increased, primarily driven by its essential role as a low alloy element in the steel industry, from nearly 0.6 Mt in the 1950s to approximately 8.5 Mt, 32.3 Mt, and 79 Mt in 1980, 2000, and 2022, respectively (United States Geological Survey (USGS), 2023).

Brazil has dominated the production of niobium, accounting for nearly 90 % of global production since the 1990s, with Canada following as the second-largest producer, contributing approximately 8.6 %. Nevertheless, due to niobium's heavy reliance on a small number of countries for mine production, its growing integration into modern, energy-efficient, low-emission technologies, and the absence of viable substitutes or substantial performance trade-offs linked to substitution, niobium has been classified as a critical material by the European Union (Grohol *et al*., 2023), the United States (U. S. Geological Survey, 2022), Australia (Australian Government Department of Industry and Science and Resources, 2023), India (India Ministry of Mines, 2023), Japan, and Canada (Graedel *et al*., 2022).

Cumulatively, over this 22-year period, the total niobium production reaches 1312.4 kt, with a predominant share of 90.1 % originating from Brazil (81 % in Araxá and 9 % in Catalão), 8.6 % from Quebec, and the remaining 1.4 % from other regions (United States Geological Survey (USGS), 2023).

In terms of niobium's future, it has been predicted that the production will exhibit a consistent upward trend over the decades. Table 3 exhibits some information about the major industries and employed processes leading to Ta and Nb products such as the metal, oxides and carbides extracted from the reference Shikika A. *et al*., 2020.

Table 3 - Major *industrial players and employed processes leading to Ta-Nb end products.*

$Ta-Nb$ plant	Location	Feed materials	High purity end products	Process	References
Ningxia Non-ferrous Metals	China	$Ta-Nb$ concentrate	Ta metal, Ta_2O_5 & Nb_2O_5	$HF-H_2SO_4$ leaching, SX with MIBK	(He *et al.*, 1997; Papp, 2008; BRGM, 2012)
Conghua Tantalum and Niobium Smeltery (CTNS)		$Ta-Nb$ concentrate	Ta_2O_5 & Nb_2O_5	$HF-H_2SO_4$ leaching, SX with MIBK	
F and X Electro-Materials Limited		$Ta-Nb$ concentrate	Ta_2O_5 & Nb_2O_5, Ta - Nb metals	$HF-H_2SO_4$ leaching, SX with MIBK	
Fogang Jiata Metals		$Ta-Nb$ concentrate	TaF_5, K_2TaF_7	$HF-H_2SO_4$ leaching, SX with MIBK	
Ningxia orient		$Ta-Nb$ concentrate	TaF_5, $TaCl_5$, K_2TaF_7	HF leaching, SX	
Global Advanced Metals	Australia	Ta ore	Ta powder, Ta_2O_5	$HF-H_2SO_4$ leaching, SX with MIBK	www.globaladvancedmetals.com

Cabot Corp.	USA	$Ta-Nb$ ore	Ta_2O_5, Nb_2O_5, Ta and Nb metal, Ta and Nb carbide.		(BRGM, 2012)
HC.Start Inc.		$Ta-Nb$ concentrate	Ta and Nb metal, Ta capacitor powder		(BRGM, 2012)
Wah Chang		Pyrochlore concentrate	Nb metal, $Fe-Nb$ alloy, and K-salt		(Papp, 2008)
Niotan Inc.		Ta_2O_5	Ta powder	Alumino thermic reduction	(BRGM, 2012)
Companhia Industrial Fluminense (CIF)	Brazil	$Ta-Nb$ ore	Ta_2O_5 & Nb_2O_5	$HF-H_2SO_4$ leaching, SX with MIBK	(BRGM, 2012), www.cif.ind.br
Solikamsk Magnesium works	Russia	Loparite minerals	Ta metal & Ta_2O_5	HF-H_2SO4 leaching, SX with TBP	(Papp, 2008; BRGM, 2012)
Ulba Metallurgical	Kazakhstan	$Ta-Nb$ concentrate	Ta metal & Ta_2O_5	HF leaching, SX	(Papp, 2008), www.ulba.kz

Irtysh Chemical and Metallurgical Works		Nb concentrate	Nb metal & Nb_2O_5	N.A.	(Papp, 2008)
Mitsui Miningand Smelting Co	Japan	$Ta-Nb$ concentrate	Nb_2O_5 & Ta_2O_5, Nb and Ta metal, Ta carbide	HF + H_2SO4 leaching, SX with MIBK	(BRGM, 2012), www.mitsui-kinzoku.co.jp
H.C.Starck GmbH and Co. KG	Germany	$Ta-Nb$ concentrate	Nb_2O_5 & Ta_2O_5, Ta and Nb metal, Ta carbide, K-salt, $Fe-Nb$ alloy	HF - H_2SO4 leaching, SX with MIBK	(Papp, 2008), www.hcstarck.com

Table 3: Overview of the economically important Ta and Nb minerals. Source: (Shikika *et al.*, Hydrometallurgy, 2020).

Figure 4 bellow illustrates the global niobium material flow analysis (MFA) spanning the years 2000 to 2022.

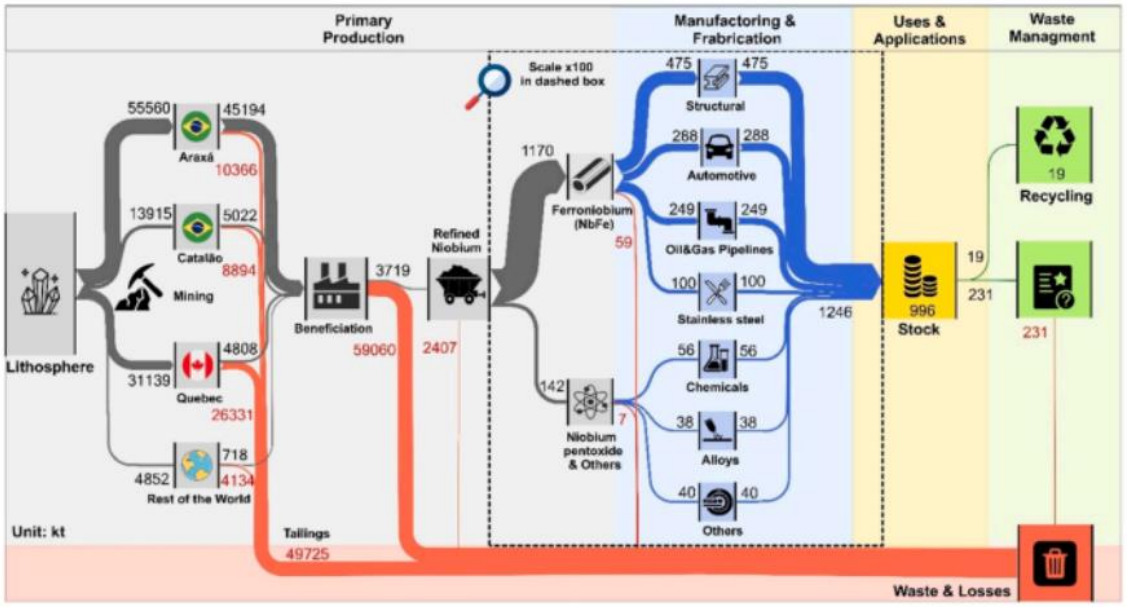


Figure 4: Worldwide dynamics of niobium by dynamic MFA from 2000 to 2022. Source: (Shikika *et al.*, Hydrometallurgy, 2020).

This limited availability is driving the need to valorise secondary raw materials containing Nb, among them tin slags, but also metallic scraps and by-products.

3.2 Chlorination of Nb_2O_5 containing materials

Chlorination of Nb_2O_5 containing materials has been studied as an alternative route for treating complex minerals and residues containing Nb and Ta such as the slags from Sn production. (Brocchi E. A. *et al.*, 2016). In that sense several Chlorine Metallurgy studies have been published in the last decades and will be described through this section, either dealing with theoretical aspects or discussing experimental results. This study comprehends some researches and articles from the years 1950 until today.

When discussing chlorination, a recognized important contribution to the field of niobium chlorination is the one by Richard S. Olsen & Frank E. Block, 1968, in *The Chlorination of Columbite in a Fluidized-Bed Reactor.* In general, reductive chlorination of metal oxides at temperatures below 550 ºC, usually follow a reaction 4 similar to, (Olsen R. S. and Block F. E., 1968)

$$MeO_2 + C + 2Cl_2 \rightarrow MeCl_4 + CO_2 \qquad [r.4]$$

However, some metal oxides such as the Nb pentoxide tend to also form oxychlorides, when reacted with carbon and chlorine, as follow in the reaction 5.

$$2Nb_2O_5 + 3C + 6Cl_2 \rightarrow 4NbOCl_3 + 3CO_2 \qquad [r.5]$$

The oxychloride can then be further chlorinated to form the oxygen-free pentachloride. As can be observed in reaction 6.

$$2NbOCl_3 + C + 2Cl_2 \rightarrow 2NbCl_5 + CO_2 \qquad [r.6]$$

In the case of niobium, the pentachloride is much preferred when compared to the oxychloride as the oxychloride condenses as a cottony mass which is difficult to handle and transport. The investigation showed that a typical columbite mineral can be easily chlorinated in a fluidized-bed reactor. Additionally, Olsen R. S. and Block F. E. affirm the recovery of Nb is almost complete in the chlorination with C presence. The carbochlorination process is generally conducted at high temperatures (800 °C – 1000 °C), where Cl_2 reacts with the metal oxide in the presence of a reducing agent in order to form the volatile desired chloride.

An interesting article, *Aspects of Chlorination and its Potencial to Produce Niobium Pentoxide*, was presented in the “Conference Jointly Sponsored by ABM and ASM”, 1984, covering the Nb_2O_5 production on a cold finger from the $NbCl_5$ previously formed, just like TiO_2 pigment is industrially formed from $TiCl_4$. The carbochlorination action on the Nb_2O_5 attends high levels of efficiency at temperature about 800 °C.

Kroll W. J., Nieberlein V. A., May S. L. and Engel C. T., studied a chlorination of a material, NbC, previously formed by the following steps: i) mineral or concentrate reduction with C at 1500 °C in an inert atmosphere and ii) chlorination in the range temperature of 400 °C – 600 °C. This innovative method has the advantage of applying the chlorination in a free oxygen material and be conducted in a relatively low temperature. However, in practical terms, it has an expensive previous reaction through the reduction of the oxidized mineral at very high temperatures for the formation of the NbC.

Another study about the chlorination of ore concentrates is from Habashi and Malinsky, 1975. They use the chlorination with the goal of produce Nb_2O_5 with technical purity from a pyrochlore (Oka, Canada) with 52.5% of Nb_2O_5 in a temperature range 500 °C – 700 °C. This concentrate demonstrates its resistance to the reactions with $HCl_{(g)}$ until 700 °C, to the direct chlorination (reaction with gaseous Cl_2) until 900 °C and to the mixture of $Cl_2 - CO$ attack until 700 °C. At 600 °C, the reaction with a mixture of $Cl_2 - SO_2$ provides approximately 60% niobium volatilized after 6 hours. Habashi and Malinsky suggest that the adequate method to treat the pyrochlore is the carbochlorination. A typical result shows that after 1 hour of reaction at 700 °C with %C around 35% in weight - w/w - provides about 96% of Nb_2O_5 conversion into $NbCl_5$.

The article, *Reduction Chlorination of Niobium Pentoxide* (Brocchi and Jeffes, 1985), discuss the possible physical mechanisms for the carbochlorination reaction, studying the effect of some system variables. It was found that a balance between temperature and percentage of carbon in the solid mixture will be responsible for different initial reactions rates.

A collection of articles related to *Chlorine Metallurgy* was presented in a review paper published by Lino R. Freitas, Eduardo A. Brocchi and Francisco J. Moura, 1989, *Applications and Potential Uses of Chlorination Methods in Extractive Metallurgy*. Another work with the same purpose was published in Mineral Processing and Extractive Metallurgy, *Halide Metallurgy of Refractory Metals* (Jena P. K. and Brocchi A. E., 1992). It explores the application of chlorine content agent in opening content refractory metals ores. Thermodynamics and kinetics aspects were discussed. The work concludes that developments in the halide metallurgy were slow due to corrosion problems, high cost of chemicals and a narrow selection range of reactor materials. However, studies in the halide metallurgy remains of interest, particularly when related to the extraction of refractory metals from lean and complex ores or slags. Based on promising research and developmental studies made on Chlorine Metallurgy, pilot plant investigations have been carried out with the purpose to evaluate its potential in large scale. (Jena P. K. and Brocchi, A. E. 1997).

González et al., 1997 confirms that the direct reaction between Cl_2 and oxides of Nb and Ta for producing the respective chlorides is not thermodynamically feasible under 1000 ºC. That's why the chlorination is performed in the presence of reducing agents such as carbon or a carbon bearing material like CO. Then, in the range of 700 °C to 800 °C, niobium chloride can be obtained along with gaseous CO/CO_2, in addition to unreacted carbon and $Cl_{2(g)}$. According to these authors, the excess carbon in the samples creates a porous surface (including unreacted carbon), and then the diffusion of chlorine gas through this surface to the inner parts of the briquette, or the diffusion of $CO_{(g)}$ and $NbCl_{5(g)}$ to leave out the sample, may be the slowest step – controlling step - of the studied reaction system. It agrees with the work of Movahedian *et al*., 2000 for the zirconium dioxide carbochlorination.

Brocchi and Moura's study of 2008, *Chlorination methods applied to recover refractory metals from tin slags*, described the sequence of metal carbochlorination at temperatures that oscillated in the range between 600 °C and 900 °C. In general, the elements kinetics is as follows: Ca reacts first, followed by Fe, then Nb, Ta, and Ti, and finally Si. This suggests that Ca and Fe have a higher tendency to react with Cl compared to Nb, while Si is the last to form chlorides. The experimental results indicate that, for any of the available tin slags, a 40 min chlorination reaction carried out at 900 °C, can transform most of the refractory metals oxides content into their chlorides.

In the study *Novel Technology for Chlorination of Niobium and Tantalum Oxides and Their Low-Grade Ore Concentrates* by Shainyan A. B. et al., (2008), an innovative energy-efficient and environmentally sustainable process was studied related to the chlorination of niobium and tantalum oxides, as well as their low-grade ore concentrates. The procedure utilizes carbon tetrachloride, CCl_4, or silicon tetrachloride, $SiCl_4$, as chlorinating agents under pressure, offering a more eco-friendly and cost-effective approach to refining these metals due to it low temperature process and knowledge of the necessary equipment. It concludes that the temperature range of the chlorination process can decrease from 800 °C -1000 °C (normal

carbochlorination) to 250 °C - 300 °C (above referenced work), therefore, contributing to minimize energy consumption.

3.3 General Chlorination: different materials and chlorinating agents

A classic work published by O. Knacke, 1970, Technische Hochschule Aachen - *On the chlorination of metal oxides* – measures partial pressures to define thermochemical investigation of systems such as U-O-Cl. According to the author, the purpose of classical chlorination is to transform insoluble compounds, such as Cu_2S, by addition of solid chlorides, like $NaCl$, into soluble salts, e.g., Cu_2Cl_2, or into volatile chlorides, through reaction with gaseous chlorinating agents such as Cl_2 or CCl_4 e.g., $SnCl_4$ or $ZnCl_2$. Hence chlorine is increasingly being used on a technical scale as a gaseous reactant to produce volatile chlorides of tin, uranium, titanium, niobium and iron from the respective oxides. This study considers two aspects of chlorination, namely, the transformation of an oxide into a volatile chloride and the reverse reaction, i.e. the re-oxidation of the chloride. In both directions, oxychlorides frequently appear as intermediary phases and tend to slow down the reaction rates. In the study of uranium dioxide, UO_2, chlorination, formation of interfering oxychlorides - e.g. $UOCl_2$ - has been observed in agreement with the equilibrium diagram, the effect of the intermediary phases is particularly grave or even catastrophic because its formation slow down the whole reaction or even stopping it. The kinetic investigations were studied in two directions. One considering the starting material preferentially as double oxides or oxide solution phases while the second concerns the chlorination of oxide particles embedded in an inert matrix.

Studies from Jena *et al*. 1986, Allain 1997 and Jena *et al*. 1997 indicate that in a gaseous mixture of $Cl_2 + CO + N_2$, the partial oxygen pressure is estimated to be approximately 10^{-28} atm at 500 °C, while for chlorination in the presence of carbon, the partial oxygen pressure is around 10^{-20} atm at the same temperature. These values clearly indicate that the C presence decreases the oxygen partial pressure.

The study named *Kinetics of chlorination of TiO_2 by Cl_2 in the presence of graphite powder* published in Mineral Processing and Extractive Metallurgy

in 1998 predicts that chlorination, either in low or high temperature range, follows the topochemical reaction model in some experimental conditions. In the lower temperature range the rate of chlorination was found to be proportional to pCl_2 and the activation energy of the process was calculated to be 130 kJ/mol. In the higher temperature range, although, the rate was found to be proportional to the square root of pCl_2 and the activation energy decreases to 12 kJ/mol (Jena P. K., Brocchi E. A. and Gameiro D.H., 1998). These activation energy values indicate that in low temperature the process tends to be chemical controlled while at high temperatures the whole reaction system is diffusional controlled.

Different chlorination agents had been studied. It is the case of the work *Kinetic modelling of CuO and Ta_2O_5 chlorination with tetrachloroethylene*, 2019. In this work was studied a thermodynamic performance evaluation of the processes from speciation diagrams for equilibrium, as well as the modelling of kinetic data associated with the chlorination of copper oxide (CuO - 923K to 1173 K) and tantalum pentoxide (Ta_2O_5 - 1073 K to 1223 K), in an atmosphere of C_2Cl_4 diluted in N_2. The diffusional model showed global activation energy for the CuO of 71.5 ± 10 kJ/mol and 62.2 ± 10 kJ/mol for Ta_2O_5, while with chemical control, for CuO, 118.0 ± 10 kJ/mol was obtained and for Ta_2O_5 a value of 119,1 ± 10 kJ/mol A derivate article from this dissertation is the work *Chlorination of tantalum pentoxide with tetrachloroethylene* by Zocatelli, T.F. Siqueira, R. C and Brocchi E. A. (2016) where the reaction with CCl_4 and C_2Cl_4 are discussed kinetically.

Also, the article *Study on the thermodynamic viability of NiO and CuO chlorination with C_2Cl_4 at high temperatures* published in Thermochimica Acta in 2017 concludes that the absence of carbon in the reacted samples is also a remarkable finding. As shown by the simulations, C_2Cl_4 has a strong decomposition tendency, thereby resulting in the formation of volatile CCl_4 and solid graphite, even at very low temperatures.

A detailed study named *A chemical thermodynamics review applied to V_2O_5 chlorination* from Brocchi E. A., Navarro R. C. S. and Moura F. J., 2013, concludes that the speciation calculations indicate that the concentration of the gas phase generated during the chlorination process is very sensitive to

variation in temperature, pCl_2 and pO_2. Finally, this study also concludes that the study of the equilibrium states achievable through the reaction between a transition metal oxide and gaseous Cl_2, can be now approached through the implementation of methods of different complexity levels. The most general one, in which the total Gibbs Free Energy of the reaction system is minimized, enables the construction of a more detailed (quantitative) picture of the equilibrium states involved. Comparing to Nb_2O_5 it is possible to affirm these both transition metals when chlorinated in a chlorine atmosphere will produce their chlorides, VCl_5 and $NbCl_5$, necessarily passing through intermediate compounds.

Chlorination and carbochlorination have already been studied (Gaballah *et al*., 1994 and Nete *et al*., 2017 and Ibrahim *et al*., 2020) and it was also studied by de Oliveira et al, 2022 in the work published in the Canadian Journal of Chemical Engineering. The authors demonstrated the possibility of tin slag carbochlorination from 800 °C. The maximum extraction observed during a chlorination process was 85% Nb and 65% Ta at a temperature of 1000 °C. Si and Ti can also be halogenated by this method, but they condensate at very low temperatures, which is favourable to separate them from Nb and Ta.

Pistorius P.C. and Ferdus Le Roux J. T. in 2002 at *Thermal Chemical* published the work *Structural changes during initial chlorination of titania slag,* which states that for industrial chlorination, the implications are that the rate's position of energy release when slag is charged to a chlorinator depend on both the heat released with the reaction (which is readily calculated from the slag composition) and the rate of the reaction (which can only be established experimentally, preferably by measuring movement of the internal reaction front with time). This article explored differences in the chlorination behaviour of two Titania slags that were studied in a laboratory chlorinator at 950 °C. The differences operated on two-time scales: within the first few minutes, nearly all of the FeO and MnO was chlorinated and then over tens of minutes the remaining material – largely TiO_2 – was chlorinated more slowly. Rapid changes occur during the initial chlorination of titania slags. These changes

are localized at a reaction front where the Ti_2O_3 is oxidized to $Ti^{4+}$and nearly all the FeO and MnO are transformed to their volatile chlorides.

In a review by Habashi, presented in the 32nd Annual Hydrometallurgy Meeting, Chloride Metallurgy, 2002, it is discussed the chlorination of oxides using carbon, C, and carbon monoxide, $CO_{(g)}$, as reducing agents, the main focus being the recovery of titanium metal from treating an Indian ilmenite to produce rutile and direct recycling of recovered chlorine.

Sombra F. S., 2015 did a theorical revision related to possible different chlorinating agents. The experimental studies involved roasting with Cl_2 and with $CaCl_2$. A derivate article from this dissertation is the work published in 2018 stating that the separation of Zn and Fe present in franklinite is viable through the late type. In a comparative approach, this analysis was based on both the reaction of isolated iron oxide (Fe-O-Cl system) and zinc oxide (Zn-O-Cl system) as well as on the reaction of the zinc ferrite itself. The work *Characterization and Chemical Processing Using Chlorinating Reagents of an Industrial Waste* has mentioned this new method as being selective and suitable for the industrial residue recycling which contains franklinite. This is due to the fact that the direct chlorination routes with $CaCl_2$ clearly present positive perspectives. At 1100 °C and with 40% of excess, the roasting allowed to practically remove 100% of Zn as a volatile chloride with 21.6% removal of Fe. It's recommended to study the roasting reaction below in order to optimize the operational conditions in the 700 °C – 1000 °C range of temperature, the reaction 7 above were performed.

$$ZnFe_2O_4 + CaCl_2 + C + O_{2(g)} \leftrightarrow ZnCl_2 + Fe_2O_3 + CaO + CO_{2(g)} \; [r.7]$$

A study presented in 2021 at The Minerals, Metals & Materials Society affirms the chlorination behaviour of a low-grade titanium slag in an $AlCl_3 - NaCl$ molten salt describes a thermodynamic analysis and an experimental procedure with their results. In this paper the chlorination behaviour of low grades titanium slag by anhydrous $AlCl_3$ in $AlCl_3 - NaCl$ was investigated. Under optimized experimental condition, the selective separation of Ti from titanium slag was achieved and 79.6% was transformed when treated at 1023

K for 3 h while other impurities remained in the chlorination residue (Dem P. *et al*., 2022).

4. RESULTS AND DISCUSSION

The bibliographic survey permits to affirm that chlorination can be considered an alternative route for value metals recovery from different kind of materials. However, before any experimental work it would be recommended a theorical approach in order to appreciate the real viability of these reaction to take place. In the other end Niobium should be seen as a good metal to be studied as it has, nowadays, a clear industrial importance and, also, its recovery should be carried out from different sources, including some residues. Microalloying steel with niobium simultaneously increases its strength and toughness. This enables the automotive industry to create lightweight vehicle designs, which leads to improved fuel efficiency and, consequently, CO_2 lower emissions (ABM, 2014).

Thermodynamics enables a quantitative assessment of the tendency of a reaction to proceed in each direction, allowing the system equilibrium composition determination and the conditions' prediction under which the desired product can be obtained. In this work, the approach to the thermodynamics of niobium pentoxide chlorination and carbochlorination primarily involves a Predominance Diagrams analysis followed by a study related to the Standard Gibbs Free Energy Diagrams and finally a review on some kinetics considerations. It is well known that through thermodynamic analysis, it is possible to assess the feasibility of a particular chemical reaction. In fact, thermodynamics allows predict of the equilibrium conversions in a closed chemical reaction system, indicating the trends and conditions that should be imposed on the system (temperature and/or concentration/partial pressure of reactants and products) to generate a chemical potential or enough driving force that enables the formation of a desired product. Therefore, it is understood that a general thermodynamic study of the niobium oxide different chlorination possibilities would be an interesting and timely initiative regarding this metal possible extractive routes.

4.1 A general view of the Nb-O-Cl system through Diagrams of Predominance

In that sense, the niobium oxygen chlorine, Nb-O-Cl, system can be first observed through the predominance diagrams. Generally, it illustrates the most thermodynamically stable species of an element, such as niobium, under different conditions, in this case, varying partial pressures of gases throughout those of oxygen (pO_2) and chlorine (pCl_2). At the straight lines or boundaries between the regions indicates the conditions when two species coexist in equilibrium as shown in the example below, as can be seen in reaction 8 and its equilibrium constant evidenced in equations [1] to [4].

$$Nb_2O_5 + Cl_2 \leftrightarrow 2NbO_2Cl + \frac{1}{2}O_2 \qquad [r.8]$$

$$K = K_{EQ} = \frac{pO_2{}^{\frac{1}{2}}}{pCl_2} \qquad [1]$$

$$logK = log(pO_2)^{\frac{1}{2}} - log(pCl_2) \qquad [2]$$

$$logK = \frac{1}{2}log\ (pO_2) - log(pCl_2) \qquad [3]$$

$$log(pCl_2) = \frac{1}{2}log(pO_2) - logK \qquad [4]$$

The mathematical demonstration above contributes to arrive at the linear equation, its angular and linear coefficient are $\frac{1}{2}log(pO_2)$ & $logK$, respectively, in order to find the equilibrium constant through the partial pressures imposed.

Predominance Diagrams for the system Nb-O-Cl at 500 ºC, 1000 ºC and 1500 ºC, are observed in the Figures 5, 6 and 7, respectively. It is important to mention that all of them are in the same scale in order to be compared. The Cartesians axes present in the 2D Predominance Diagram for Nb-O-Cl System are partial pressure of O_2 as the axis of abscissas and partial pressure of Cl_2 as the axis of ordinates. These diagrams help visualize the stability of Nb different compounds at varying temperature and chlorine pressures.

4.1.1 Nb-O-Cl System at 500 °C

In the Predominance Area Diagram at 500 ºC presented in the Figure 5 it is observed the presence of Nb_2O_5, NbO_2Cl and $NbCl_5$ within three distinct stability regions. It shows the presence of the specie Nb_2O_5 from $pO_2 = 10^{-30} atm$ to $pO_2 = 1\ atm$ while pCl_2 goes from $10^{-16}\ atm$ to $10^{-2} atm$. Then, Nb_2O_5 is stable from very low oxygen partial pressures and up to high chlorine partial pressures.

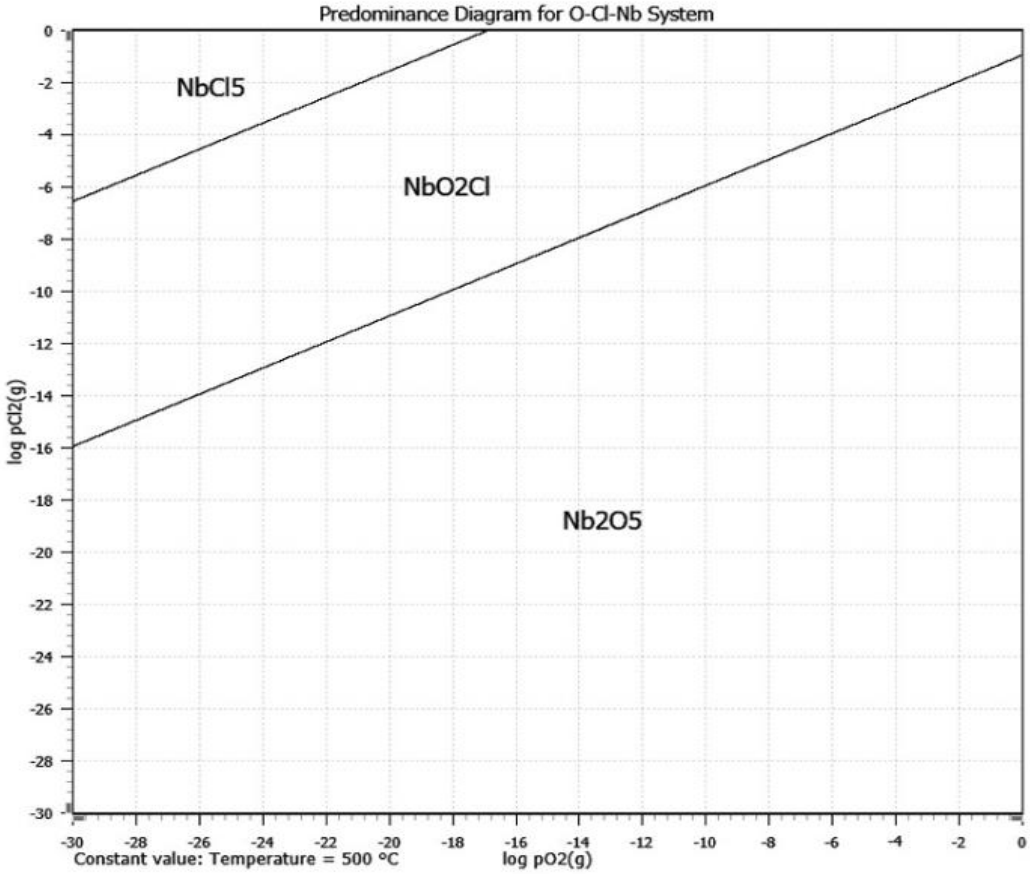


Figure 5: Predominance Area Diagram for the system Nb-O-Cl at 500 ºC extracted from HSC 10 Chemistry.

The boundaries between the regions are straight lines, indicating that the transitions between stable compounds are dependent on the ratio and magnitude of $\log pCl_2$ and $\log pO_2$. $NbCl_5$ is only stable at high chlorine partial pressures and low oxygen partial pressures. This is logical, as this compound is rich in chlorine and has no oxygen. NbO_2Cl is stable in the intermediate region while $NbCl_5$ is only formed at high chlorine partial pressures.

The straight lines on the diagram represent the equilibrium conditions for reactions between the compounds. For example, the boundary between

the $NbCl_5$ and NbO_2Cl regions represent the conditions where these two species coexist in equilibrium. A change in the partial pressures across this line will cause a phase transition from one stable compound to another. It's possible to predict that at 500 ºC, Nb_2O_5 is dominant, with limited formation of Nb chlorides and no presence of Nb metal.

4.1.2 Nb-O-Cl System at 1000 °C

In the Predominance Area Diagram at 1000 ºC presented in the Figure 6 it is observed the presence of Nb, NbO, NbO_2, Nb_2O_5, $NbCl_{2.33}$, $NbCl_{2.67}$, $NbCl_{3.13}$, $NbCl_5$ & NbO_2Cl. Compared to the 500 °C diagram, the 1000 °C diagram shows a wider variety of stable niobium compounds. As the temperature increases, more species, including different niobium oxides and chlorides, become thermodynamically favoured. The chlorination process may have more intermediaries' products being formed until the desired one.

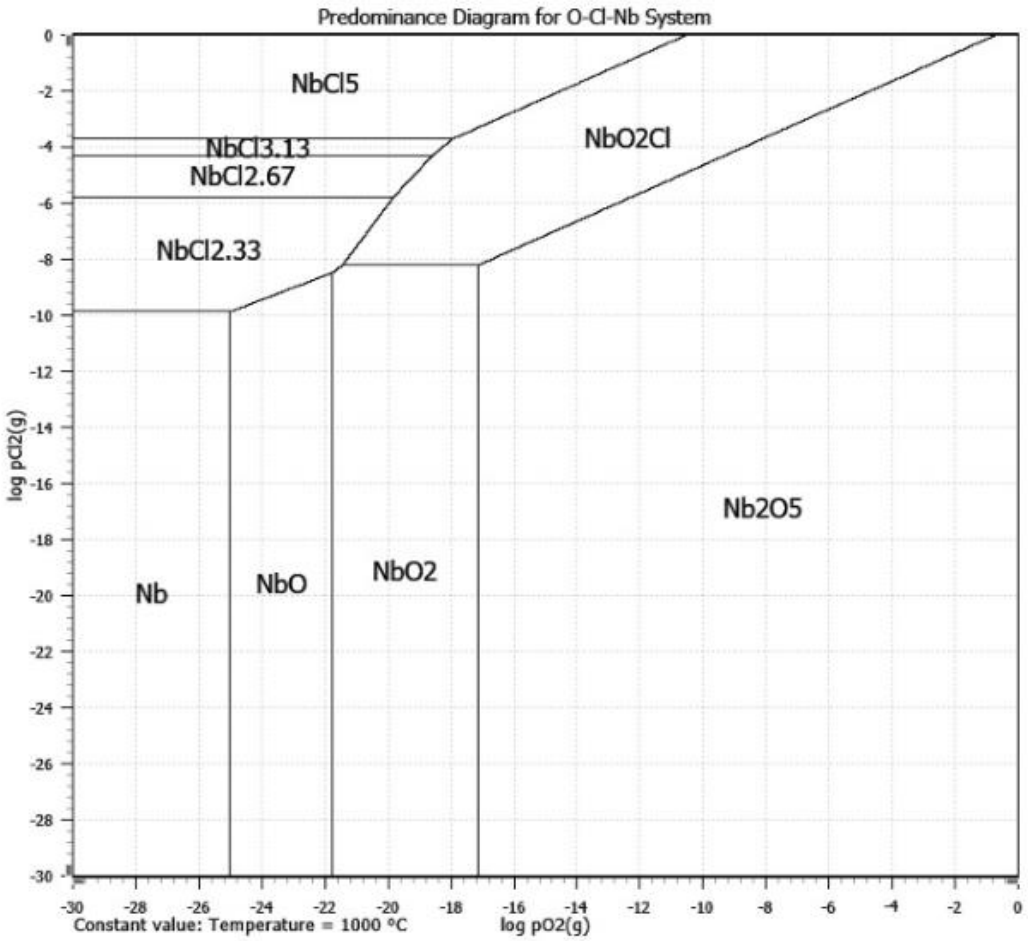


Figure 6: Predominance Area Diagram for the system Nb-O-Cl at 1000 ºC extracted from *HSC 10 Chemistry*.

Niobium metal, Nb, is stable at extremely low partial pressures of both oxygen and chlorine but as the oxygen partial pressure increases, the stable phases transits from niobium metal to its oxides: first NbO, then NbO_2, and finally Nb_2O_5. The boundaries between these oxide phases are vertical lines, indicating that these transitions are predominantly controlled by the oxygen partial pressure. As the chlorine partial pressure increases (and oxygen is low), niobium forms various chlorides, such as $NbCl_{2.33}$, $NbCl_{2.67}$, $NbCl_{3.13}$, and $NbCl_5$. The stability of these compounds increases with chlorine pressure. The compound NbO_2Cl forms at intermediate partial pressures of both oxygen and chlorine, representing a stable mixed oxide-chloride phase, this formation retards the process of producing $NbCl_5$.

4.1.3 Nb-O-Cl System at 1500 °C

In the Predominance Area Diagram at 1500 ºC presented in the Figure 7, it is observed the presence of Nb, NbO, NbO_2, Nb_2O_5, NbO_2Cl, $NbCl_{2.33}$ and $NbCl_5$. The window of Nb is bigger compared to the ones of lower temperature and the formation of $NbCl_5$ at high chloride partial pressure goes up to $pO_2 = 10^{-8}\ atm$.

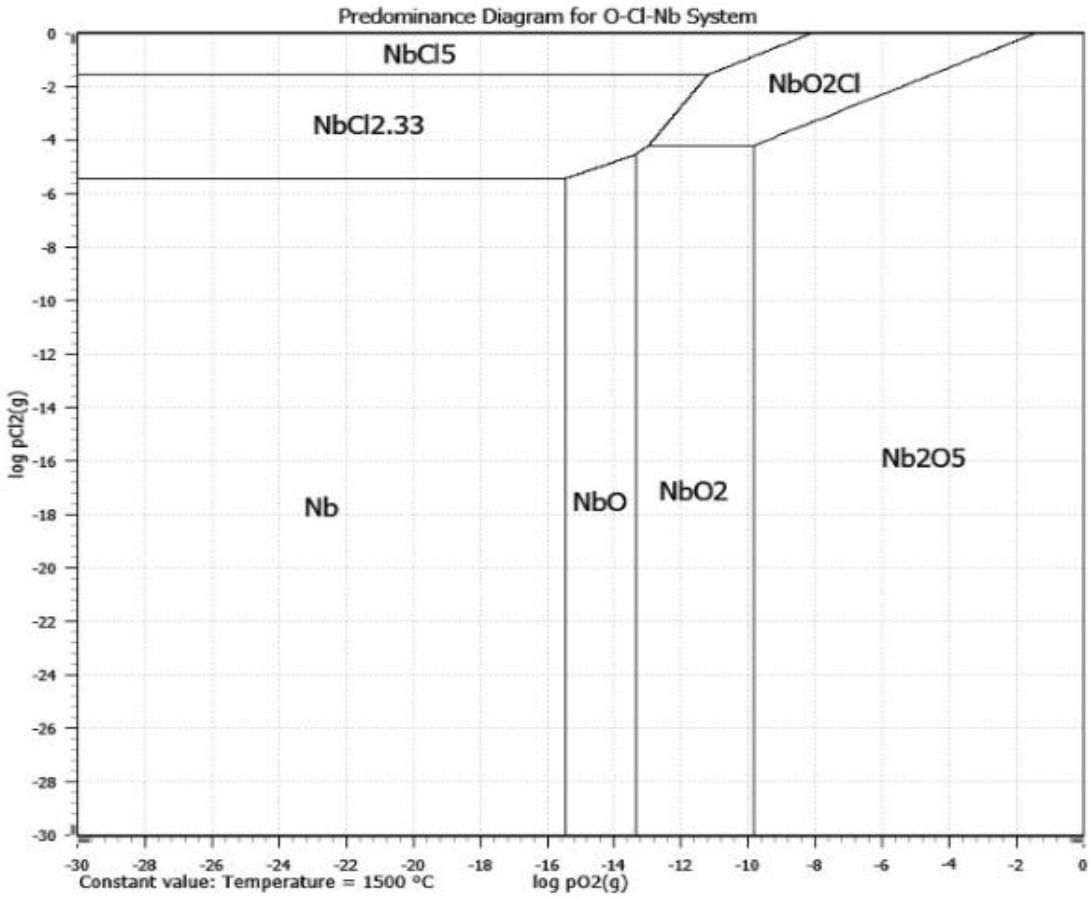


Figure 7: Predominance Area Diagram for the system Nb-O-Cl at 1500 ºC extracted from *HSC 10 Chemistry*.

Based on the provided predominance diagrams for the Nb-O-Cl system it is possible to conclude that the temperature has a significant impact on the species formation as new stable phases appears when its increased. In general term the chlorination is favoured at high temperatures. It can be also be observed that the formation mechanism of $NbCl_5$ from Nb_2O_5 will inevitably, pass through intermediate species. However, the following thermodynamic approach in this work will be conducted based on the Gibbs Free Energy Variation of the different Nb_2O_5 chlorination reactions, starting with direct

chlorine action followed by this reaction in the presence of a reducing agent, C, CO & H_2, and by using alternative chlorinating reagents.

4.2 A comparison between the action of different chlorinating agents through Standard Gibbs Free Energy

In the previous section it could be seen the large number of niobium chlorides and oxychlorides species formation which are dependent on the temperature and imposed reaction atmosphere, $\boldsymbol{pO_2 \times pCl_2}$. Still, considering that the desired product in a chlorination process is the $\boldsymbol{NbCl_5}$, all the following reactions will be studied as such, so the entire possible intermediate products formed will not be considered. This procedure is also more appropriate for any kind of comparisons between the selected reactions.

Then, the Nb_2O_5 chlorination tendency will be evaluated in this section by the Standard Gibbs Free Energy, the thermodynamic driving force - ΔG^0, which means the variation energy difference between the standard state going to the equilibrium state, as shown in equation [5].

$$\Delta G^0 = G_{eq} - G^0 \qquad [5]$$

A negative value of this difference is a good indication that the reaction may occur while a positive value causes an opposite impression. It can be said because, actually, the reaction occurrence, or not, will be given by the energy value difference between a general imposed state and the equilibrium state.

So, it is well known in equation 6 that,

$$\Delta G = \Delta G^0 + \Delta G' = \Delta H - T\Delta S \qquad [6]$$

Where, in equation 7 and equation 8,

$$\Delta G^0 = -RTlnK_{eq} \qquad [7]$$

$$\Delta G' = RTlnQ \qquad [8]$$

In a practical point of view K_{eq} represents the situation to where the reaction wants to go, the equilibrium state. While, Q represents the operational conditions in the reactor. Mathematically K_{eq} and Q, are respectively, the equilibrium constant and the reaction coefficient. It is easy to notice that the

reaction may take place whenever $K_{eq} > Q$ as ΔG will be negative. Therefore, any reaction may occur even with $\Delta G^0 > 0$ since $\Delta G' < 0$ and greater than ΔG^0. Taking all these comments into consideration is important to look at the equilibrium constant value which is a function of temperature. Theoretically it is always possible to make a reaction to occur, just stablishing $Q < K_{eq}$. Nonetheless, when K_{eq} is very small, such as bellow 10^{-4} it will be practically impossible to impose an operational condition where $Q < K_{eq}$ (Brocchi and Lino, 1994). This will be exemplified below, in the section 4.2.1.1, for a 10^{-25} equilibrium constant value.

As said before, the comments above in this section 4.2 aims to give an easy and practical understanding of the variation energy concepts and the search for the equilibrium conditions, contributing in some way to the didactics related to this subject. Also, it is worthwhile to mention the recent work, *A simple chemical equilibrium algorithm applied for single and multiple reaction systems,* by Moreira *et al*., 2024, where an alternative method was proposed to predict chemical equilibrium in different reactions states.

4.2.1 The effect of a reducing agent presence

4.2.1.1 Chlorine Direct Action and the C effect as the reducing agent

Again, it can be said here that possible intermediate products will not be considered as a thermodynamic comparison is always more appropriate considering the same product $NbCl_5$ for the selected reactions studied in this work.

The Ellingham Diagram represented in the Figure 8 show four reactions 9, 10, 11 and 12 respectively.

$$Nb_2O_{5_{(s)}} + 5Cl_{2_g} \leftrightarrow 2NbCl_{5_{(l)}} + \frac{5}{2}O_2 \quad (Direct\ chlorination\ in\ blue) \quad [r.9]$$

$$CO_{2(g)} + C_{(s)} \leftrightarrow 2CO_{(g)} \qquad (\text{Boudouard}\ in\ orange) \qquad [r.10]$$

$$Nb_2O_{5_{(s)}} + \frac{5}{2}C + 5Cl_{2_g} \leftrightarrow 2NbCl_{5_{(l)}} + \frac{5}{2}CO_{2(g)} \qquad (in\ grey) \qquad [r.11]$$

$$Nb_2O_{5_{(s)}} + 5C + 5Cl_{2_g} \leftrightarrow 2NbCl_{5_{(l)}} + 5CO_{(g)} \qquad (in\ yellow) \qquad [r.12]$$

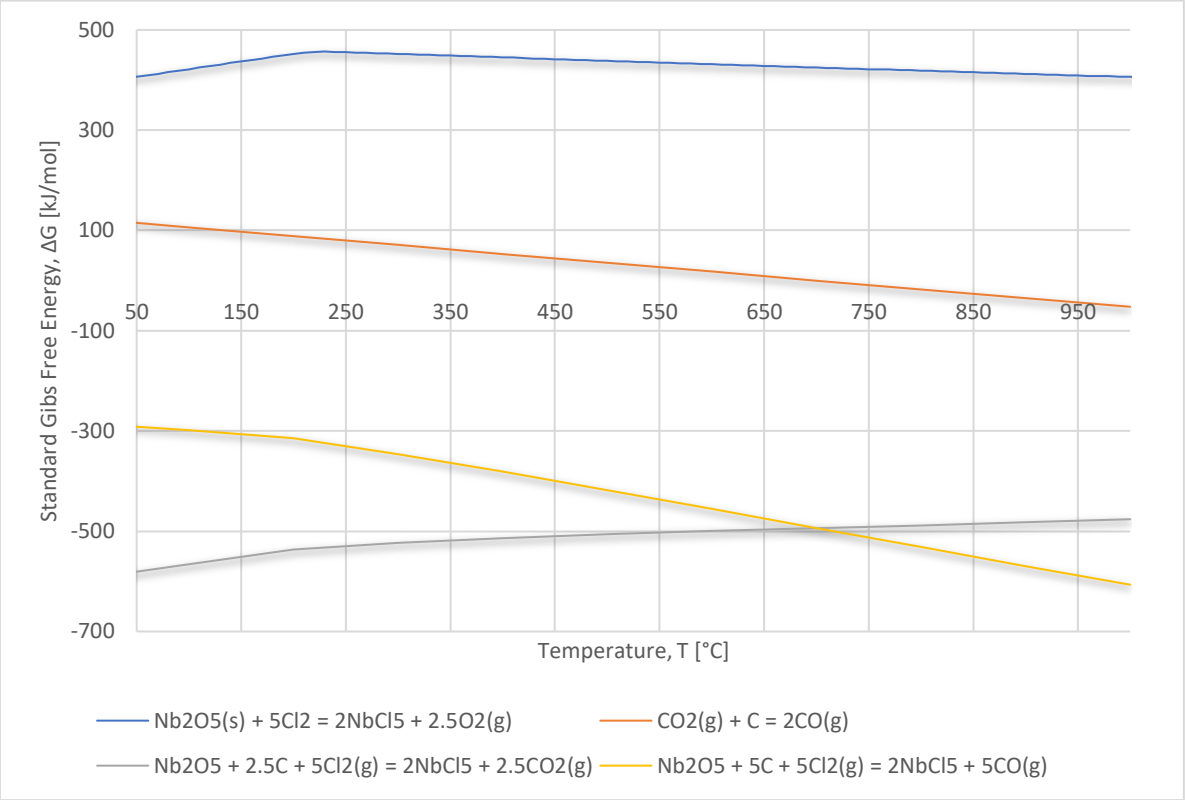


Figure 8: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for direct chlorination.

From the curve presented in Figure 8, it is possible to observe that the direct chlorine action on niobium pentoxide, Nb_2O_5, exhibits high positive ΔG^0 values across the entire temperature range. Consequently, their equilibrium constants are very low, indicating that the conversion for direct chlorination reactions is minimal or nearly negligible even after the $NbCl_5$ becomes gaseous at approximately 250 ºC, when the entropy of the products increases favoring the formation of them because the inclination of the ΔG curve goes down when the product entropy increases causing the ΔG value to become even more negative due to the increasing of the $-T\Delta S$ value as can be observed in equation 6.

This fact can be mathematically exemplified by the following calculations at 800 °C.

Consider the reaction 13,

$$Nb_2O_5 + 5Cl_2 \leftrightarrow 2NbCl_5 + \frac{5}{2}O_2 \qquad [r.13]$$

$$K\,[800℃] = 3.982 \cdot 10^{-25}$$

The K value is extremely low and will not permit any practical formation of $NbCl_5$, as shown in the calculations below, based on Table 4.

	Nb_2O_5	Cl_2	$NbCl_5$	O_2
Start [mol]	1	*5*	-	-
Conversion [mol]	*X*	*1-x*	*2x*	*2.5x*
Equilibrium [mol]	*1-x*	*5(1-x)*	*2x*	*2.5x*

Table 4: Resume of the reaction involving Nb_2O_5, Cl_2, $NbCl_5$ and O_2.

In Table 4, where x is the molar quantity reacted or generated. Assuming the gas phase has a pressure of one atmosphere over the system and behaves ideally, we have in equation 9 and 10,

$$P_T = P_{NbCl_5} + P_{O_2} + P_{Cl_2} = 1atm \quad [9]$$

$$P_i = P_{y_i} \cdot P_T \quad [10]$$

where y_i is the molar fraction of gas i.

The total number of moles in the gas phase is presented in equation 11,

$$n_T = 5(1-x) + 2x + \frac{5}{2}x = 5\left(1 - \frac{1}{10}x\right) \quad [11]$$

Therefore, the partial pressures of the gases are exposed in equations 12, 13 and 14,

$$P_{NbCl_5} = \frac{\frac{4}{10}x}{\left(1 - \frac{1}{10}x\right)} \quad [12]$$

$$P_{O_2} = \frac{\frac{5}{10}x}{\left(1 - \frac{1}{10}x\right)} \quad [13]$$

$$P_{Cl_2} = \frac{1-x}{\left(1 - \frac{1}{10}x\right)} \quad [14]$$

After all, the equation 15 solves with the K value the conversion,

$$K = \frac{{P_{O_2}}^2 \, {P_{NbCl_5}}^2}{{P_{Cl_2}}^5} = \frac{\left[\frac{\frac{5}{10}x}{\left(1-\frac{1}{10}x\right)}\right]^2 \cdot \left[\frac{\frac{4}{10}x}{\left(1-\frac{1}{10}x\right)}\right]^2}{\left[\frac{1-x}{\left(1-\frac{1}{10}x\right)}\right]^5} = 3.982 \cdot 10^{-25} \qquad [15]$$

Using MATLAB this equation 15 can be easily solved and provides x in equation 16,

$$x = \ 8.36 \cdot 10^{-6} = 8.36 \cdot 10^{-4} \ \% \qquad [16]$$

It can then be said that practically there is no conversion in this case, to increase the efficiency of chlorination, there are two options. The first is to raise the temperature, an alternative that is practically unfeasible due to the requirement for very high temperatures. The second is to reduce the oxygen potential, which is viable through the addition of a reducing agent, such as C, CO or H_2.

Several authors have observed that the presence of carbon will reduce the propensity for oxide formation and favours the production of chlorides by providing a low oxygen potential environment (Brocchi 1983, Jena *et al*. 1986, Pasquevich *et al*. 1992, Andrade *et al*. 1999, Esquivel *et al*. 2003, Movahedian *et al*. 2000, Shainyan *et al*. 2008, Gavíria *et al*. 2010).

When C is the reducing agent the percentages of $CO_{(g)}$ and $CO_{2(g)}$ vary with temperature. For temperatures above 800 °C, the predominant gaseous species will be $CO_{(g)}$, while for temperatures below 600 °C, it will be $CO_{2(g)}$, as can be seen in the intersection of the lines at the same temperature where ΔG^0 for the Boudouard reaction is zero.

So, the reactions III and IV are carbochlorination forming $CO_{2(g)}$ or $CO_{(g)}$, respectively. Both of them are thermodynamically favourable over the entire temperature range studied, as its ΔG is consistently negative and will be discussed further in this section. However, for kinetic reasons the reaction is much more efficient at temperatures higher than 800 °C (Brocchi 1983 and Lino 1984).

4.2.1.2 The CO effect as the reducing agent

Figure 9 exposes the variations in Standard Gibbs Free Energy, $\Delta G^0 \times T$, for the reactions forming niobium pentachloride, $NbCl_5$, during carbochlorination with CO as observed in reaction 10. It can be observed that CO can also be used as reducing agent as the Gibbs Free Energy remains very negative in the whole temperature range with the equilibrium constant being, in both cases, very high.

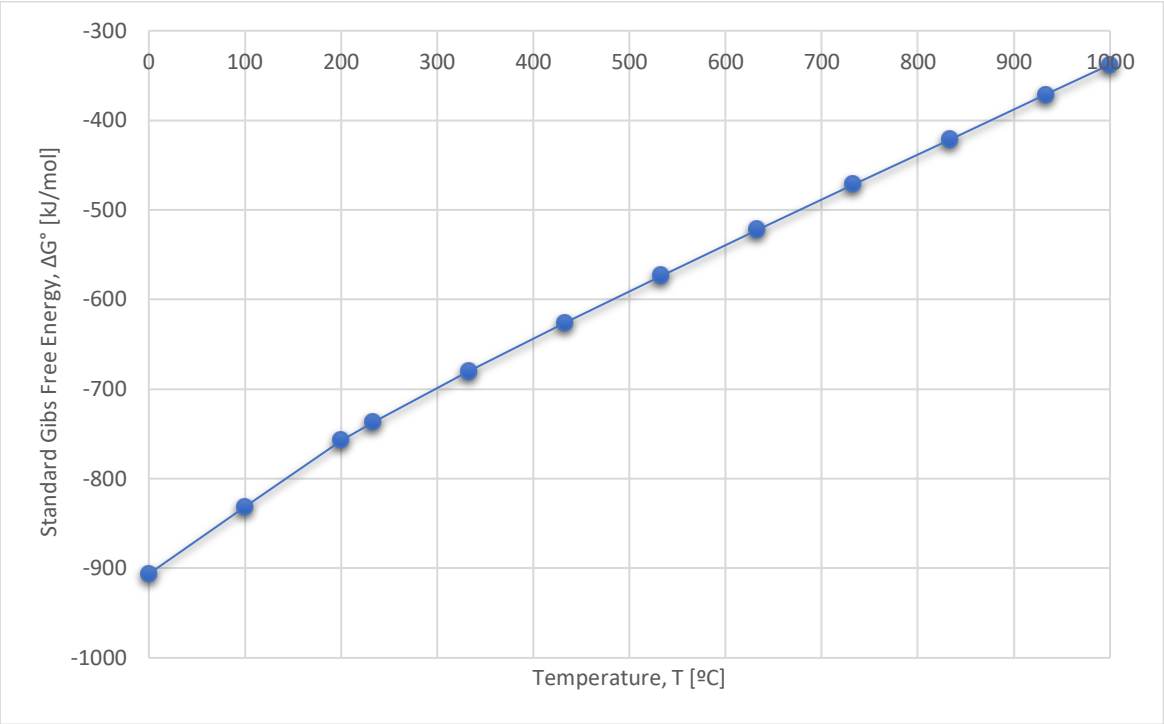


Figure 9: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], using $CO_{(g)}$ as the reducing agent.

It is interesting to call attention that the equilibrium constant decreases through increasing temperature (Tables 5 & 6) for the reactions 10 and 11 because in these cases ΔG^0 is less negative due to the presence of more gaseous species in the reactants than in the products, $\Delta S < 0$.

$$\boldsymbol{Nb_2O_{5(s)} + \frac{5}{2}C + 5Cl_{2(g)} \leftrightarrow 2NbCl_5 + \frac{5}{2}CO_{2(g)}} \qquad [r.10]$$

$T\ [°C]$	K
500	$1.72 \cdot 10^{+34}$
700	$3.40 \cdot 10^{+26}$
1000	$3.58 \cdot 10^{+19}$

Table 5: Equilibrium constant, K_{EQ}, at specific temperatures when adding C as the reduction agent.

$$\boldsymbol{Nb_2O_{5(s)} + 5CO + 5Cl_{2(g)} \leftrightarrow 2NbCl_5 + 5CO_{2(g)}} \qquad [r.11]$$

$T\ [°C]$	K
500	$1.42 \cdot 10^{+37}$
700	$3.08 \cdot 10^{+24}$
1000	$7.22 \cdot 10^{+13}$

Table 6: Equilibrium constant, K_{EQ}, at specific temperatures when adding $CO_{(g)}$ as the reduction agent.

A detailed study related to the chlorination of Nb_2O_5 content in pyrochlore concentrates was carried out by (Freitas and Brocchi, 1988). In this work was also enclosed a kinetic comparison between the two reductive agents, C and CO, letting it clear that the using of a solid carbon is much more effective in terms of a niobium conversion to $NbCl_5$ under a temperature range between 650 °C – 850 °C.

4.2.1.3 The H_2 effect as the reducing agent

Again, it can be observed in Figure 10 that H_2 can also be used as a reducing agent. A thermodynamic tendency comparison with the use of CO is given in it. Although the negative ΔG^0 values are smaller when compared with the use of CO, as observed in reaction 12, the equilibrium constants presented in Table 7 are within the same magnitude order, very high, and it has the advantage of producing H_2O. However, any decision about the best reducing agent will have to take into consideration a kinetic study.

$$\boldsymbol{Nb_2O_{5(s)} + 5H_{2(g)} + 5Cl_{2(g)} \leftrightarrow 2NbCl_5 + 5H_2O_{(g)}} \qquad [r.12]$$

$T\ [°C]$	K
500	$3.33 \cdot 10^{+37}$
700	$8.41 \cdot 10^{+27}$
1000	$5.22 \cdot 10^{+19}$

Table 7: Equilibrium constant, K_{EQ}, at the specific temperatures when adding $H_{2(g)}$ as the reduction agent.

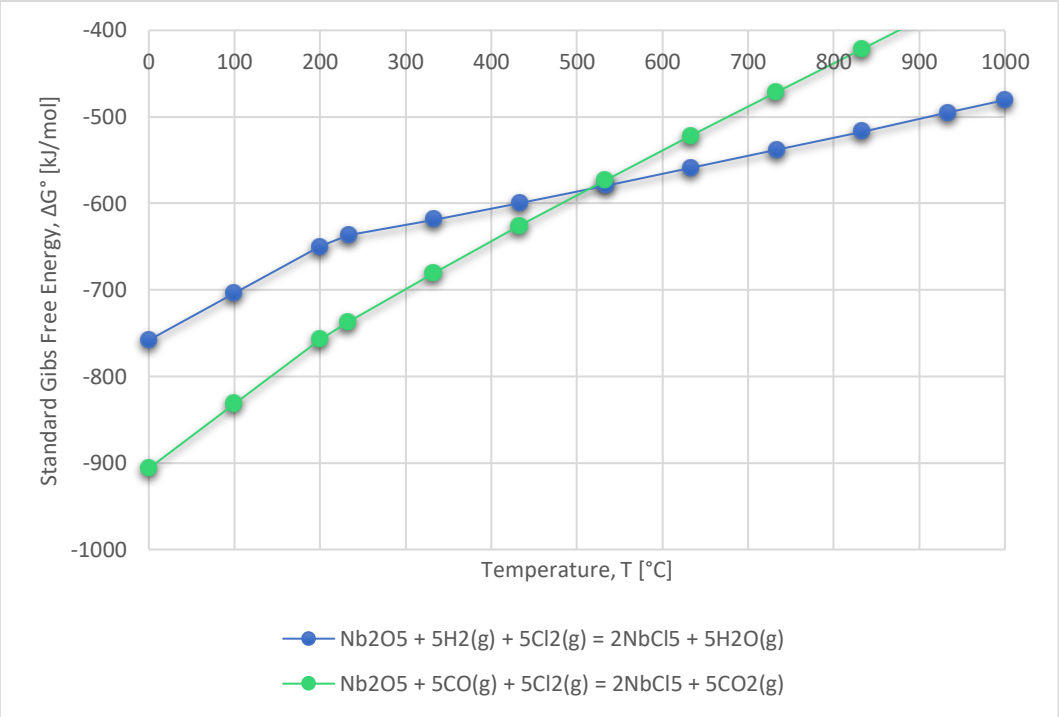


Figure 10: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], using $H_{2(g)}$ & $CO_{(g)}$ as the reducing agent.

4.2.2 Chlorination through alternative chlorine bearing gaseous reagents

4.2.2.1 Hydrogen Chloride, HCl

$$\boldsymbol{Nb_2O_5 + 10HCl \rightarrow 2NbCl_5 + 5H_2O} \qquad [r.13]$$

The $\Delta G^0 \left[\frac{kJ}{mol}\right] \times T\ [°C]$ diagram for the Nb_2O_5 chlorination with $HCl_{(g)}$ is presented in Figure 11. It can clearly be observed that the reaction 12 has no tendency to occur and become even less favourable as the temperature increases due to a negative ΔS. The positive ΔG values are associated with very high equilibrium constants as can be observed in Table 7, indicating that $NbCl_5$ will not be formed through the $HCl_{(g)}$ direct action. This fact is confirmed by the work of Habashi and Malinskia, 1975, which studied this reaction process with a Canadian pyrochlore Nb_2O_5 content up to 700 °C.

However, it is valuable to comment that at low temperature the same chlorination may be used to separate Nb from others common elements in minerals and residues, such as Si, Fe and Zn. For instance, Figure 11 illustrates the action of $HCl_{(g)}$ over SiO_2, Fe_2O_3 and ZnO. In that figure it is possible to observe that the $SiCl_4$, $FeCl_3$ and $ZnCl_2$ should have a high thermodynamic formation driving force, it means a preference to be formed. In that case, the chlorination process could be used for separation of these elements either as gaseous gasification, $SiCl_4$, $ZnCl_2$, $FeCl_3$ (chlorination above 300 °C) or by a further selective solubilization ($FeCl_3$ liquid chloride is formed by chlorination bellow 300 °C). Then, $HCl_{(g)}$ may be used to form different metal chlorides leaving behind the niobium as the original pentoxide, making possible again a further separation amongst the content elements in the starting material. Nonetheless it has to be considered the corrosive aggressivity of this reaction system with $HCl_{(g)}$ presence.

Although, $HCl_{(g)}$ may be dissociated, it is interesting to comment that it will only happens at high temperatures, near to 2000 °C, as can be seen in Figure 12. It can also be observed that the entropy change between products and reagents is close to zero because they have the same moles number of gaseous species.

$$\boldsymbol{Nb_2O_5 + 10HCl \rightarrow 2NbCl_5 + 5H_2O} \qquad [r.13]$$

$T\ [°C]$	K
500	$1.26 \cdot 10^{-27}$
700	$3.22 \cdot 10^{-22}$
1000	$4.70 \cdot 10^{-23}$

Table 8: Equilibrium constant, K_{EQ}, at the specific temperatures for HCl direct chlorination.

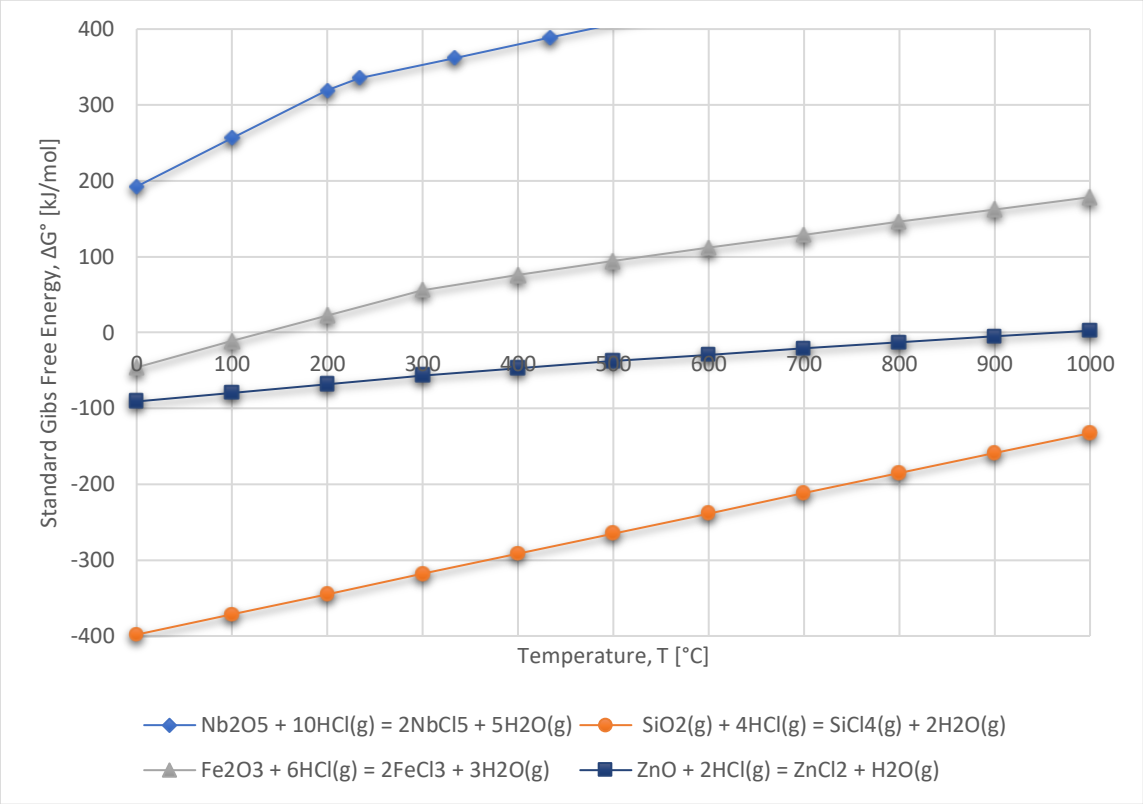


Figure 11: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for direct chlorination with $HCl_{(g)}$.

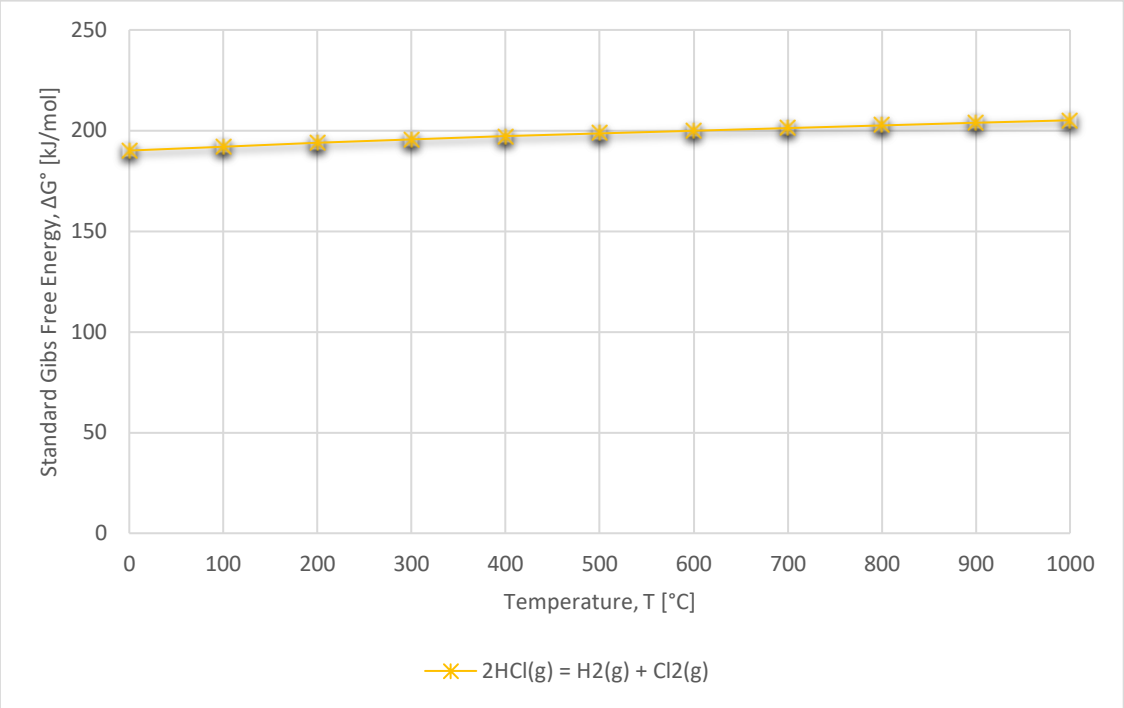


Figure 12: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for $HCl_{(g)}$ dissociation.

4.2.2.2 Sulphide Chloride, SCl_2

An evaluation was also conducted regarding the use of SCl_2 as a chlorinating agent as showed in Table 9 and Figure 13 and observed in reaction 15.

$$\boldsymbol{Nb_2O_{5\,(s)\,\&\,(g)} + 5SCl_{2(l)} \leftrightarrow\ 2NbCl_5 +\ 5SO_{2(g)}} \qquad [r.15]$$

$T\ [°C]$	K
500	$1.05 \cdot 10^{-13}$
700	$2.10 \cdot 10^{-5}$
1000	$2.52 \cdot 10^{+2}$

Table 9: Equilibrium constant, K_{EQ}, at the specific temperatures for SCl_2 chlorinating agent.

Still within this work purpose, it can be observed that the thermodynamic Nb_2O_5 sensibility to this particular gaseous specie should be only significative at temperatures just below 1000 °C. There is no reference available about this type of chlorination.

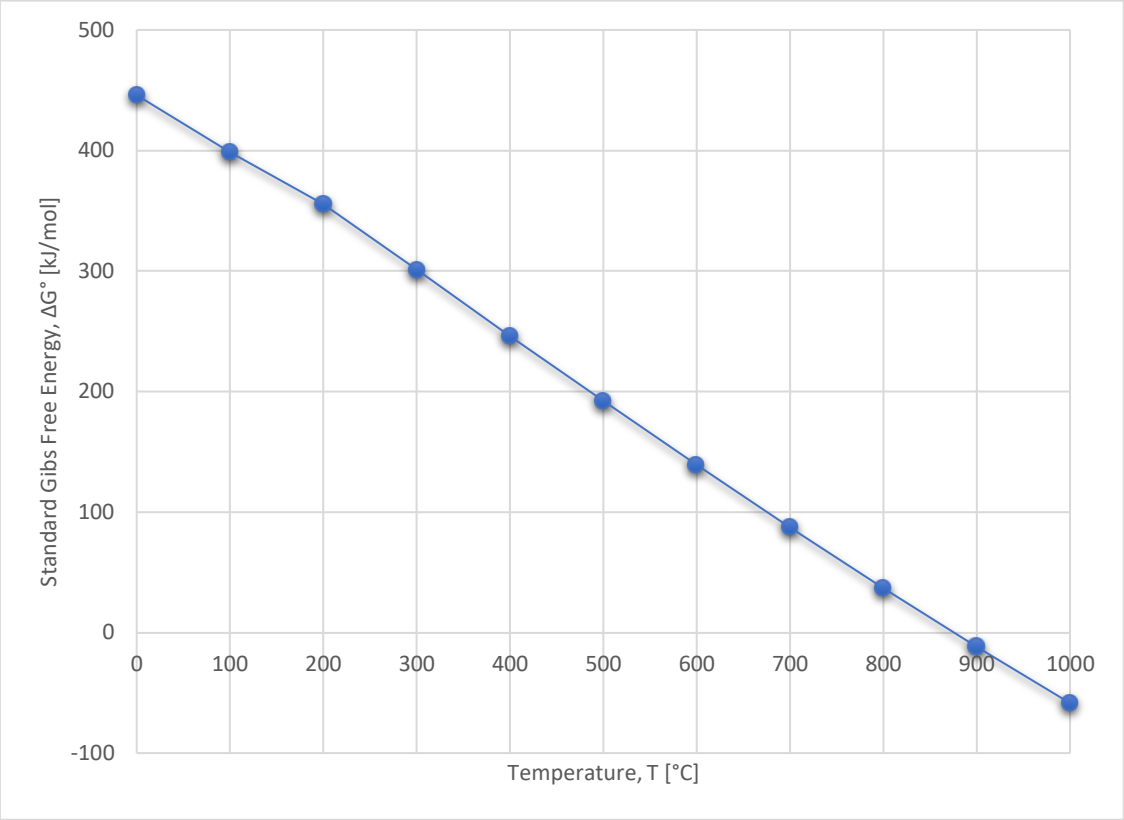


Figure 13: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for direct chlorination with $SCl_{2(l)}$.

4.2.3 Chlorination through alternative chlorine bearing liquid reagents

4.2.3.1 Carbon Tetrachloride, CCl_4

$$\boldsymbol{Nb_2O_5 + \frac{5}{2}CCl_4 \rightarrow 2NbCl_5 + \frac{5}{2}CO_2} \qquad [r.16]$$

Ellingham diagram for the reaction 16 is shown in Figure 14. It exposes that the reaction has a thermodynamic tendency to occur. It can also be seen by the equilibrium constant values given in Table 10.

In fact, this kind of study has already been carried out together with a kinetics appreciation and a mechanism proposal (Jena *et al*., 2008). The using of CCl_4 has the advantage of being applied in a temperature range, ≅ 500 °C, below the usual carbochlorination, ≅ 1000 °C, in order to get 100% conversion of Nb_2O_5. Nevertheless, it has to be also considered the operational aspects regarding the set-up of the required equipment's since it may not easy to build up as the already used industrial features.

$$Nb_2O_5 + \frac{5}{2}CCl_4 \rightarrow 2NbCl_5 + \frac{5}{2}CO_2 \qquad [r.16]$$

$T\ [°C]$	K
500	$3.35 \cdot 10^{+38}$
700	$1.10 \cdot 10^{+35}$
1000	$9.77 \cdot 10^{+31}$

Table 10: Equilibrium constant, K_{EQ}, at the specific temperatures for CCl_4 chlorinating agent.

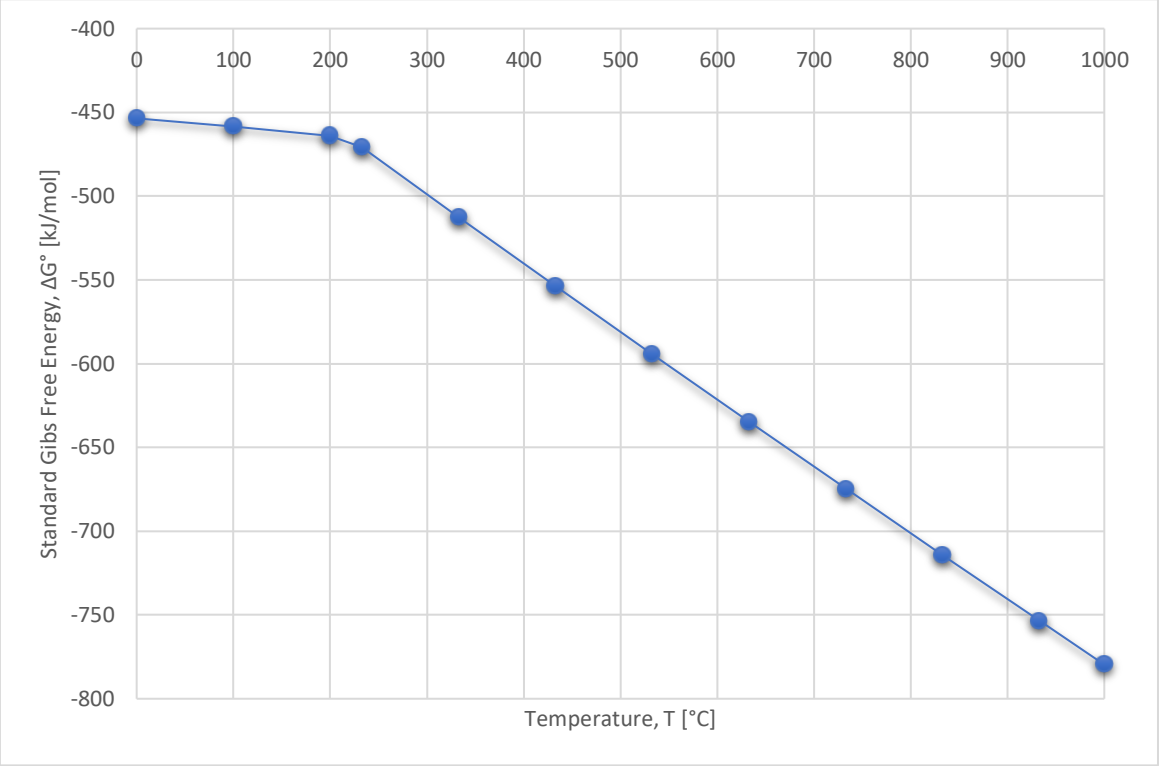


Figure 14: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for direct chlorination with $CCl_{4(l)}$.

4.2.3.2 Dicarbon Tetrachloride, C_2Cl_4

The use of $C_2Cl_{4(l)}$ would be very similar to the $CCl_{4(l)}$ as both show a clear thermodynamic favourability exposed in Figure 14 & 15 and Tables 10 & 11 as observed in the reaction 17. It is also observed a decrease in the ΔG value with an increasing temperature. It happens because even considering that the chlorides - $CCl_{4(l)}$ & $C_2Cl_{4(l)}$ - will dissociate the reaction entropy variation is positive. After, 250 °C there are seven gaseous moles in the products.

As mentioned in section 4.2.2.1 this type of chlorination could also be considered to be applied over different metals aiming their separation. It was

studied in the work, *Study on the thermodynamic viability of NiO and CuO chlorination with C_2Cl_4 at high temperatures,* by Navarro *et al*., 2016.

$$\boldsymbol{Nb_2O_5 + \frac{5}{4}C_2Cl_4 \leftrightarrow 2NbCl_5 + 5CO} \qquad [r.17]$$

$T\ [°C]$	K
500	$1.65 \cdot 10^{+44}$
700	$3.31 \cdot 10^{+43}$
1000	$3.05 \cdot 10^{+42}$

Table 11: Equilibrium constant, K_{EQ}, at the specific temperatures for $C_2Cl_{4(l)}$ chlorinating agent.

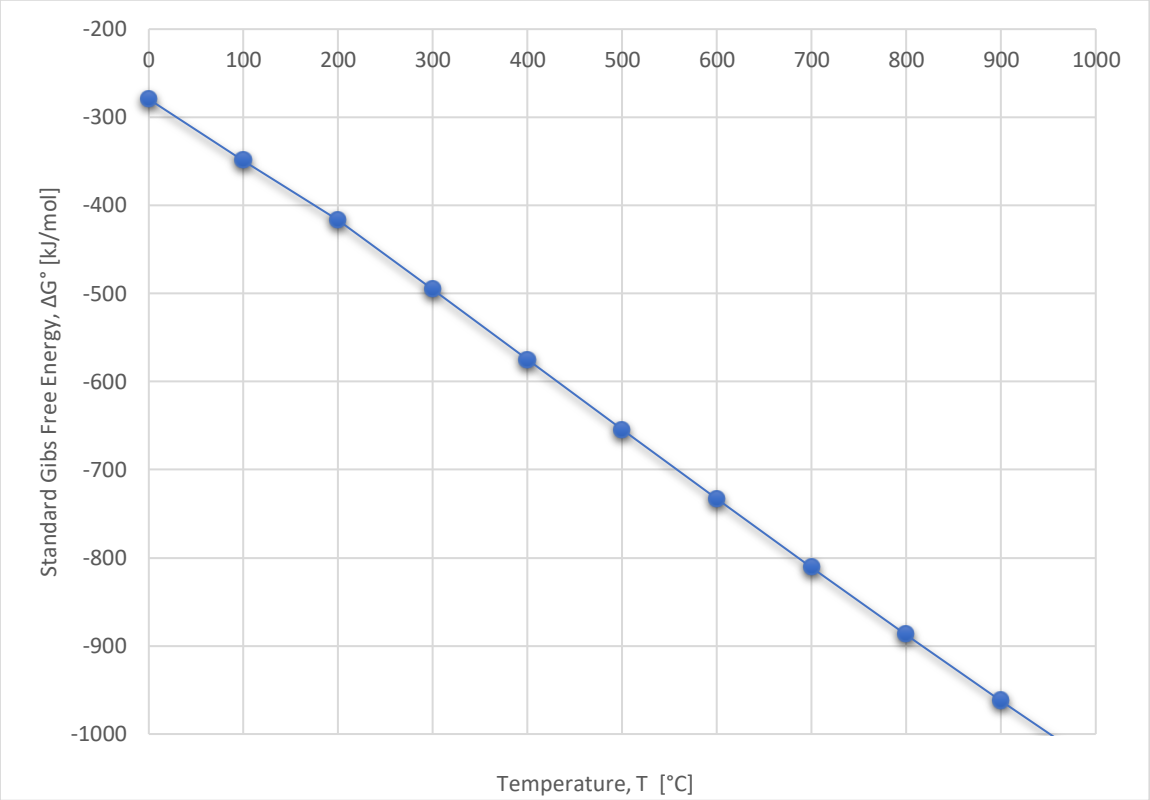


Figure 15: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for direct chlorination with $C_2Cl_{4(l)}$.

4.2.4 Chlorination through alternative chlorine bearing solid reagents

The effectiveness of these type of reagents will be appreciated through the action of four species KCl, $NaCl$, $MgCl_2$ and $CaCl_2$. It is illustrated in Figures 16, 17, 18 and 19 & Tables 12, 13, 14 and 15, respectively.

4.2.4.1 Potassium Chloride, KCl

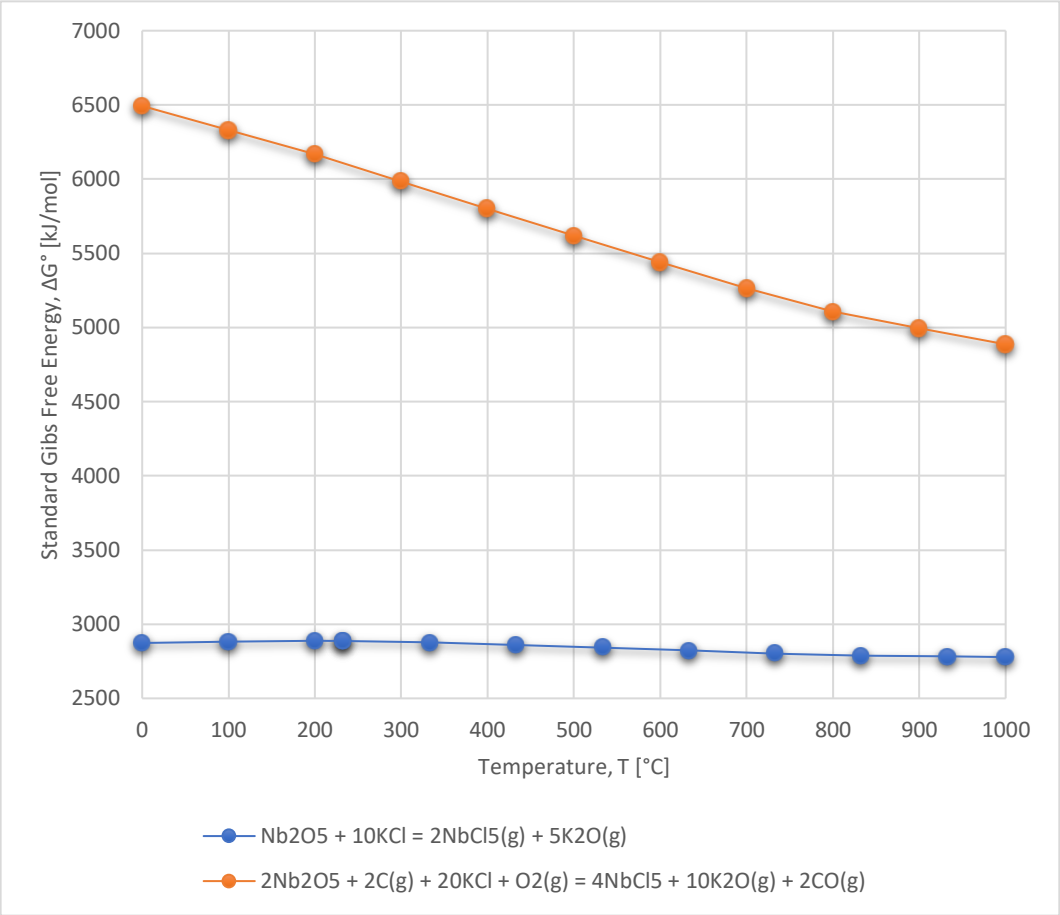


Figure 16: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for chlorination with $KCl_{(s)}$.

$$\boldsymbol{Nb_2O_5 + 10KCl \leftrightarrow 2NbCl_{5(g)} + 5K_2O} \qquad [\boldsymbol{r.18}]$$

$T\ [°C]$	K
500	$2.130 \cdot 10^{-212}$
700	$2.254 \cdot 10^{-132}$
1000	$1.004 \cdot 10^{-114}$

Table 12: Equilibrium constant, K_{EQ}, at specific temperatures for KCl chlorinating agent.

4.2.4.2 Sodium Chloride, $NaCl$

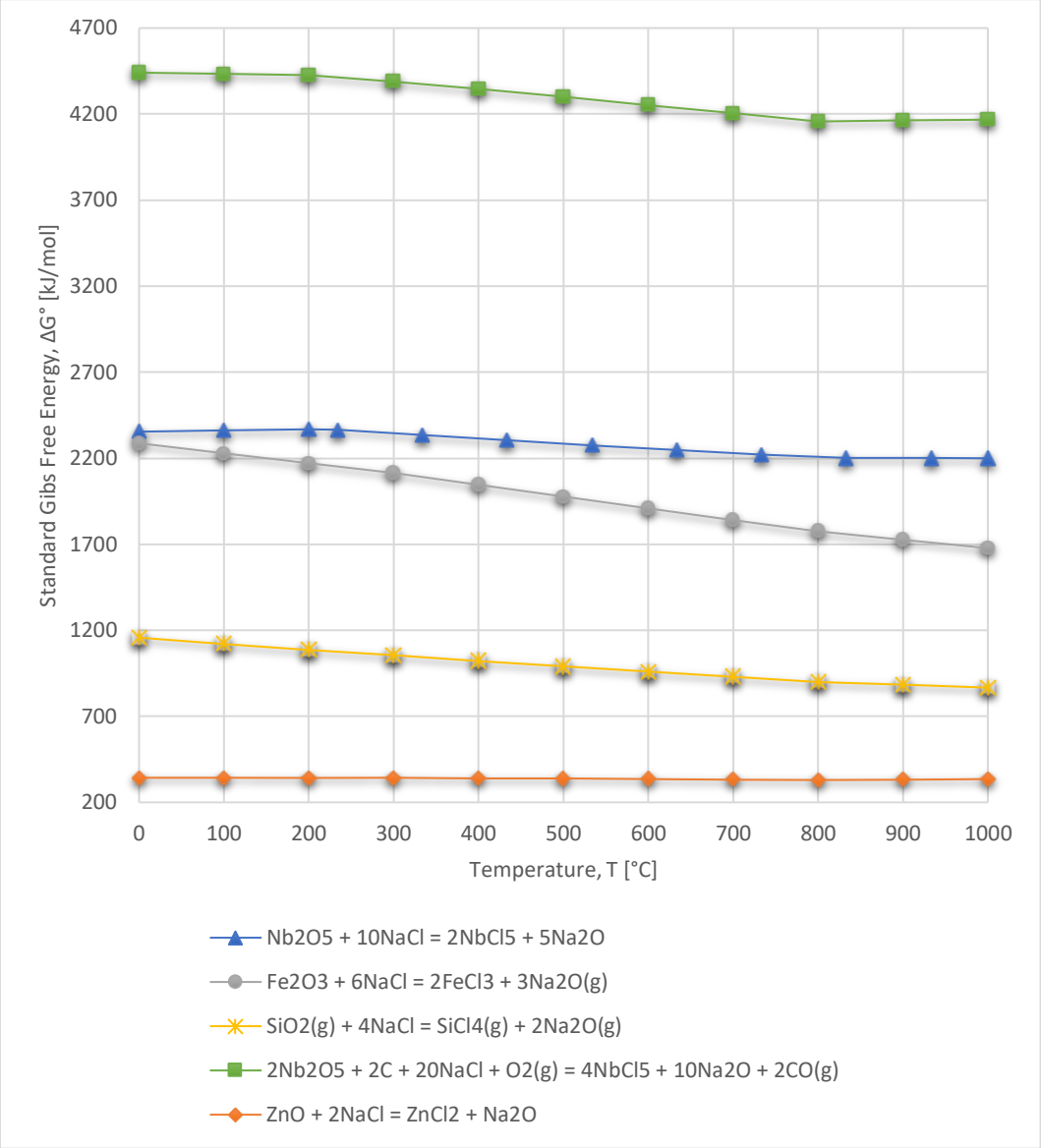


Figure 17: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for chlorination with $NaCl_{(s)}$.

$$\boldsymbol{Nb_2O_5 + 10NaCl \leftrightarrow 2NbCl_5 + 5Na_2O} \qquad [r.19]$$

$T\ [°C]$	K
500	$4.25 \cdot 10^{-148}$
700	$6.50 \cdot 10^{-116}$
1000	$5.57 \cdot 10^{-91}$

Table 13: Equilibrium constant, K_{EQ}, at specific temperatures for $NaCl$ chlorinating agent.

4.2.4.3 Magnesium Chloride, $MgCl_2$

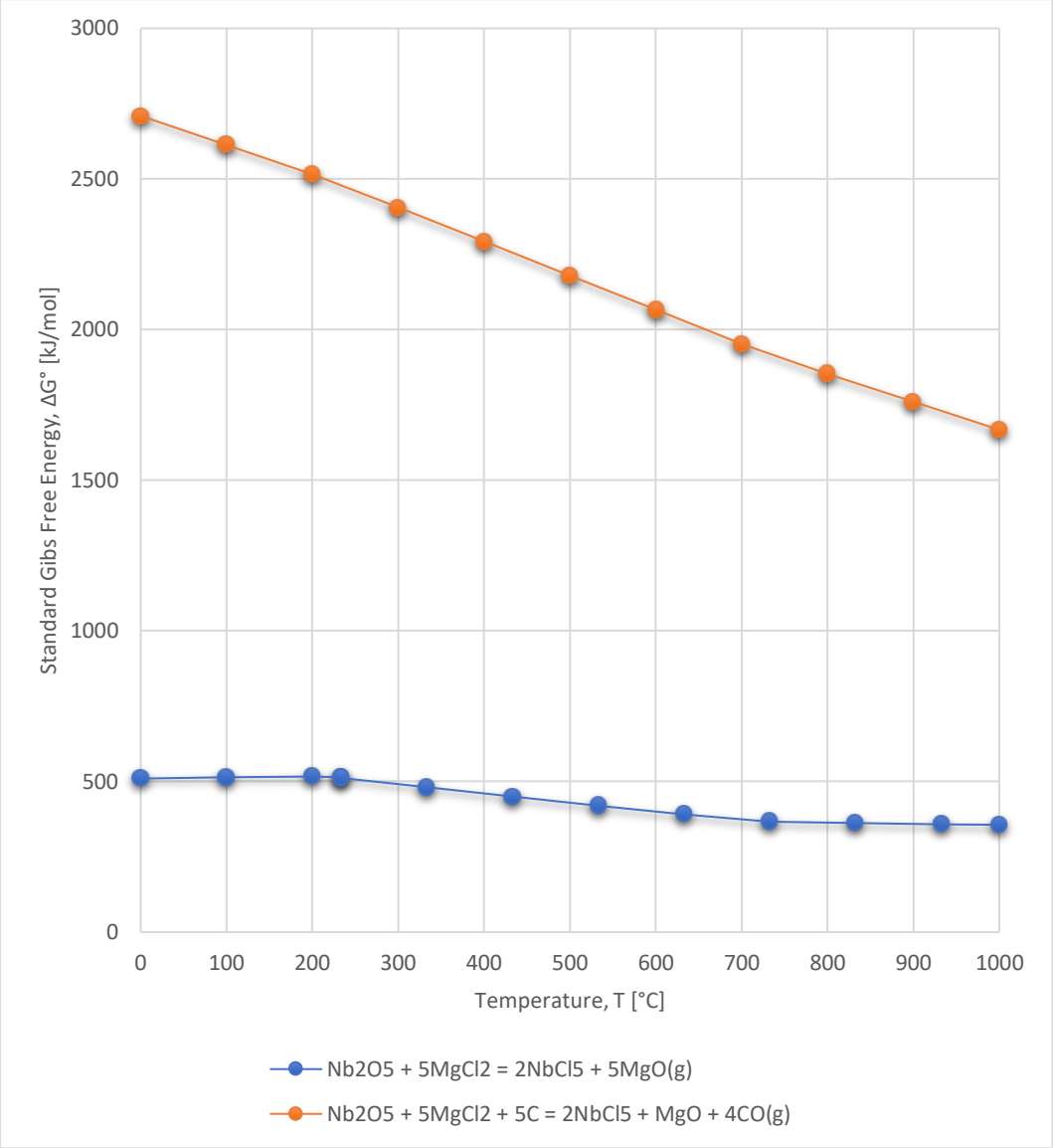


Figure 18: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for chlorination with $MgCl_{2(s)}$.

$$\boldsymbol{Nb_2O_5 + 5MgCl_2 \leftrightarrow 2NbCl_{5(g)} + 5MgO_{(g)}} \qquad [r.20]$$

$T\ [°C]$	K
500	$5.77 \cdot 10^{-28}$
700	$8.14 \cdot 10^{-20}$
1000	$2.37 \cdot 10^{-15}$

Table 14: Equilibrium constant, K_{EQ}, at specific temperatures for $MgCl_2$ chlorinating agent.

4.2.4.4 Carbonate Chloride, $CaCl_2$

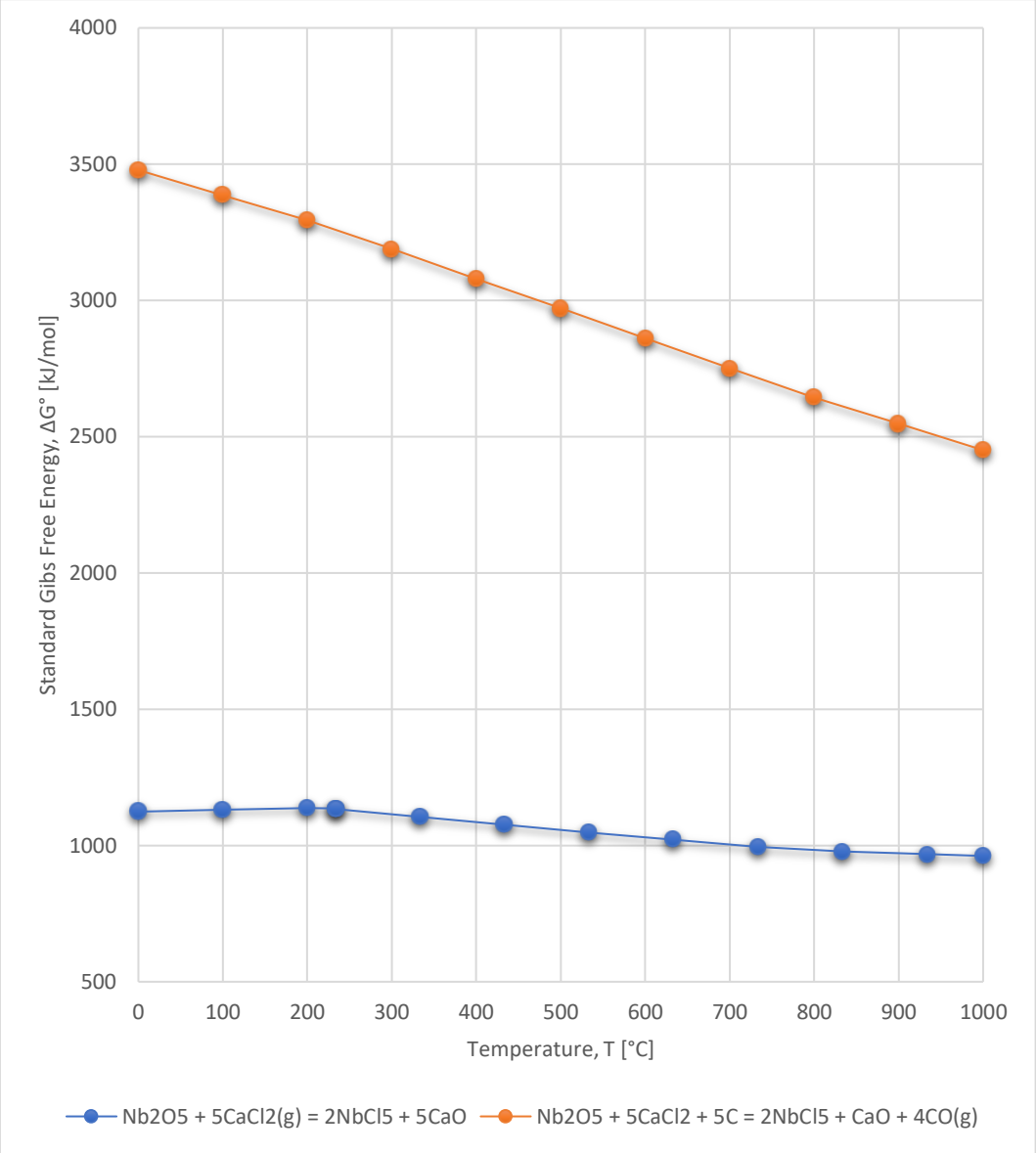


Figure 19: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for chlorination with $CaCl_{2(s)}$.

$$\boldsymbol{Nb_2O_5 + CaCl_2 \leftrightarrow 2NbCl_5 + 5CaO} \qquad [r.21]$$

$T\ [°C]$	K
500	$1.28 \cdot 10^{-68}$
700	$2.38 \cdot 10^{-52}$
1000	$3.50 \cdot 10^{-40}$

Table 15: Equilibrium constant, K_{EQ}, at specific temperatures for $CaCl_2$ chlorinating agent.

It can be observed through the previous figures and tables that the action of all chlorides over Nb_2O_5 is difficult to occur. Even with the presence of a reducing agent, $C_{(s)}$, for the all cases listed before the chlorination remains

unavailable, providing an even greater Standard Gibbs Free Energy. It is interesting also to notice, that even for some other oxides Fe_2O_3, SiO_2 and ZnO the action of these chlorides may not be viable, as studied for the use of $NaCl$ (Figure 17). It shows a different approach in comparison to the discussion related to the use of $HCl_{(g)}$ where a possible separation was mentioned.

Considering that this work has the purpose to discuss the chlorination process as a whole and its thermodynamic evaluation when applied to Nb_2O_5 it is valid to finalize this chapter mentioning that the action of chlorine content agents has to be thermodynamically studied encompassing, whenever there are data available, the compound where the metal values are located and not the reaction with the pure oxides. It is the case of the franklinite (zinc ferrite: $ZnFe_2O_4$) where the chlorination can be used to separate these two metals as emphasized in the work by Santos et al., 2015. In fact, that possibility is shown respectively in Figure 20 and Tables 16 & 17 where it can be seen that both, $NaCl$ and $CaCl_2$ will react with the franklinite producing a water insoluble Fe_2O_3 and a soluble $ZnCl_2$.

$$\boldsymbol{ZnFe_2O_4 + CaCl_2 + C + O_{2(g)} \leftrightarrow ZnCl_2 + Fe_2O_3 + CaO + CO_{2(g)}} \quad [r.22]$$

$T\ [°C]$	K
500	$2.43 \cdot 10^{+2}$
700	$1.11 \cdot 10^{+2}$
1000	$2.58 \cdot 10^{+1}$

Table 16: Equilibrium constant, K_{EQ}, at specific temperatures for chlorination of $ZnFe_2O_4$ with $CaCl_2$.

$$\boldsymbol{ZnFe_2O_4 + 2NaCl + C + O_{2(g)} \leftrightarrow ZnCl_2 + Fe_2O_3 + Na_2O + CO_{2(g)}} \quad [r.23]$$

$T\ [°C]$	K
500	$2.43 \cdot 10^{+2}$
700	$1.11 \cdot 10^{+2}$
1000	$2.58 \cdot 10^{+1}$

Table 17: Equilibrium constant, K_{EQ}, at specific temperatures for chlorination of $ZnFe_2O_4$ with $NaCl$.

4.2.4.5 Franklinite, $ZnFe_2O_4$

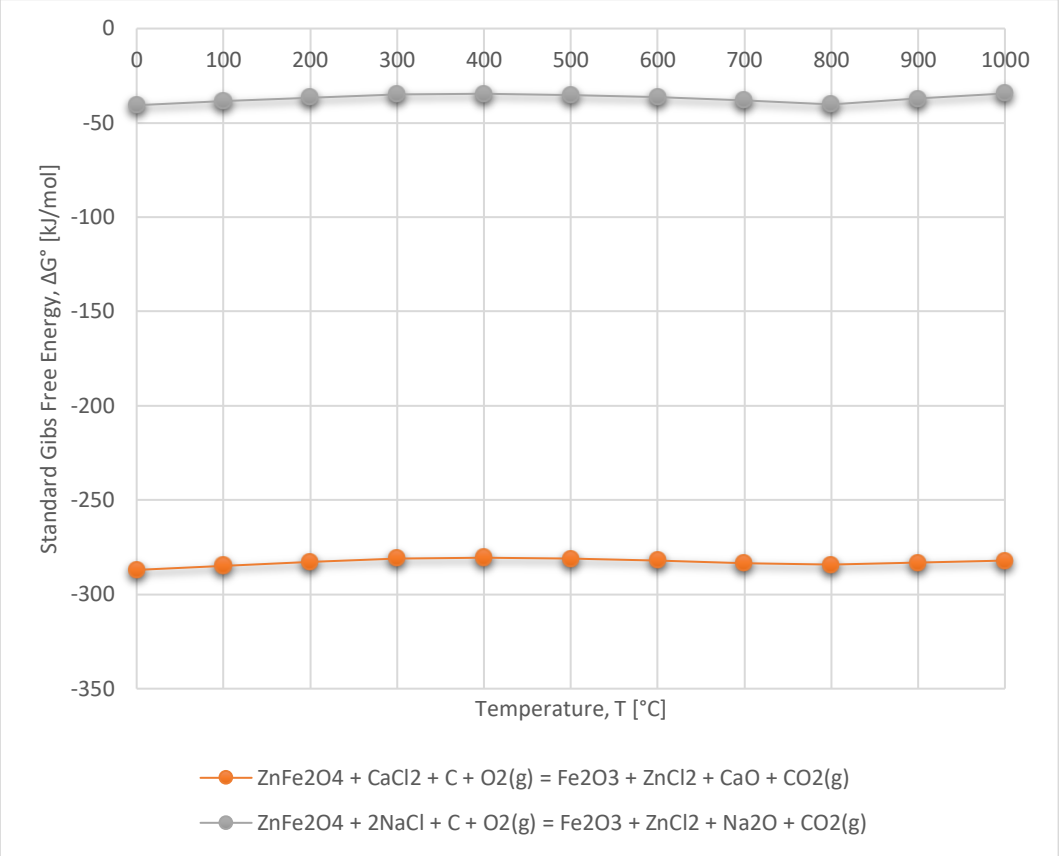


Figure 20: Variation of the Standard Gibbs Free Energy, ΔG° [kJ/mol]) x Temperature [ºC], for chlorination with $ZnFe_2O_4$.

4.3 A kinetic appreciation and the physical aspects transformations of the Nb_2O_5 carbochlorination - $Cl_2 + C$

Thermodynamics can be applied to predict the operational conditions under which the desired product can be obtained as it is based on the reaction equilibrium composition. It is well known that thermodynamic data alone does not provide any objective information regarding the required time to a significative conversion be achieved, which is, obviously, a fundamental data for a process viability. It is stablished by kinetics studies considering both variables effects of the reaction rate and the physical-chemical transformation mechanism. Also, based on these, a mathematical model can be developed incorporating mass transport phenomena and so, providing a detailed knowledge of the reaction system.

With the aim of contribute to develop, in the future, a mathematical model for the kinetics of this chlorination process, the following approach examines the physical chlorination behaviour of Nb_2O_5 samples, focusing primarily on the variables of temperature, initial carbon percentage (%Ci), and solid porosity.

This approach is based on the findings of Brocchi E. A., 1984, in the study *Reduction Chlorination Reactions of Niobium and Tantalum Oxide Containing Materials*. It considered diverse experimental conditions such as temperatures varying from 700 °C to 900 °C, porosity from the percentage of 28%, 46% and 83% and initial carbon percentage from 9% to 40%, also exposed surface area, pellet depth and chlorine partial pressure - these two last variables were not appreciated in this present study.

Therefore, regarding the Nb_2O_5 carbochlorination, $Cl_2 + C$, the following sections will present a variable effect on the oxide conversion.

(1) The solid structural transformations over time and the type of transformation according to the values of temperature - T;

(2) Initial carbon percentage in the solid mixture - %Ci;

(3) Porosity of the sample - ε;

4.3.1 The effect of operational variables

With the aim of showing some particular experimental conditions where the Nb_2O_5 conversion varies from 50% to near 100% as well as to see some variables effect on the carbochlorination kinetic (e.g. initial rate), Figures 21, 22 & 23 are presented.

It is clearly seen in Figure 21 that a sample with 83% porosity (loose powder) and 40% carbon in the solid mixture will have above 90% Nb_2O_5 reacted at 700 °C in 60 minutes and at 800 °C in 20 minutes. For samples with 28% porosity of the pellet and 40% initial carbon in the mixture the conversion of Nb_2O_5 can vary from 40% at 700 °C in 30 minutes to about 90% at 800 °C in 15 minutes as shown in Figure 22. The activation energy for this condition was calculated to be Ea = 76.6 kJ/mol. Depending on the experimental conditions the activation energy varies. This value for samples with 83% porosity and 9% Ci is 156.5 kJ/mol. The effect of temperature was studied using the Arrhenius relationship and show that for experiments with easy chlorine penetration at 83% porosity the apparent activation energy is smaller than that for experiments with difficult chlorine penetration at 28% porosity.

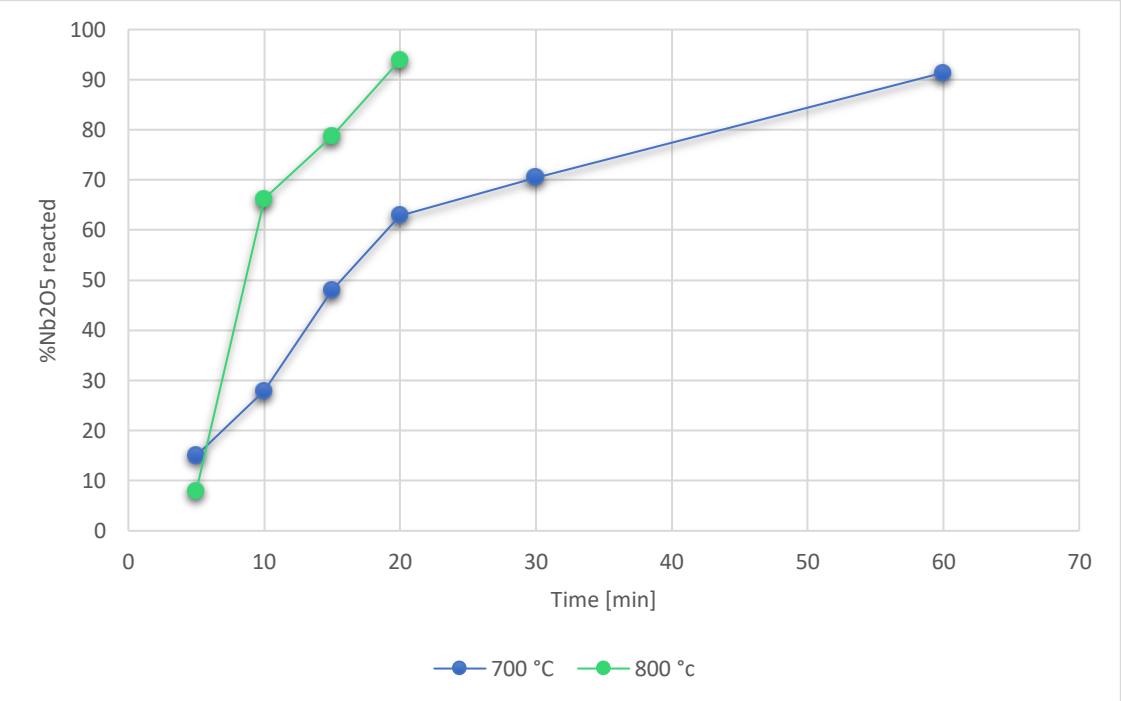


Figure 21: Effect of the Temperature.

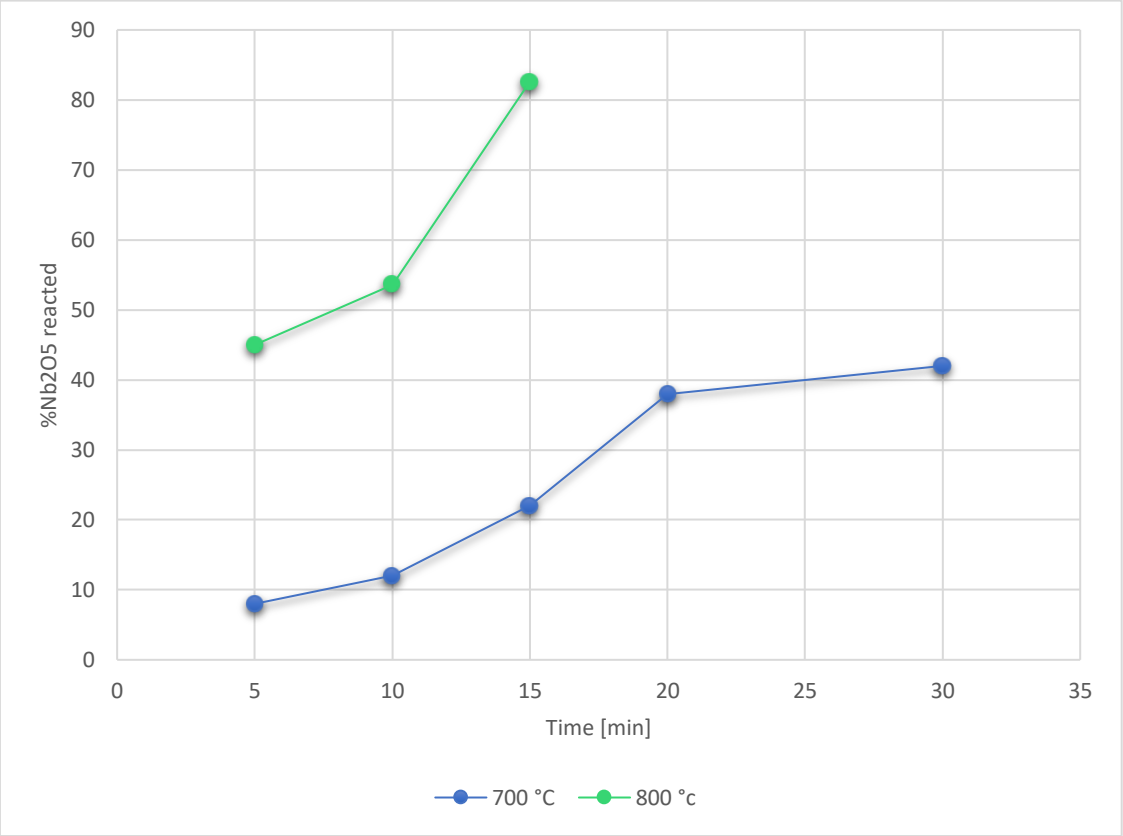


Figure 22: Effect of the Temperature with 28% pellet porosity.

Experimental were also conducted with different exposed area to the chlorine flow observed in Figure 23. In this case is very interesting to mention that for high temperature (800 °C) and high initial carbon (40%) the exposed area effect on the initial rate is very clean while for low temperature (700 °C) and low initial carbon (9%) there is no effect of the exposed area. This fact is a clear indication that depending on the experimental conditions the chlorine will easily penetrate, or not, to the inner parts of the solid mixture, as well will be discussed in the following section. This fact is well in accordance with the previous discussion.

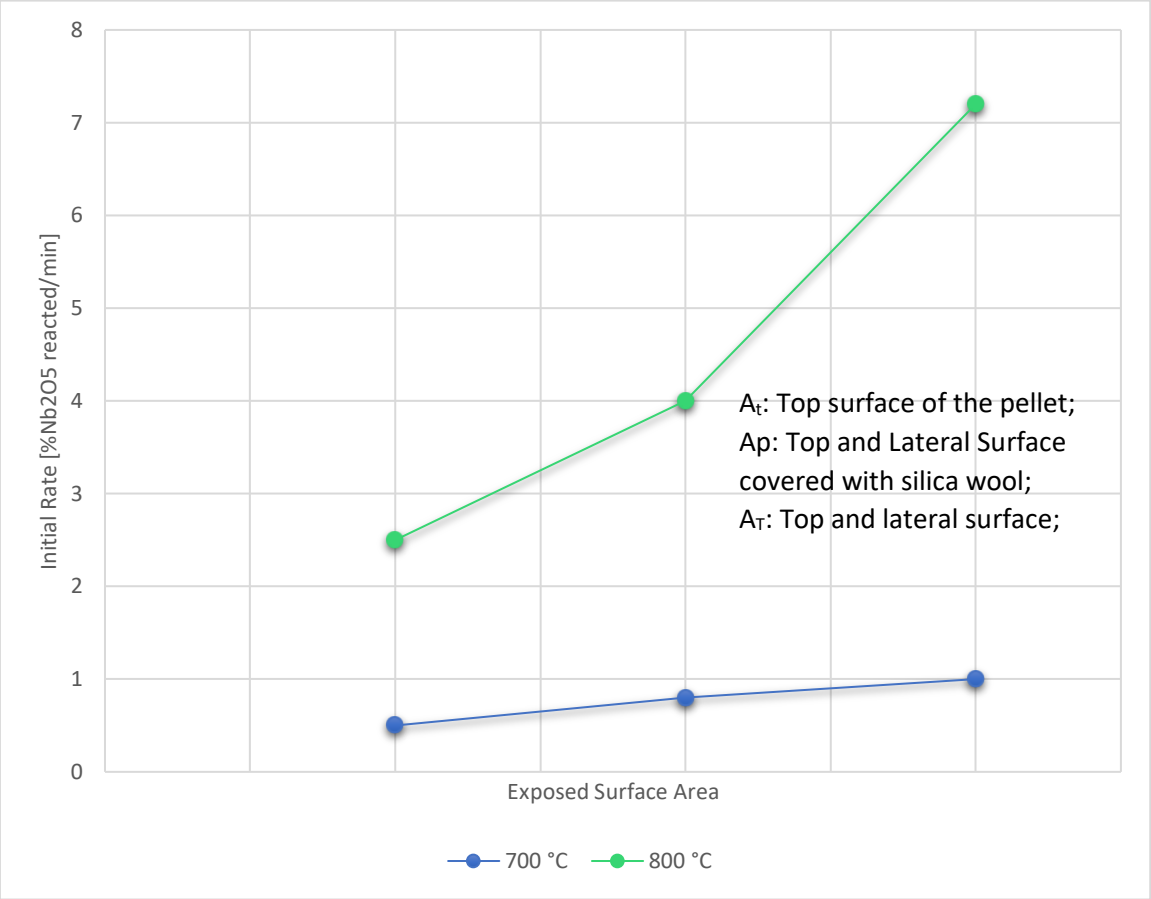


Figure 23: Effect of exposed surface area on the initial rate.

The effects of varying the sample porosities were observed between 700 ºC and 800 ºC, in most cases increasing porosity proportionate high initial reaction rates. This is probable due to the greater ease chlorine's penetration into the bulk of the pellet at higher porosities. The phenomenon caused by porosity rise will provoke a general chemical controlling in a gas-solid reaction. However, at high temperature, such as 800 ºC, the porosity effect may decrease and the chemical reaction will take place, anyway, at the exposed solid superficial area to the inner parts of the sample.

It is understood that a niobium pentoxide carbochlorination general overview on the overall kinetic behaviour, as provided in the last section of this chapter, may provide valuable insights for the development of a future mathematical model.

4.3.2 The physical structural evolution through time

Taking into consideration the previous section it is important to call attention that the effect of the experimental variables on the Nb_2O_5 conversion levels is not the only aspect to be considered in terms of full chlorination process knowledge. It can be said, that the solid structural evolution through time may be completely different for the same percentage of Nb_2O_5 converted to chloride. So, a conversion of 50% may have been achieved through three completely different internal mechanism and then providing three solids with completely different structures. This occurs because, for instance, at high temperatures and low porosity, the chlorine will react immediately with the available surface while at low temperature and high porosity, the chlorine will penetrate to the inner parts of the solid mixture, $Nb_2O_5 + C$.

Therefore, the conversion levels profiles through the sample depth over time will be different and Figure 24 shows that theoretically. The theorical expected behaviour for a 50% Nb_2O_5 reacted in the whole sample encompassing all the pellet depth is clearly observed in Figure 24. Perceive in,

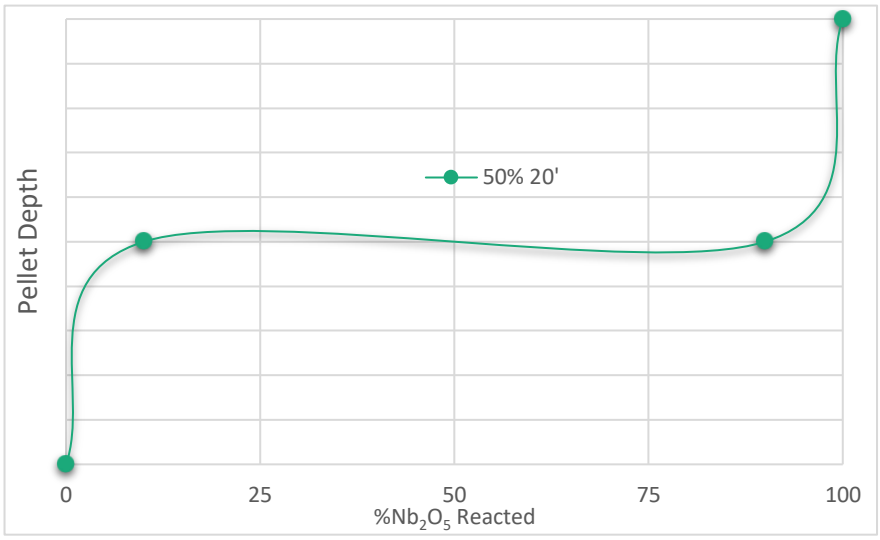
(a) all the Nb_2O_5 reacts only in the sample's upper layers – difficult chlorine penetration;

(b) all the Nb_2O_5 reacts from the top to the bottom sample's layers – regular facility for chlorine penetration;

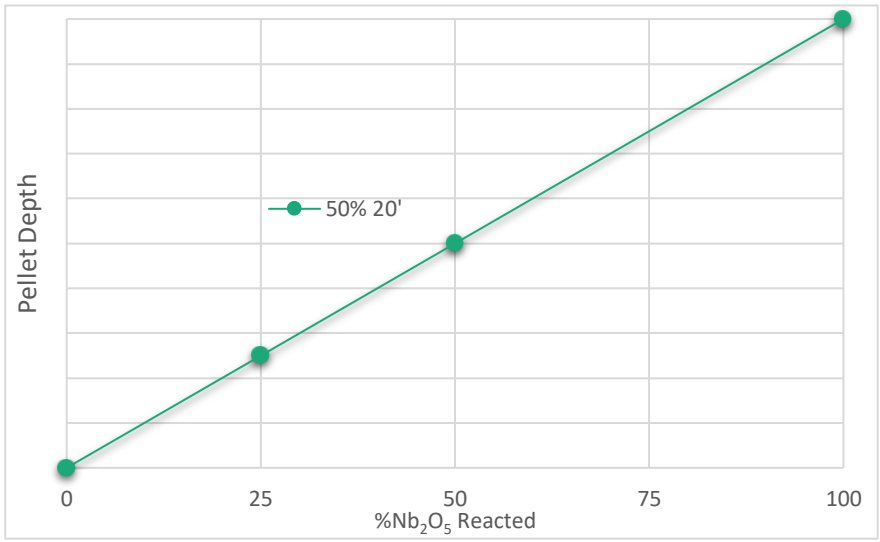
(c) all the Nb_2O_5 reacts equally from top to bottom of the sample layers – easy chlorine penetration;

It is related to the proposed mechanism reaction control in each theoretical frame which will be diffusional, mixed and chemical, respectively. This approach will be discussed in section 4.3.3 and presented in Figure 26.

(a)



(b)



(c)

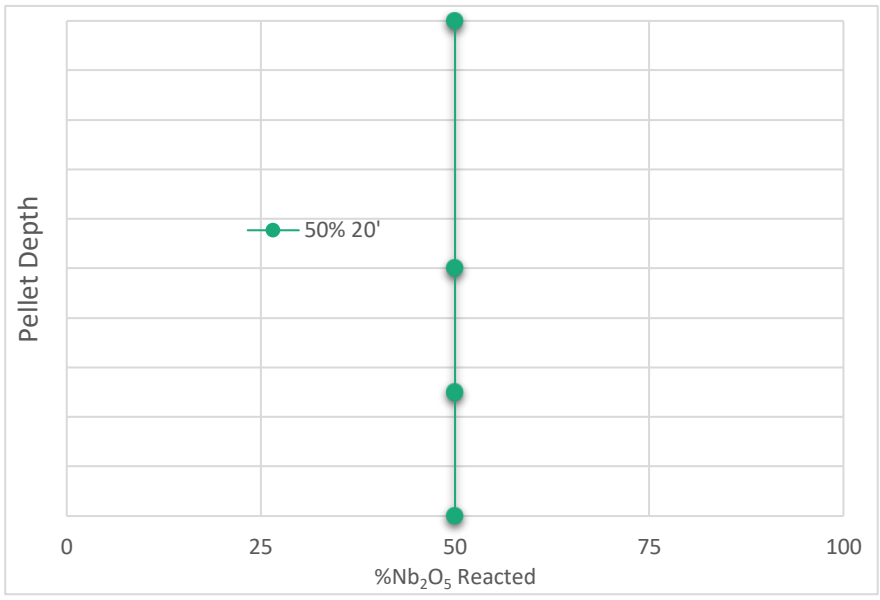


Figure 24: Theorical Percentage of Nb_2O_5 reacted against pellet depth. (a) Diffusional control, (b) Mixed control, (c) Chemistry control.

Specifically, the Figure 25 represents the $\%Nb_2O_5$ reacted through the pellet depth in an interval of time which was experimentally obtained. It is important to mention that a comparison can be made for all the reactions with approximately 50% of Nb_2O_5 reacted observed in the blue curves in a specific period of time, being 38 minutes to 120 minutes at the specific operational conditions applied.

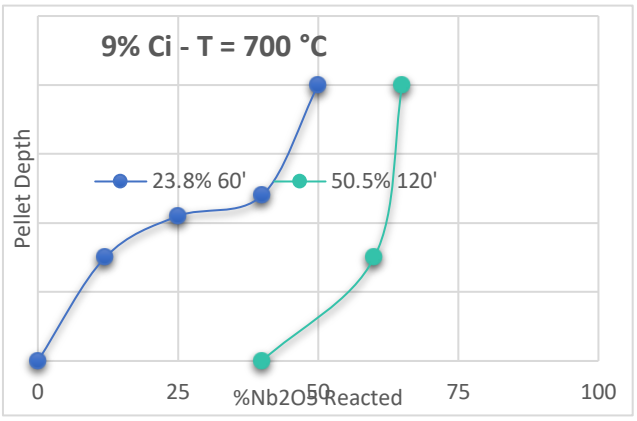
In order to contribute didactyly Figure 25 represents the real aspect behaviour expected of the $\%Nb_2O_5$ reacted in function of the pellet depth.

In the first case, showed in Figure 25 (a), the diffusional mechanism predominates due to obvious reasons – low porosity and high temperature. It represents the whole briquette, when the porosity is not still so big, the chlorine, Cl_2, reacts mainly in the superficial so fast that consumes all the Nb_2O_5 present in the top layers of the pellet, so the curve is a linear horizontal line near to 100% of the Nb_2O_5 reacted in the pellet's top.

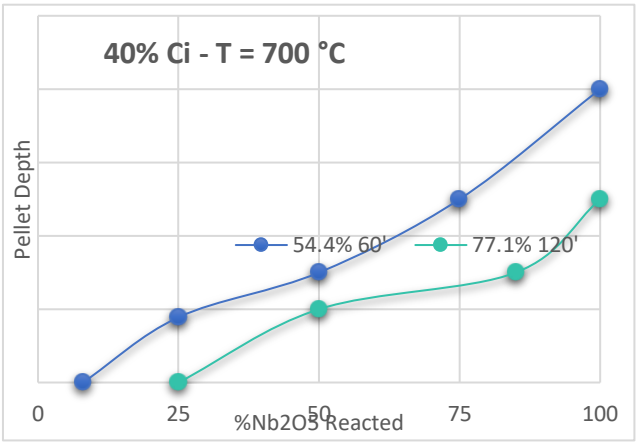
In the second case, showed in Figures 25 (b) and 25 (c), a linear horizontal line indicates that the Nb_2O_5 conversion goes from 100% in the pellet's top to 0% in the pellet's bottom. It can be clearly seen that these experimental curves are very similar to the theoretical behaviour as observed in Figure 24 (b).

In the third case, showed in Figure 25 (d), it can be seen that the removal of Nb_2O_5 as chlorides occurs preferentially in the top layers of the sample indicating a difficult chlorine penetration to the inner parts of the sample.

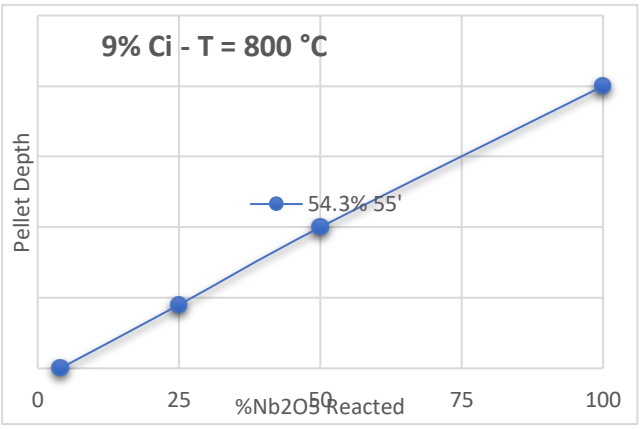
(a)



(b)



(c)



(d)

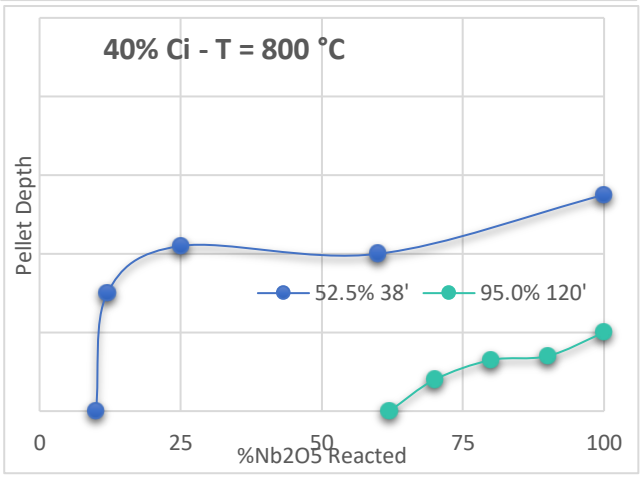


Figure 25: Percentage of Nb_2O_5 reacted against pellet depth, porosity 28%, $pCl_2 = 1atm$, & h = 10mm, (a) 9% Ci & T = 700 °C, (b) 40% Ci & T = 700 °C, (c) 9% Ci & T = 800 °C, (d) 40% Ci & T = 800 °C.

Therefore, it can be seen that the progress of the reaction may take place either through a uniform conversion throughout the solid, favoured by low temperature, high porosity and low %C, or through a sharp reaction front moving to the interior of the solid, favoured by high temperature, low porosity and high %C. Intermediate conditions results in a reaction patter lying to between these two extremes.

Table 18 below resume what was discussed above about Mechanism's Control reaction respecting to the variable's temperature - T, porosity - ε of the sample and initial percentage of carbon - %Ci.

Chemical Control	Mixed Control	Diffusional Control
low T	intermediate T	high T
high ε	intermediate ε	low ε
low %C	intermediate %C	optimum %C

Table 18: Contribution of the variables temperature, porosity and initial carbon content on the possible types of the whole reaction mechanism control.

As commented in the section 2 of this work, Figure 26 illustrates a proposal for the general physical mechanism of the Nb_2O_5 carbochlorination progress based on the reaction rate in each layer of the sample.

When the depth of the initial partially reacted layer is greater the diffusion is high when compared with the rate of chemical reaction and the chemical regimes will predominate. It should also be noted that the overall rate of niobium oxide volatilization may be constant during a certain time. It is also suggested that the maximum rate of niobium pentoxide volatilized in each pellet layer decreases for deeper layers. This fact can be explained by the existence of a chlorine concentration profile through the pellet since the reaction rate in each layer may be proportional to the corresponding chlorine concentration, and the chlorine has to pass through a partially reacted layer with excess of carbon in order to reach the bottom parts of the pellet. If the material left in the top of the sample does not offer any resistance to the passage of the chlorine, then the rate of transformation at each of the deeper layers would be determined by available chlorine that crosses each of them. The effect of the chlorine diffusion is not important in determining the overall reaction rate when the conversion takes place evenly in the whole sample from

the very beginning of the chlorine admission. A uniform concentration of the chlorine throughout the sample can be rapidly attained and the rate of Nb_2O_5 gasified from each layer is basically the same. However, this rate will decrease after a certain time due to an increasing poor contact between the solids until when the porosity reaches a critical value which will causes the collapse of the charge.

When the amount of Nb_2O_5 reacted in the top sections of the sample is greater than in the bottom the analysis carried out suggests that after the admission of chlorine there is a rapid formation of a partially reacted layer which acts as a reaction front. The rate of conversion of Nb_2O_5 in the top of this layer decreases due to a decreased extent of contact between niobium oxide and carbon observed by an increased porosity while in the bottom layer the rate of niobium oxide conversion increases up to a certain critical value when the increasing porosity becomes more significant despite the higher concentration of chlorine. At this point, the reaction front has already moved to a deeper portion of the pellet and may reach it before all the niobium oxide present in the top of the pellet has been reacted.

The depth of the initial partially reacted layer is a function of the chlorine penetration through the sample which in turn is a function of the chemical reaction rate of the chlorine with the top layer and the porosity. When this velocity is high and the porosity is low the chlorine reacts in a thin layer because it cannot move to the inner parts of the pellet. Also, in this case the overall reaction rate decreases continuously due to changes in the structure, such as an increasing porosity, from the top to bottom layers of the sample.

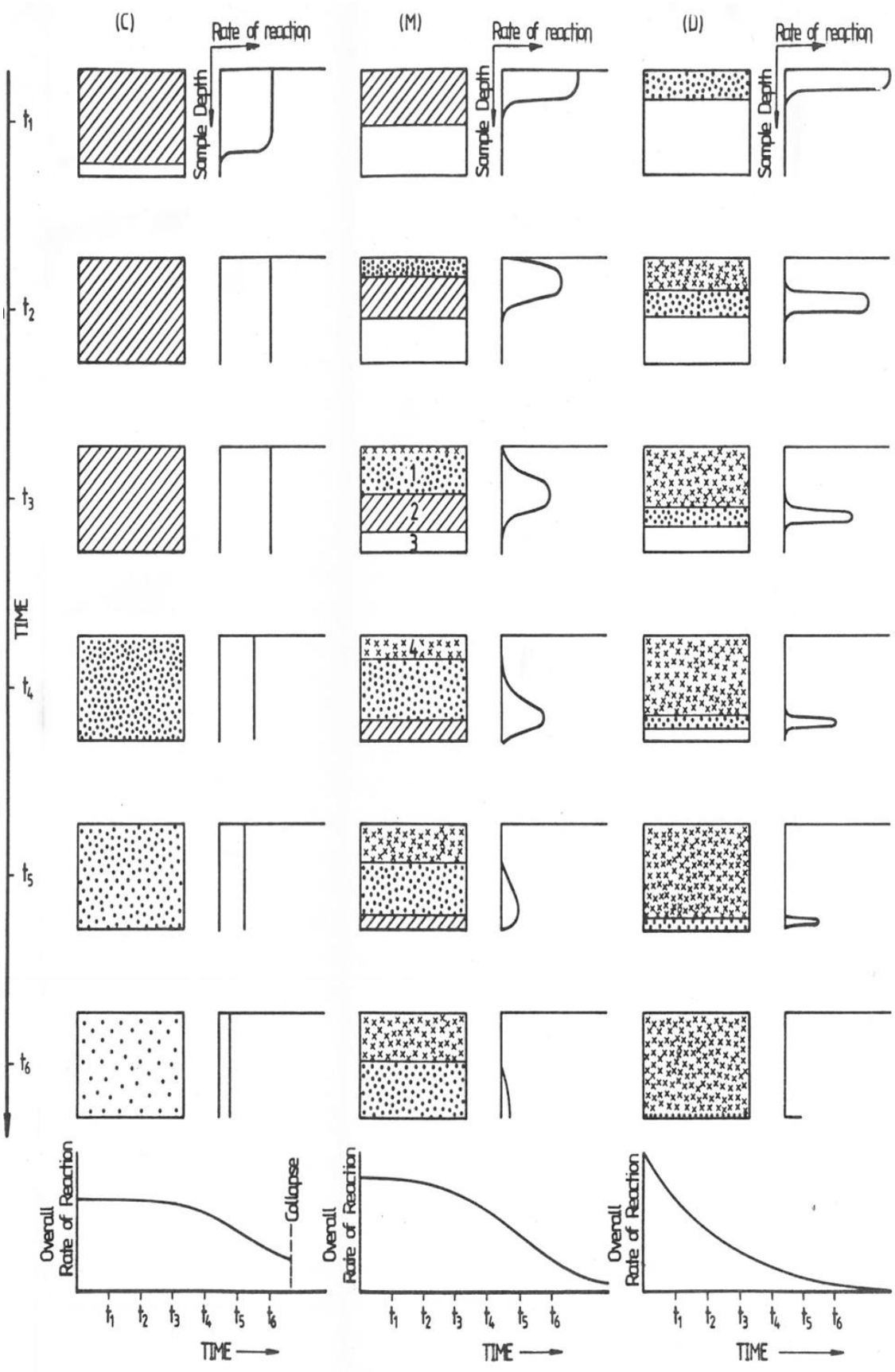


Figure 26: Progress of the reaction zones through samples showing the changes in the reaction rates of each layer as a function of time. Source: (Brocchi E. A., Reduction chlorination reactions of Niobium and Tantalum Oxide containing materials, 1983).

Figure 26 can be easily understood if it is considered the information below related to the reaction's zones and mechanism control,

I - Reaction Zones

(1) Well reacted zone – the rate in each layer decreases due to increasing porosity.

(2) Reacting zone.

(3) Unreacted zone.

(4) Completely reacted zone.

II – Mechanism Control

(C) Deep Initial Chlorine penetration - Reaction takes place evenly through the whole sample – Chemical Control.

(M) Intermediate initial chlorine penetration – Reaction front moves to the bottom of the sample – Mixed Control.

(D) Poor initial penetration – Formation of a sharp reaction front – Diffusional Control.

The progress of the reaction may therefore take place through a uniform conversion of niobium pentoxide throughout the chlorination charge (favoured by low temperature, low %C and high porosity) or through a sharp reaction front moving the interior of the solid mixture which is favoured by high temperature, high %Ci and low porosity. Intermediate conditions result in a reaction pattern lying between these extremes.

As a resume of the above discussion, follow a brief description explaining column by column of the Figure 26,

Column I – In the first one exposed in Figure 26, Cl_2 keeps entering to the inner parts of the sample from t_1 to t_6. However, the rate of reaction is decreasing after t_3 and the overall rate, given by the area inside the figures decreases as shown in t_4. This effect is explicit in the behaviour of the Time x Overall Rate Reaction curve when it can also be seen the collapse of the sample due to its attained high porosity.

Column II – In the second one exposed in Figure 26, Cl_2 enters partially into the sample reacting mainly in the top layers but also in deep layers. From t_1 to t_3 there is still layers not reacted at the bottom and it can also be observed that the overall reaction rate, given by the area inside the figures decreases from t_2 to t_6. It represents the intermediate case between the two extremes, high penetration from the beginning observed in column I and no penetration observed in column III. This effect is explicit in the behaviour of the Time x Overall Rate Reaction curve when it can also be seen the decrease of the overall rate from t_3.

Column III – In the third one exposed in Figure 26, Cl_2 reacts with Nb_2O_5 mainly in the top layers due to low porosity and high temperature. Then, it can be seen that the rate of reaction became zero in the top layers after a certain time. The chlorine increasing difficulty to reach the bottom layers causes a decrease in the overall reaction rate from t_1. This effect is explicit in the behaviour of the Time x Overall Rate Reaction curve when it is observed the fall of the overall reaction from the first moment.

4.3.3 A general theorical proposal based on temperature, %Ci and porosity in order to provide a general representation of how the reaction proceeds in the body of the chlorination charge

Since the Nb_2O_5 carbochlorination reaction behaviour is determined by a balance between the most important variables of the system the observations of the combined effect of temperature, $\%C_i$ and porosity of the solid mixture on the progress of the reaction can be analysed in order to provide a general representation of how the reaction front flows to the inner parts of the solid charge in the mixture with $Nb_2O_5 + C$.

i) Under conditions of high temperatures and $\%C_i$ the chemical reaction takes place rapidly resulting in poor chlorine penetration into the solid mixture even when it is formed of loose powder.

ii) At low temperatures and $\%C_i$ the chemical step is slow and the reaction may take place throughout the pellet to the same extent independently of the porosity of the solid mixture.

iii) Under intermediate conditions, increasing porosity will increase chlorine penetration into the solid charge due to a poor $Nb_2O_5 - carbon$ contact which causes the chemical reaction to be slow so that access of the chlorine into deeper section occurs.

iv) The importance of $\%C_i$ and porosity of the solid mixture determining the overall behaviour of the system decreases for increasing temperature. It follows that for increasing temperature lower values of $\%C_i$, at any porosity, or higher values of the charge porosity, at any $\%C_i$, may be sufficient to maintain the overall reaction behaviour under the same mechanism.

These considerations are illustrated in a general representation of the behaviour system. Figure 27 shows how the balance between temperature, $\%C_i$, and porosity may determine the progress of the reaction throughout the chlorination charge, $Nb_2O_5 + C$.

Also, in the same figure are presented three areas, which are,

C Area: Uniform reaction throughout the charge – Chemical Control.

M Area: Intermediate Behaviour – Mixed Control.

D Area: Formation of a sharp reaction front – Diffusional Control.

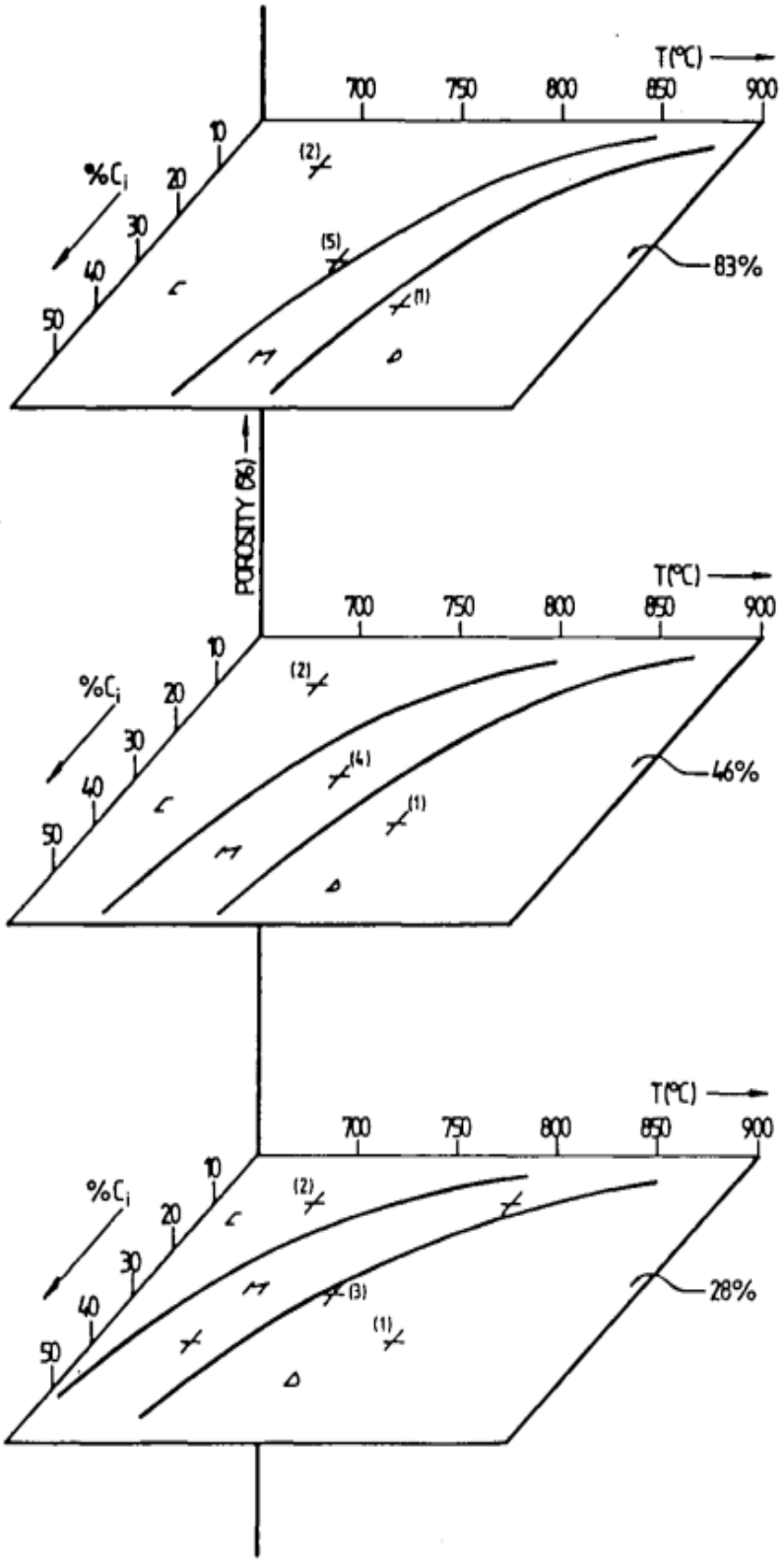


Figure 27: General Representation of how the reaction proceeds in the body of the chlorination charge (h=10mm) according to the values of temperature, $\%C_i$ and porosity of the solid mixture. Source: (Brocchi E. A., Reduction chlorination reactions of Niobium and Tantalum Oxide containing materials, 1983).

5. CONCLUSIONS

Considering the purposes of this work, as mentioned in section two, the conclusions can be divided into three segments.

5.1 Updated data related to Niobium resources, applications and general perspectives

Niobium natural availability remains concentrate in the Brazil's already know reserves, keeping this country with clean prominence in the mining and niobium containing material production international scenario. But it is also recognised that alternatives sources of the metal will have to be considered in the future or as soon as possible.

Due to its properties either as metal or as a component in diverse types of materials, such as alloys and carbides, the applications of niobium have been expanded to new and modern technologies as those in the fields aero or space constructions, general buildings and energy such as batteries electrodes.

Niobium metal extraction from natural resources seems to have a stablished production route which is finished through the Nb_2O_5 reduction with Al followed, whenever required, by electron beam refining. Also, others important Nb content products, such as different grades of Nb_2O_5 and $FeNb$ alloys, have their production routes well accepted by the main market consumers.

5.2 Chlorination possibilities and thermodynamic studies in the Niobium metallurgy scenario

The halide metallurgy seems to be an attractive alternative process for the extraction of refractory metals. Then, chlorination should be considered as a process to be applied for recovering niobium metal from different materials such as slags and other industrial residues.

In that sense it is fundamental the choice of the chlorinating agent which can provide an adequate separation either through selective reactions forming volatile chlorides or by the selective formation of soluble chlorides. The former

case was exposed as a possible alternative route to separate Zn and Fe content in franklinite.

It seems to be a tendency that the halide metallurgy will be considered as an alternative process for the extraction of refractory metals and chlorination route stand amongst them. In that sense, chlorination should be considered as a process to be applied for recovering value metal from different materials such as slags and industrial residues, essentially materials containing Nb_2O_5.

In terms of niobium, it was clearly observed that carbochlorination ($C + Cl_2$) as well as the use of CCl_4 or C_2Cl_4 are efficient Nb_2O_5 chlorinating agents to form gaseous $NbCl_5$ while the other investigated reagents have no tendency to chlorinate the Nb_2O_5. However, some of them, such as $NaCl$ and $CaCl_2$, can be applied to form soluble metal chlorides to be separated from the unreacted Nb_2O_5 in a further step of an eventual process route.

5.3 A contribution for the kinetics and physical transformation of the Nb_2O_5 carbochlorination

An important conclusion is related to the experimental results which show a clear possibility of a 100% Nb_2O_5 conversion in less than 2 hours under different operational conditions, such as 800 °C and 20 % initial carbon in the solid mixture.

The effect of the sample available surface for the chlorine flow on the initial rate is related to the experimental conditions. For easy chlorine penetration this effect is irrelevant showing that the Nb_2O_5 removal occurs, from the beginning, through the whole sample (from top to bottom). For all experimental conditions where the initial reaction rate is proportional to the exposed area it can be said that the chemical step is very fast and the chlorine has difficulty to penetrate into the solid sample.

The initial depth of the chlorine penetration into the sample depends on the operational conditions. For fast chemical reaction in the sample top layers (high temperature and good solid contact) the depth of this zone is small and the reaction front to the inner parts of the sample is a sharp horizontal line. However, for experimental conditions where the chlorine can easily penetrate

into the sample (low temperature and high porosity) the reaction front will tend to be a vertical line. In the intermediate conditions the reaction front will follow a diagonal line. That observation is clearly exemplified for a 50% Nb_2O_5 conversion and was also observed through experimental measurements (Figure 24).

It was proposed a mechanism for the penetration of chlorine into the sample as function of the experimental conditions, discussing the reaction rate in each layer of the sample as well as the overall reaction evolution of the Nb_2O_5 conversion (Figure 26).

According to the values of temperature, % initial carbon and porosity, the reaction progress through different mechanisms. It is proposed that for easy initial chlorine penetration the whole system would be chemically controlled while for difficult penetration it will move to diffusion controlled. Between these conditions a mixed control takes place (Figure 27).

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