

# Partition Behavior of Niobium between Carbon Saturated Iron and Slags from the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-MgO}$ system

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## Abstract

Equilibrium studies were conducted to further understand the partition behavior of niobium between carbon saturated iron and the lime-alumina-silica-magnesia slag system with change in basicity in the temperature range 1773- 1873K. The behavior of niobium in this range of slag composition is of interest to those who use ferroniobium to alloy steel during ladle metallurgy. . Small variations in slag composition caused the activity coefficient for niobium pentoxide in the slag to change by over an order of magnitude and the activity coefficient of  $\text{NbO}_{2.5}$  was found to be a strong function of optical basicity. The measured data were used, in conjunction with literature values for the activity of niobium in steel, to predict the niobium partition under secondary steelmaking conditions. This showed that niobium losses to the slag under these conditions may be significant and the erratic nature of industrial niobium recoveries may be explained by the strong sensitivity to slag composition. The Temperature dependence of the activity coefficient of niobium pentoxide was found to be positive which requires an unusually large contribution from the entropy of mixing to justify the measured activity coefficient.

## Introduction

Niobium is added to steel in small amounts to improve yield strength while maintaining desirable toughness and ductility(1). Its addition can also increase corrosion resistance and creep resistance in steel grades for use in high temperature service (2).

During ladle steelmaking the recovery of ferroniobium tends to be erratic(1), although there has been little by way of explanation for this behaviour reported in the literature. There have been several studies of niobium recovery relating to the ferroalloy production, and oxidation to remove niobium from pig iron(3-7). There have been some studies that relate to steelmaking conditions but none using calcium aluminate slags typical of those used in ladle metallurgy.

It has been consistently found that niobium behaves as an acidic oxide, with increased partitioning on the addition of iron oxide, lime, soda or other basic components to the slag. Even small changes in slag composition and atmosphere can affect large changes in niobium partition between slag and metal. Tsukihashi et. al. found that adding 2%  $\text{NaO}_2$  to the slag resulted in

partition increases of up to two orders of magnitude, in the  $\text{CaO-Na}_2\text{O-CaF}_2\text{-SiO}_2$  system at 1573K.

In work done by Inoue et. al. in the  $\text{MgO}_{\text{sat}}\text{-Fe}_t\text{O-SiO}_2\text{-Nb}_x\text{O-MnO}$  system, the activity coefficient of niobium pentoxide did not change significantly with slag composition(7). It should be noted that this occurred at high oxygen potentials, as the iron content of the slag was as much as 50%. Under conditions of carbon saturation the activity of niobium is reduced, effectively increasing recovery in the metal.

The kinetic behavior of niobium has been studied in the  $\text{Fe}_2\text{O}_3\text{-CaO-SiO}_2$  system(3), in the  $\text{Fe}_2\text{O}_3\text{-CaO-CaF}_2\text{-B}_2\text{O}_3$  system(4), in the  $\text{Fe}_2\text{O}_3\text{-CaO-B}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3\text{-NaCO}_3\text{-B}_2\text{O}_3$  systems(6), in the  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  system(8), and in the  $\text{NaCO}_3\text{-Fe}_2\text{O}_3$  and  $\text{CaO-CaF}_2\text{-Fe}_2\text{O}_3$  systems(9). The partition behavior of niobium has been studied by Inoue et. al. at 1873K between liquid iron and the  $\text{MgO}_{\text{sat}}\text{-FeO-SiO}_2\text{-NbO}_x\text{-MnO}$  system(7). Tsukihashi et. al. studied the partition between carbon saturated iron and the  $\text{CaO-CaF}_2\text{-SiO}_2\text{-Na}_2\text{O}$  system at 1573K(10). To the knowledge of the present authors these two studies comprise the only published data in the temperature range is applicable to the steel ladle, and no data is available for the magnesia saturated-lime-alumina-silica slag system is normally used in secondary steelmaking.

During steelmaking there are other alloying elements present which will partition preferentially depending on the activity of oxygen ions in the slag(7,9). There has been much debate over the definition and quantification of the activity of the  $\text{O}^{2-}$  ion, which cannot be thermodynamically measured. In addition, the oxygen ion activity is contributed to, collectively by all components of the slag, and cannot be defined by only one compound or reaction. Various weighted ratios with the sum of the basic components, over the sum of the acidic components have been used(11). These empirical ratios are useful for comparison, and while based on a qualitative fundamental understanding of the thermodynamics of the oxide ion activity, they do not normally work over a wide range of composition. Others have avoided using an ion activity term by using the ratio of slag capacities(10), which eliminates the problematic term, and gives a basis of comparison. This method is limited to systems in which the standard, usually a carbonate species, is soluble over a range of concentration. In recent years the concept of optical basicity developed by Duffy and Ingram(12), has been employed to define the oxide ion activity. This concept defines the electron donor power of slag components compared with that of pure  $\text{CaO}$ , and in theory compares all slags on the same basis. However, practical experience shows that this theory does not give an entirely consistent picture across a wide range of slag systems and there remains some debate over the optical basicity values chosen for individual oxides(11). Table 1 compares proposed values for common components of steelmaking slags. It is clear there is consensus for  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  but  $\text{FeO}$  is still in some doubt. The appropriate value for  $\text{FeO}$  appears to depend on its use. (For phosphorus partition 0.51 works well(11), but for sulfur the recommended value 1.03 is best(13).) In the present work the generally accepted values have been used, as we are mainly concerned with components that are not in doubt.

## Experimental Method

All experiments were carried out in a tube furnace heated electrically by lanthanum chromite elements. The composition of the gas mixture inside the furnace was controlled using electronic mass flow controllers and monitored by gas chromatography. Carbon dioxide was removed from carbon monoxide using ascarite (sodium hydroxide on a non-fibrous silicate carrier) and moisture was removed from carbon monoxide and argon, using drierite (anhydrous calcium sulfate) and silica gel. Argon was deoxidized by passing it over copper turnings at 873K. See Figure 1 for diagram of furnace set up.

The alloy used in this study was prepared from hydrogen reduced iron, and ferroniobium supplied by Lake Erie Steel Company Ltd. The level of niobium in the ferroalloy was 65.7 wt%. The iron powder and ferroniobium mixture was pre-melted in a graphite crucible using an induction furnace.

The slag compositions used in this study were prepared from reagent grade lime, alumina, silica and magnesia. The slag material was also pre-melted using an induction furnace and then quenched in air. If the slag was not uniform in color or texture it was ground and remelted to ensure homogeneous composition. After being broken up in a shatter box, the powdered slag was heated to 1273K for three hours to remove any carbon acquired during initial melting.

Five grams of metal and 0.75 grams of slag were placed in a graphite crucible with an inner diameter of 12 mm and depth of 20mm. The crucible was held at the bottom of the furnace until the required gas composition was reached. It was then raised into the hot zone, supported by an alumina rod. When the prescribed time had elapsed the crucible was lowered out of the hot zone into the cooling chamber and was flushed with argon using high flow rates to ensure efficient quenching.

## **Chemical analysis**

Metal samples were cleaned to remove excess graphite, and cut into pieces approximately 0.3 grams in size. Samples were dissolved in a solution of one part hydrochloric acid, one part nitric acid and two parts distilled water. The niobium content of the metal was determined using Inductively Coupled Plasma (ICP).

Slag samples were ground and then sieved using a 64  $\mu\text{m}$  mesh to remove any metal from the slag. This technique has been found to be very effective in removing metal particles from slag(14). Following this, slag samples were heated to 1327K for forty five minutes to remove carbon prior to fluxing. Sodium carbonate and sodium borate were the fluxing agents used in conjunction with sodium bromide as a de-wetting agent. When the slag had fully dissolved, and while it was still molten, it was deposited in a solution of nitric acid and distilled water. The niobium content of the slags was determined at Stelco, while the bulk composition was determined on campus, also using ICP.

## Results and Discussion

Table 2 shows the starting compositions of the slags which were used in estimating time required to reach equilibrium between the lime-alumina-silica-magnesia system and carbon saturated iron at 1873K.

Figure 2 shows the partition behavior of the third slag composition with time. This figure compares the partition calculated from analysis of slag and metal with partitions calculated from slag analysis and a mass balance to determine the metal composition. In this case we see fairly good agreement, however there is more scatter in the values obtained from metal analysis. Solutions were filtered to remove carbon prior to analysis and it is believed that some undissolved niobium carbide was also trapped on the filter paper, resulting in a low value for niobium in the metal. Therefore the slag analysis, and metal composition calculated from the slag analysis are deemed to be more reliable. In addition, the slag analysis is believed to be accurate over that of the metal, as the entire slag sample was analyzed where only a small portion of the metal was taken. The following data relating to niobium metal content were determined by mass balance unless otherwise stated.

Similar behavior was observed with all three slags. Initially there was a high partition to the slag, followed by a decrease to the final equilibrium level. The initial peak is likely due to an increase in oxygen potential which results from the oxide coating on the alloy material used. Under these conditions equilibrium was reached in approximately four hours.

The log of metal content in the slag is shown as a function of reciprocal temperature in Figure 3 for the second slag composition. These results are somewhat confusing as they show no clear trend with temperature. However, if we examine the slags in terms of their real, rather than nominal composition, we find a very different picture. The activity of  $\text{NbO}_{2.5}$  was calculated from the metal content and the oxygen potential in the furnace. This was then used to calculate the activity coefficient of  $\text{NbO}_{2.5}$  in the slags, as shown in Figure 4. This showed that there is a considerable change in the activity coefficient of  $\text{NbO}_{2.5}$  with minor changes in the slag composition, which explains the apparent erratic behavior in Figure 3. In fact the data follows the same trend with remarkable consistency. Figure 4. shows the activity coefficient as a function of optical basicity for niobium content (in the metal) from 0.41% - 1.20% at 1773, 1823 and 1873K. The authors had some misgivings in plotting data over such a small range of optical basicity, however the data fits the expected linear trend and is consistent at all temperatures. This clearly shows that the activity of niobium-pentoxide is very sensitive to minor changes in slag composition. This is consistent with the findings of Tsukihashi et. al. who showed that a 2% change in slag composition altered the partition ratio by two orders of magnitude. This result has an important implication for steelmakers as it shows that minor changes in slag composition may create large changes in niobium recovery. Figure 4 also shows that as temperature increases, the activity coefficient decreases. This is contrary to normal expectations for solution behaviour but is probably related to the fact that the dissolved species is considerably different from the solid oxide used as the standard state.

As shown in Figure 5, for a given amount of niobium in the metal, the activity of the

oxide increased as the temperature decreased. Therefore greater losses of niobium to the slag are expected at lower temperatures. The dependence of the activity coefficient on temperature is illustrated in Figure 6. Using equation (1) the heat of mixing of niobium pentaoxide ( $\text{NbO}_{2.5}$ ) in the slag was estimated from the data to be approximately 586kJ/mol.

$$\partial R \ln \gamma / \partial 1/T = \Delta H^M_i \quad (1)$$

Again the positive enthalpy is contrary to normal expectation and requires a rather large entropy of mixing term to account for the measured activity coefficient. The spread in activity coefficient values, which exists between the differing metal compositions at higher temperatures does not appear at the lower temperature of 1773K.

The free energy of formation of niobium pentoxide, from gaseous oxygen and niobium in carbon saturated iron, was estimated from  $\gamma^0_{\text{Nb(s)}} = 0.44$  at 1873K(15) and the standard state free energy of formation for niobium pentoxide listed by Turkdogan(16), assuming regular solution behavior.

$$\begin{aligned} \text{Nb}_{(1\text{wt}\%)}(\text{s}) + 5/4 \text{O}_2(\text{g}) &= \text{NbO}_{2.5}(\text{s}) \\ \Delta G^0_{\text{NbO}_{2.5}} &= -931.4 + 0.252 T \quad (\text{kJ/mol}) \end{aligned} \quad (2)$$

The activity coefficient for niobium was calculated from the interaction coefficients for niobium,  $e^{\text{Nb}}_{\text{Nb}} = 0.006$  (17), and  $e^{\text{Csat}}_{\text{Nb}} = -0.12$ . The latter coefficient was estimated from the interaction of niobium on carbon saturated iron using the well established relation:

$$\epsilon^i_B = 2.303M_{\text{Wi}} ((\%A/M_{\text{WA}}) + (\%i/M_{\text{Wi}}))e^i_B \quad \text{where} \quad \epsilon^i_B = \epsilon^B_1 \quad (3)$$

and  $\epsilon^{\text{Csat}}_{\text{Nb}} = -7.0$  as proposed by Huang(18).

From the above relations, and the measured niobium content in the slag, the activity coefficient of niobium pentoxide  $\gamma_{\text{NbO}_{2.5}}$  was calculated at 1873K for the three slags used in this study. Figure 4 shows the linear relationship which exists between the log of the activity coefficient, and the optical basicity of the slag. Dissolution of the pentoxide into the slag can be described by



As  $X_{\text{NbO}_{2.5}} = X_{\text{NbO}_4^{3-}}$  the equilibrium constant for Equation 4 can be expressed as follows:

$$\log K = \log \gamma_{\text{NbO}_4^{3-}} - \log \gamma_{\text{NbO}_{2.5}} - 3/2 \log a_{\text{O}^{2-}} \quad (5)$$

and rearranged so that

$$\log \gamma_{\text{NbO}_{2.5}} = \log \gamma_{\text{NbO}_4^{3-}} - 3/2 \log a_{\text{O}_2} - \log K \quad (6)$$

where  $\gamma_{\text{NbO}_4^{3-}}$  and  $K$  are assumed constant, and  $R^*T^*2.303 \log a_{\text{O}_2}$  is proportional to  $\Lambda$ ,

therefore

$$\log \gamma_{\text{NbO}_{2.5}} = C_1 \Lambda + C_2 \quad (7)$$

the log of the activity coefficient of niobium pentoxide can be expressed as a linear function of the optical basicity. Experiments to this point have used slags within a narrow range of optical basicity, however the observed trend is as expected.

Figure 7 shows the predicted partition behavior of carbon saturated iron and that of low carbon steel, as a function of reciprocal temperature. A common value for the steel niobium content (0.08%),  $K$  constant from equation (1) and activity coefficients  $\gamma_{\text{NbO}_{2.5}}$  at 1773, 1823 and 1873K were used to calculate the mole fraction of niobium pentoxide  $X_{\text{NbO}_{2.5}}$  according to the following equation

$$X_{\text{NbO}_{2.5}} = (K * h_{\text{Nb}} * \text{PO}_2^{5/4}) / \gamma_{\text{NbO}_{2.5}} \quad (8)$$

where  $h_{\text{Nb}}$  and  $\text{PO}_2$  values were estimated according to the conditions of steel and carbon saturated iron. This in turn was used to determine a partition ratio. Experimental values of  $h_{\text{Nb}} = 0.018$  and  $\text{PO}_2 = 4.0\text{E-}16$  were used for carbon saturated iron, and an estimated activity of  $h_{\text{Nb}} = 0.080$  and partial pressure  $\text{PO}_2 = 2.5\text{E-}14$  were used for steelmaking conditions. The value of niobium content in the metal was chosen to be similar to that of some grades of steel, and the oxygen potential was calculated from an assumption of equilibrium with 4ppm O in steel. Though. In the case of carbon saturated iron, carbon reduces the activity of niobium, keeping the partition low, the oxygen potential has more of an effect on the level of niobium in the slag according to this comparison.

## Conclusions

The partition behavior of niobium was investigated at 1873K between carbon saturated iron and the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO slag system. The results obtained are summarized as follows:

Partition behavior was similar for different slag compositions, with initially large partitions that reached equilibrium in approximately four hours.

The activity coefficient of  $\text{NbO}_{2.5}$  was found to be very sensitive to slag composition, decreasing with increasing optical basicity.

The temperature dependence of the activity coefficient was positive which is contrary to normal expectations. More work is required to clarify this result.

Niobium partition ratios calculated for secondary steelmaking conditions show that significant niobium losses are likely, and, given the strong sensitivity of  $\gamma_{\text{NbO}_{2.5}}$  to slag composition, these losses are likely to be erratic.

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Table 1. Optical Basicity Values

	Recommended	Calculated from Pauling Electronegativities	Calculated from Electron Densities
Al <sub>2</sub> O <sub>3</sub>	0.605	0.66	0.6
CaO	1.0	1.0	1.0
MgO	0.78	0.92	0.78
SiO <sub>2</sub>	0.48	0.47	-
FeO	1.0	0.94	0.51

Table 2. Nominal Slag Compositions

	CaO wt%	Al <sub>2</sub> O <sub>3</sub> wt%	SiO <sub>2</sub> wt%	MgO wt%
Slag 1	45.0	39.6	5.4	10.0
Slag 2	65.5	16.4	8.1	10.0
Slag 3	46.5	22.1	21.4	10.0



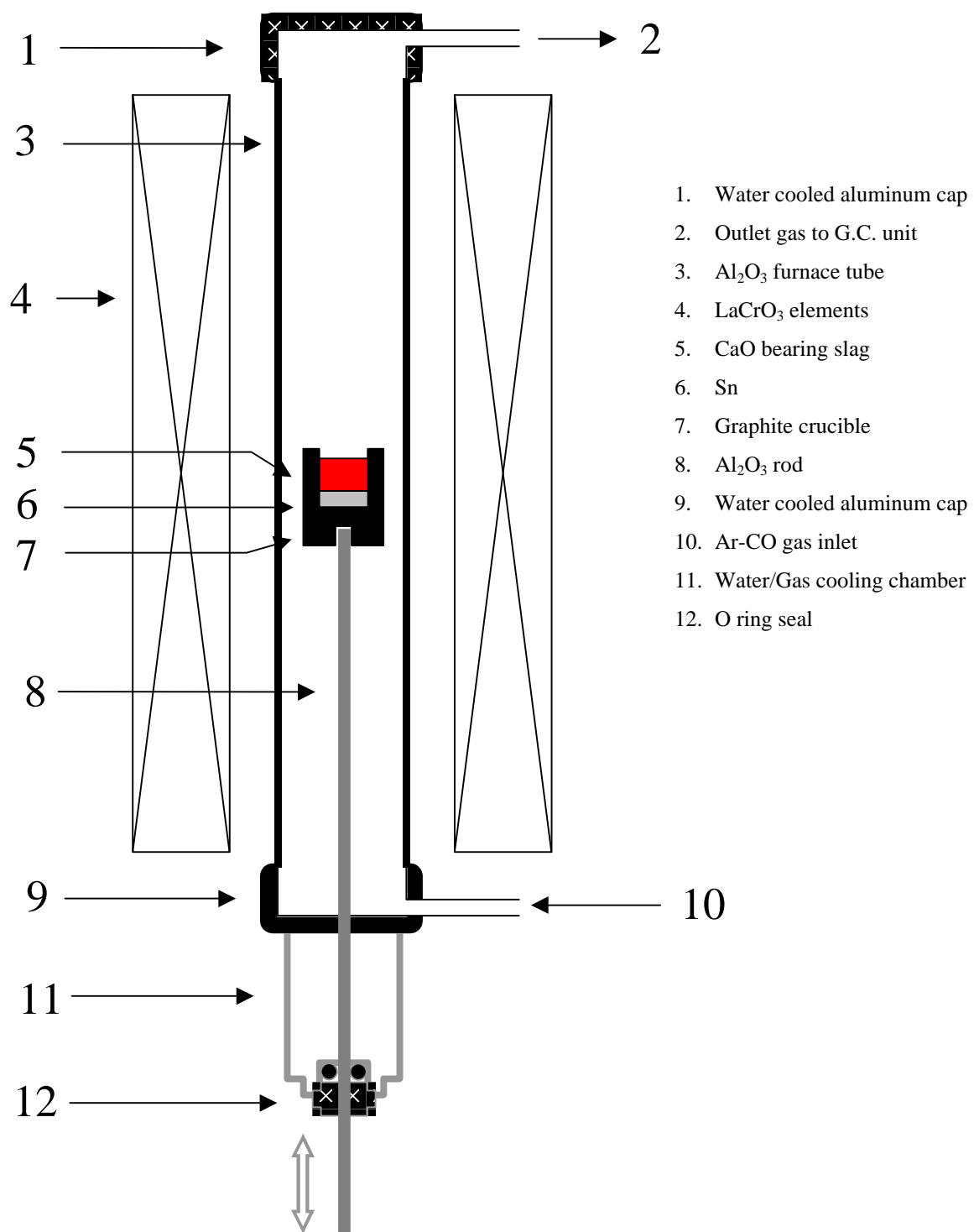
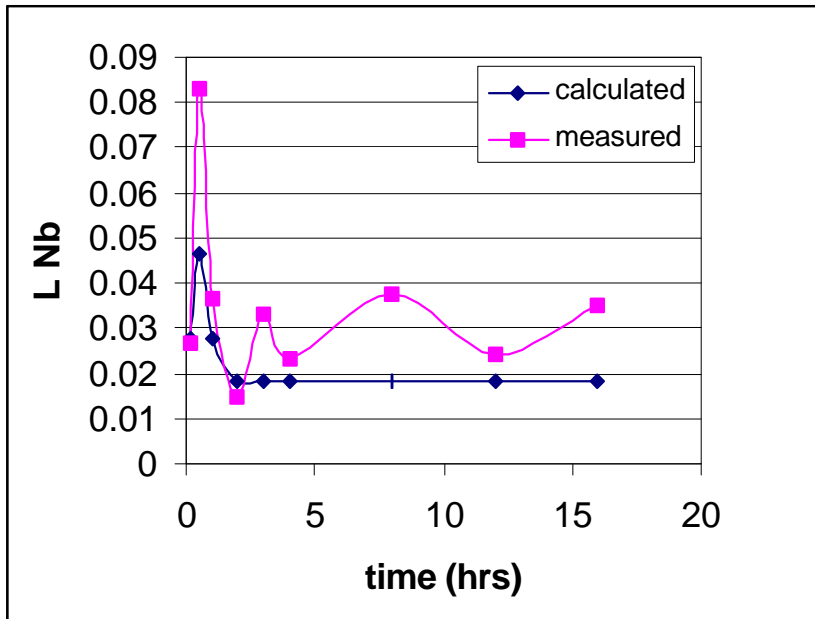
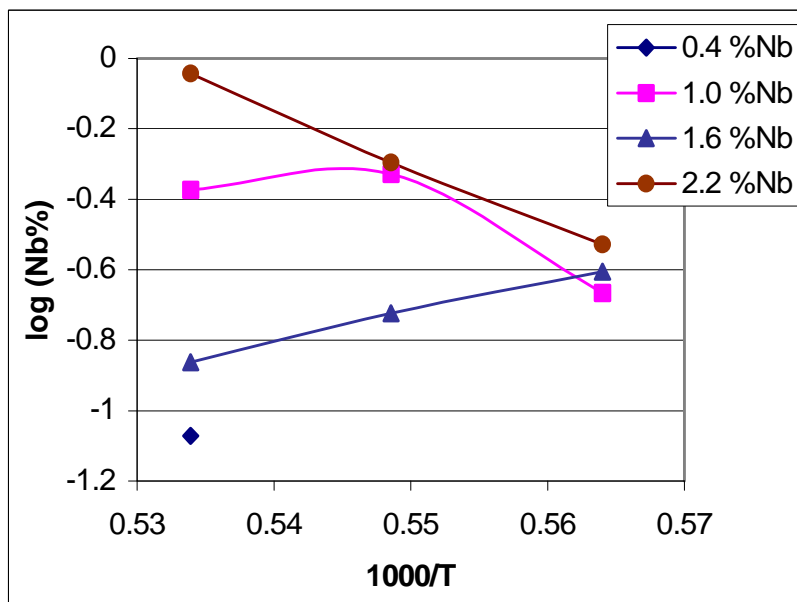


Figure. 1: Diagram of Furnace



**Figure 2.** Niobium partition, comparing values calculated using metal and slag analysis, with values determined using metal compositions calculated by mass balance.



**Figure 3.** Log wt% niobium in the slag as a function of reciprocal temperature, for different starting concentrations of niobium in metal.

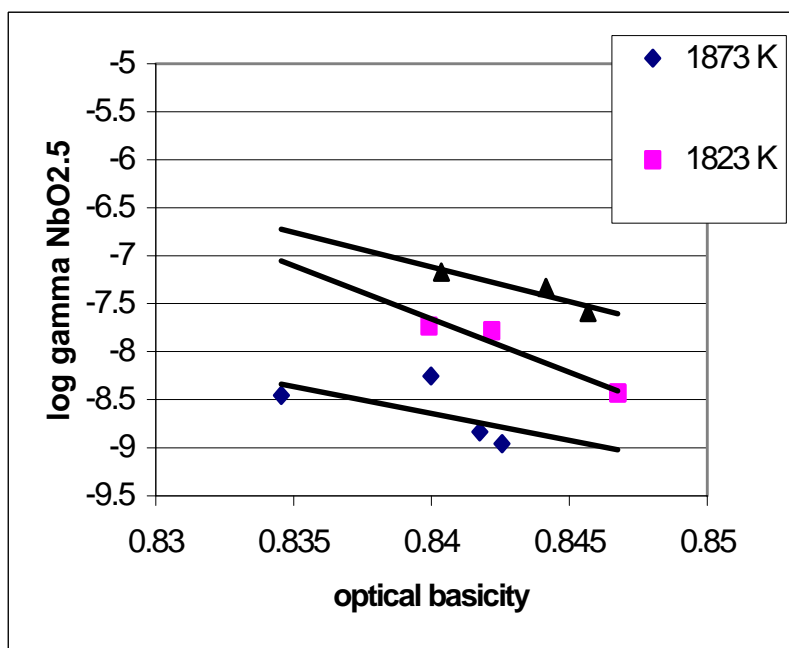


Figure 4. Log activity coefficient of niobium pentoxide as a function of optical basicity of the slag, at different temperatures.

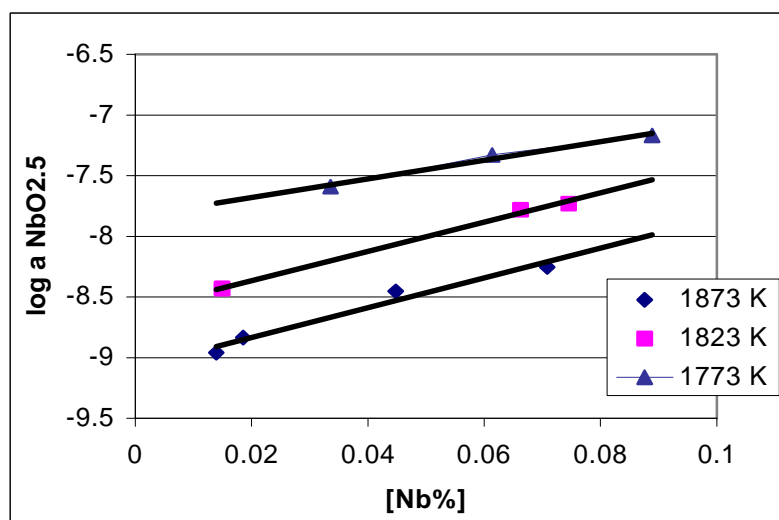


Figure 5. Log of the activity of niobium pentoxide as a function of the niobium in the metal.

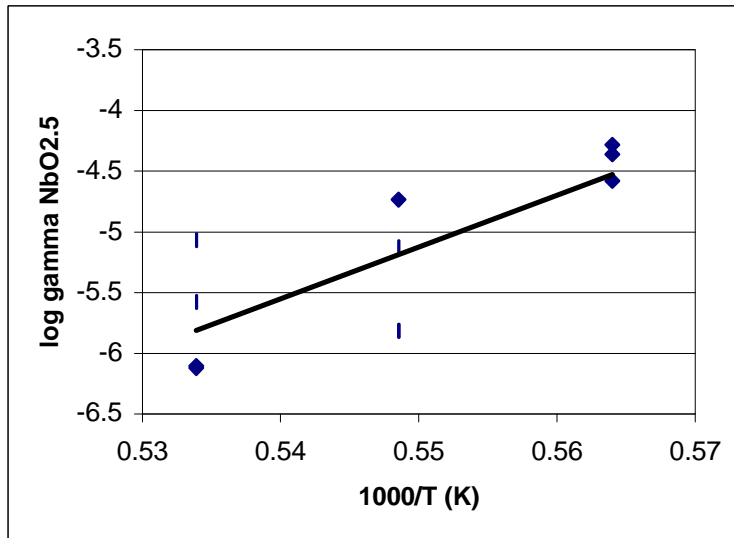


Figure 6. Log of activity coefficient of NbO<sub>2.5</sub> as a function of reciprocal temperature, for the second slag composition.

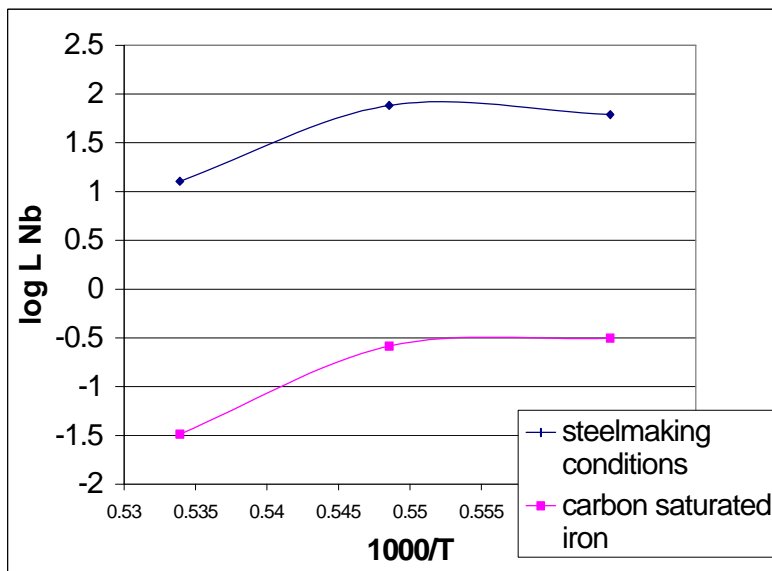


Figure 7. Plot of calculated partition for carbon saturated iron and low carbon steel based on activity coefficients found in this work.