6. Equilibrium simulation calculations

6.1. Introduction

Ferrovanadium can be produced from trivalent oxide (V_2O_3) by reduction with aluminium in an electric arc furnace, adding iron in the form of scrap, and lime (CaO) to flux the alumina (Al_2O_3) which is produced by reduction of vanadium oxide. Incompatibility between the refractory and the Al_2O_3-rich slag results in excessive refractory wear. (Industrial slag contains 3-15 % MgO). The effect of MgO on the activity coefficient of $VO_{1.5}$ is not known, but MgO does affect the Al_2O_3 activity. Al_2O_3 is expected to fix the oxygen activity in the slag. Calculations were performed assuming equilibrium to hold between Al_2O_3 and $VO_{1.5}$ in the slag, and Al and V in the metal. The effect of temperature, aluminium activity and MgO content of the slag on oxidic vanadium loss were considered. The activity of Al_2O_3 in CaO-MgO-Al_2O_3 slags and Al activity in Al-Fe-V melts were estimated using a software package of Chemsage (Chemsage,1999).

6.2. Results and discussion

The Chemsage software package was utilized to estimate the activities of species in liquid ferrovanadium and CaO-Al_2O_3-MgO slags. This Solgasmix free energy minimizer uses free energy correlations of all the pure species as well as correlations describing their respective interactions in binary systems. Using these correlations with a mixing model enables the user to estimate activities of species in different melts. The first simulation calculations aimed to compare activities obtained using the software package and experimentally determined activities. The activity of $AlO_{1.5}$ as a function of the mole fraction $AlO_{1.5}$ in $AlO_{1.5}$-CaO slags, published by Rein et al(1965) and the estimated activities using the Chemsage software package are shown in figure 70. Reference states were pure solid V, MgO, CaO and Al_2O_3, pure liquid Al and Fe.
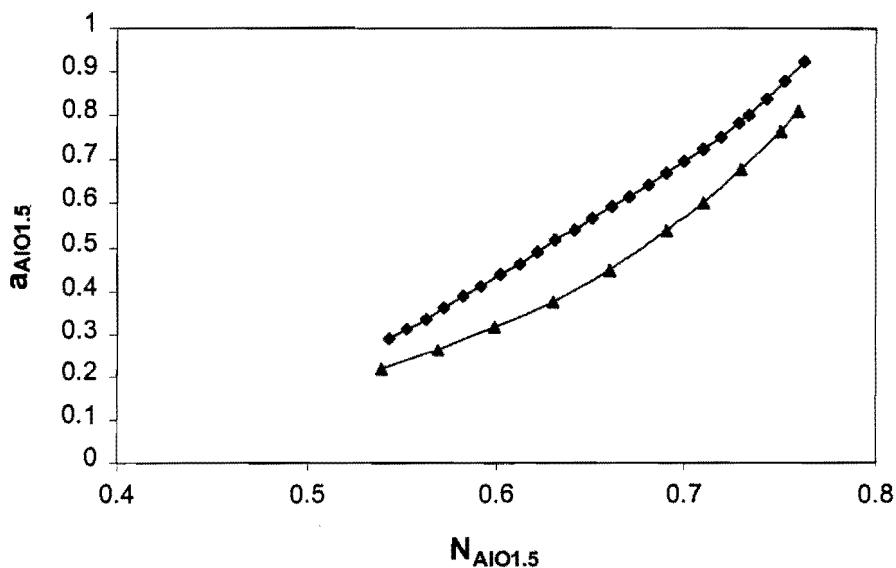
Figure 70: Activity-composition relations of $AlO_{1.5}$ on $AlO_{1.5}$-CaO slags at 1650°C. The triangles show the calculated data points using the Chemsage package and the diamond data markers, the published activities of Rein et al.(1965). Reference states were pure solid CaO and Al_2O_3.

Some error is associated with the published activities of Rein et al since the data were only graphically represented in the published paper. Nevertheless, the graph indicates that the estimated activities for the $AlO_{1.5}$-CaO binary system using the Chemsage software package compares well to the Rein et all published data. Activities in the ternary Al_2O_3-CaO-MgO system were tested against data published in the Slag Atlas(Verein Deutscher Eisenhüttenleute,1995).

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Figure 71 shows the activity of MgO in the system Al_2O_3-CaO-MgO at 1687°C.

(b)

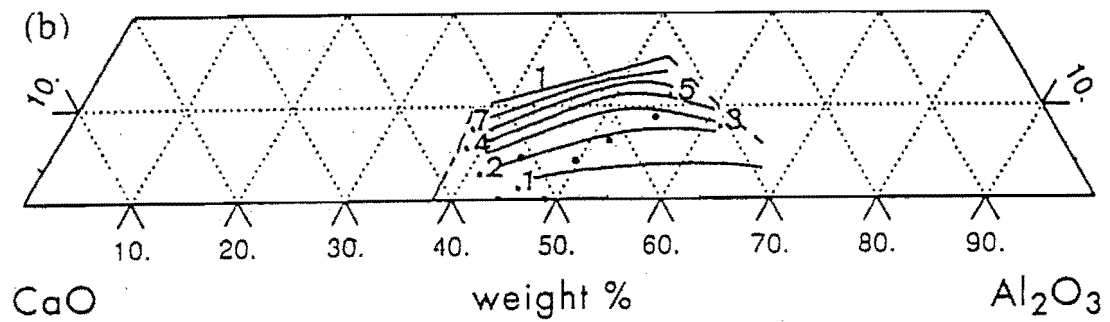10.   20.   30.   40.   50.   60.   70.   80.   90.

CaO   weight %   Al₂O₃

Figure 71: Activity of MgO in the system Al₂O₃-CaO-MgO with the solid lines showing the published activity (Verein Deutscher Eisenhüttenleute,1995) and the data points the estimated activities of 0.2 for different slag compositions utilizing the Chemsage software. Reference states were pure solid MgO, CaO and Al₂O₃.

Figure 71 illustrates that the estimated activities compare remarkably well with the published data. (A large activity coefficient of MgO in MgO-CaO-Al₂O₃ slags is expected because MgO has unit activity at around 12% MgO).

With confidence in the abilities of the Chemsage software to estimate the activities of species in the CaO-MgO-AlO₁.₅ system, the ternary system, illustrated in figure 70, was constructed.
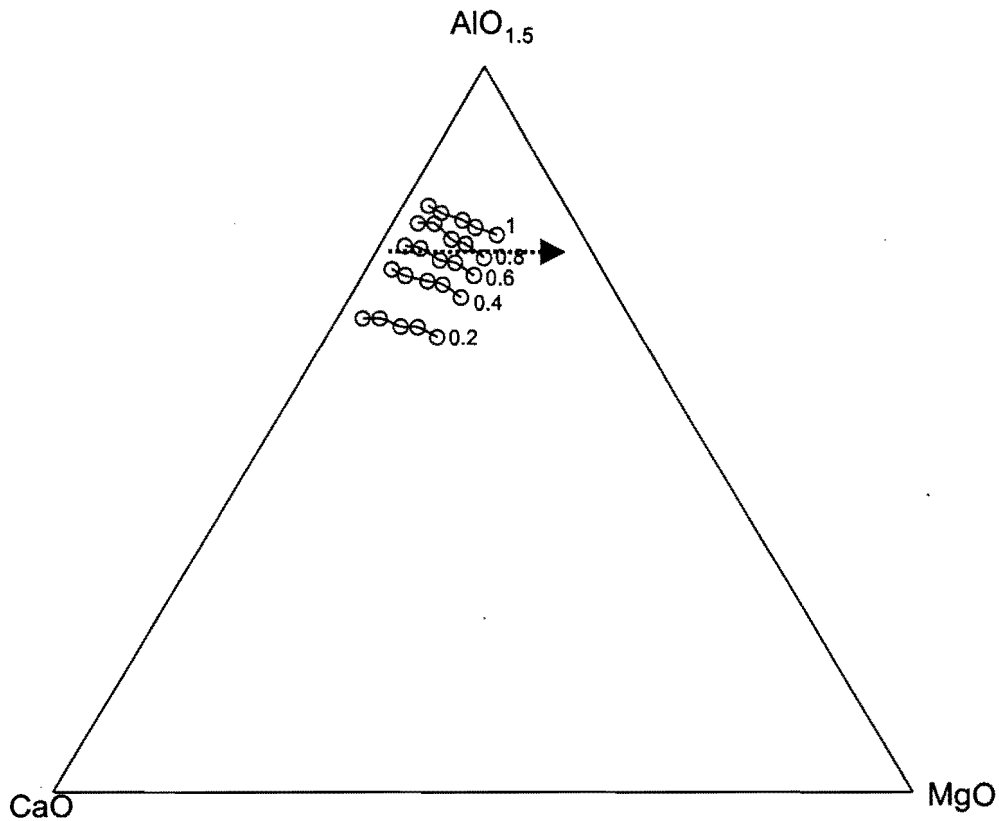
AlO$_{1.5}$

1
0.8
0.6
0.4
0.2

CaO

MgO

Figure 72: Activity of Al$_2$O$_3$ in the system AlO$_{1.5}$-CaO-MgO. Compositions plotted as mole fractions of AlO$_{1.5}$, CaO and MgO. Reference states were pure solid CaO, MgO and Al$_2$O$_3$ at 1973 K.

This graph indicates that the activity of AlO$_{1.5}$ is somewhat increased by MgO for a constant $\dfrac{MgO + CaO}{AlO_{1.5}}$ (mole basis) ratio. Thus, MgO substitutes CaO in the slag resulting in the slag composition changing along the broken line shown in figure 72. The effect on the oxidic vanadium loss of this increasing in the AlO$_{1.5}$ activity by MgO will now be quantified. Calculated vanadium losses to the slag - based on the measured activity coefficients – are presented in figure 73. This figure gives the predicted mass percentage of vanadium oxide in the slag and the total mass of vanadium lost to the slag as oxide, per tonne of ferrovanadium. The calculations were performed by assuming equilibrium to

hold between Al_2O_3 and $VO_{1.5}$ in the slag, and Al and V in the metal. (See third reaction in Table 18.) The Chemsage software was utilized to estimate the activity of aluminum in ferrovanadium. A ferrovanadium composition of 80% V, 1.5% Al and balance Fe, a typical average composition of ferrovanadium produced by the South African producer, was chosen to estimate the aluminum activity. Appendices 10 and 12 contain the calculated activities of Al and Al_2O_3 as a function of ferrovanadium and slag composition. It was further assumed that the aluminum content of the ferrovanadium remains constant, independent of the slag composition. This assumption is supported by industrial data, see figure 62, that the aluminum content of ferrovanadium is not strongly influenced by the slag composition. The other main assumption is a total mass of Al_2O_3 of 800kg per tonne of ferrovanadium. All the calculations were performed at 1973K. The basicity of the slag is expressed as follows:

$$Basicity = \frac{N_{CaO} + N_{MgO}}{N_{Al_2O_3}} \qquad (45)$$

With N_i = mole fraction of species i in the slag.

It was assumed that the effect of MgO on $\gamma_{VO_{1.5}}$ is similar to that of CaO (on a molar basis).
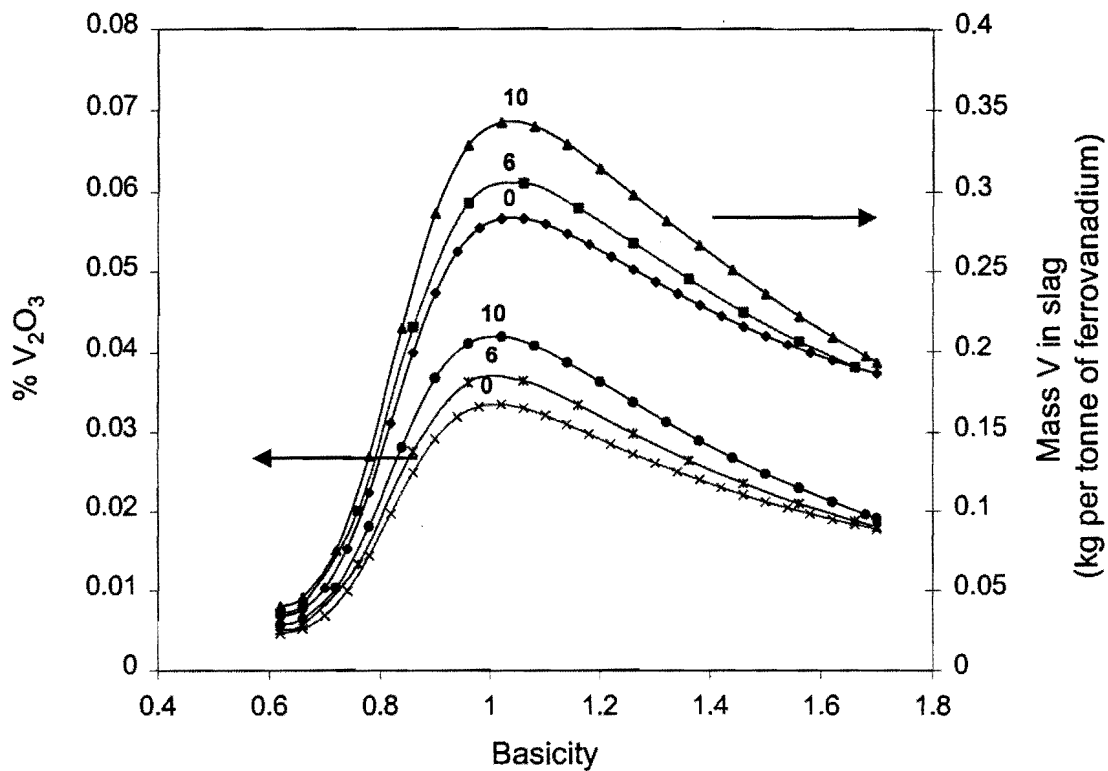
Figure 73: Predicted effect of slag composition on the soluble vanadium loss to the slag, based on activity data given in figure 49 and in Appendices 10 and 12. A constant ferrovanadium composition of 80% V, 1.5% Al and the balance Fe rendering the aluminum and vanadium activities to be 0.00539 and 0.834, respectively. A total mass of Al_2O_3 of 800kg per tonne of ferrovanadium was assumed. The V_2O_3 content of the slag and the total vanadium loss to the slag are shown for different MgO contents at 1973K. The numbers depict the respective mass percentages of MgO in the slag. Reference states were pure solid V, MgO, CaO and Al_2O_3, pure liquid Al and Fe.

The predicted relationships in figure 73 show a strong effect of slag basicity on soluble vanadium losses. At low slag basicities, a small increase in the basicity yields a large increase in vanadium losses, as a result of the sharp decrease in the vanadium oxide activity coefficient.

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At higher basicity, the continued decrease in the Al_2O_3 activity (giving a lower oxygen activity at constant aluminum activity) while the $VO_{1.5}$ activity coefficient remains nearly constant, result in somewhat lower predicted vanadium oxide levels in the slag.

Figure 71 further shows MgO retained in the slag to be detrimental to the soluble vanadium loss to the slag. The strong effect of slag basicity on the $VO_{1.5}$ activity coefficient for low basicity slags (Basicity < 0.8) overshadows the small effect of MgO on the activity of Al_2O_3. MgO somewhat increases the activity of Al_2O_3 (at a constant basicity) resulting in lower oxygen activities at a constant aluminum activity. The detrimental effect of the dissolution of the refractory lining and fettling material, and the subsequent uptake of MgO is mainly related to the change of the slag basicity. In addition to the cost associated with the dissolution of the magnesite refractory lining, the uptake of MgO from the lining further increases the soluble vanadium loss to the slag. This confirms that ways have to be found to retard the dissolution of the magnesite refractory lining, which may include fettling with crushed slag or using dolomite instead of lime, rather than with MgO-rich fettling materials.

The typical V_2O_3 content of industrial slag samples (see section 5.2.2.2.) is between 1 and 3% (mass percentage) for high-alumina slags. The calculated vanadium yield (figure 73) is much higher than for the industrial slag samples. The lower oxidic vanadium content predicted is mainly attributed to the aluminum activity estimation, which appears a factor 10 too high. The calculated effect of slag composition on the loss of vanadium oxide assuming activity of aluminium in ferrovanadium chosen to yield vanadium oxide contents of the same order as those measured for industrial slags is shown in figure 74. All the assumptions previously made still hold.
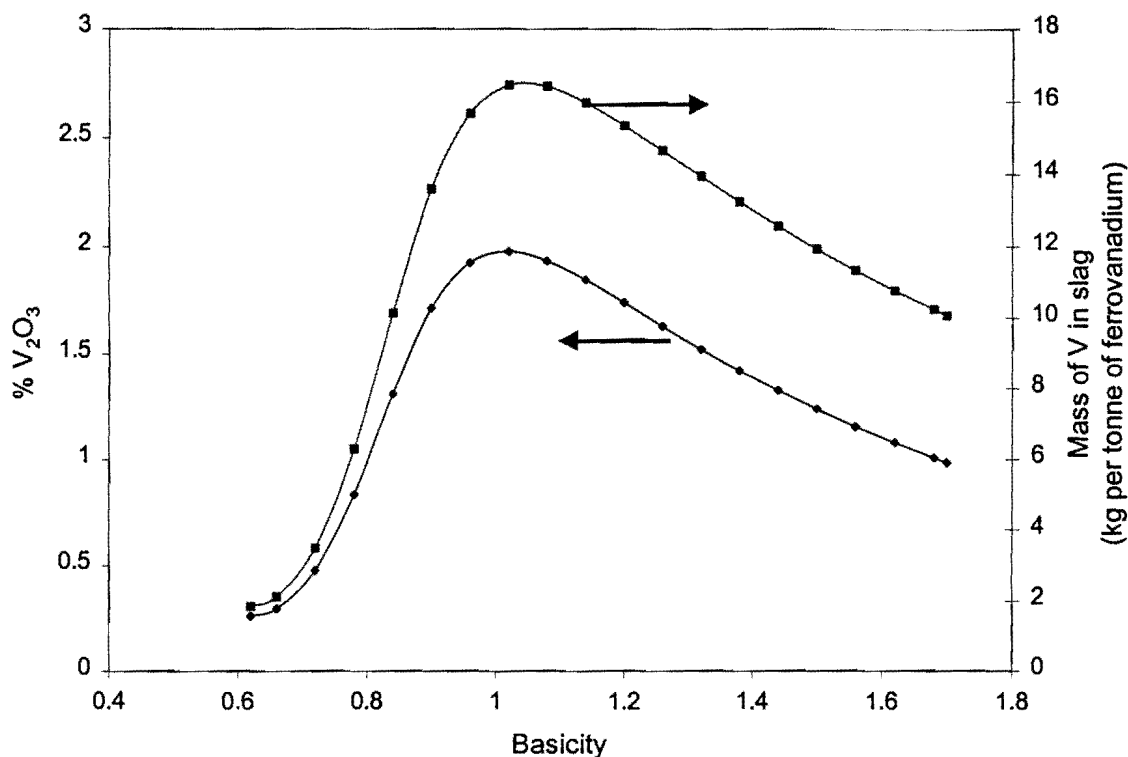
Figure 74: Predicted effect of slag composition on the soluble vanadium loss to the slag, assuming a constant activity of a_{Al}=0.0002 to yield the same vanadium oxide content as previously measured for industrial slag. Activity data given in figure 49 and Appendices 11 and 13 were used to perform the calculations. A total mass of Al_2O_3 of 800kg per tonne was assumed. The V_2O_3 content of the slag containing 10 % MgO and the total vanadium loss to the slag are shown for 2073K.

This figure clearly indicates that a factor 10 change in the aluminum activity will result in a factor 100 change in the mass of vanadium in the slag due to the quadratic dependency on the activity of aluminum in the equilibrium constant (see Table 18). The activity of aluminum in ferrovanadium cannot be fully quantified using the Chemsage software package and uncertainties on the order of the magnitude of the activity coefficient still remain. Experiments should ideally be performed to determine the activity coefficient of aluminum in ferrovanadium. By knowing the activity of aluminum in ferrovanadium the

oxidic vanadium losses to the slag can be fully quantified. Despite the uncertainties of the Chemsage aluminum activity estimates, the values generated using the software package will be used, (due to the lack of better correlations) for the remainder of the simulation calculations to illustrate the effect of temperature and aluminum content of ferrovanadium on the oxidic vanadium loss.

Calculated vanadium losses to the slag, showing the influence of the aluminum content of the ferrovanadium, are presented in Figure 75. This calculation was performed assuming a constant MgO content in the slag of 10%. In addition to this, a ferrovanadium composition with constant vanadium content of 80% V was assumed. All the calculations were performed at 1973K. A constant mass of Al_2O_3 of 800kg was assumed (based on the mass balance shown in Figure 5) which implies that the slag mass increases as the slag basicity is increased. The other main assumption is that the aluminum content of the ferrovanadium remains constant, independent of the slag composition, which is supported by plant data.
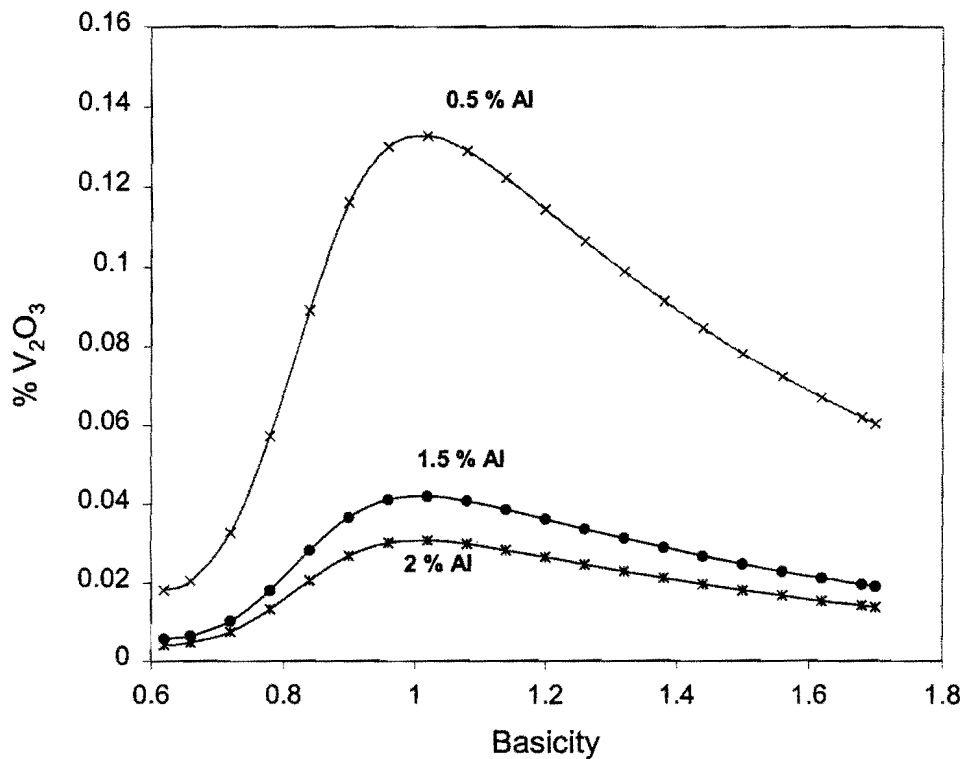
Figure 75: Predicted effect of the aluminum content of the ferrovanadium on the soluble vanadium loss to the slag equilibrated at 1973K. Constant MgO content of the slag and vanadium content of ferrovanadium of 10% and 80%, respectively, and a total mass of Al_2O_3 of 800kg per tonne of ferrovanadium were assumed.

The predicted relationship in figure 75 shows, in addition to the strong effect of slag basicity, also a strong effect of the aluminum content of ferrovanadium on vanadium losses. A 1% decrease, from 1.5% Al – 0.5% Al, in the aluminum levels of the ferrovanadium will increase the mass percentage vanadium in the slag from $\approx 0.04\%$ to $\approx$ 0.13%. This strong effect is due to the quadratic dependence of a_{V2O3} on a_{Al} in the equilibrium constant expression. This strong effect of aluminum further underlines the necessity to perform equilibrium experiments to fully quantify the aluminium effect on soluble vanadium losses.

The predicted effect of temperature on the soluble vanadium losses to the slag is shown in figure 76. In all the calculations a MgO content of 10% MgO in the slag was assumed. A constant ferrovanadium composition of 80% V, 1.5% Al and the balance Fe was used to estimate the vanadium and aluminum activities utilizing the Chemsage software package. In these calculations, it was assumed that the $VO_{1.5}$ activity coefficients are not strongly dependent on temperature for the entire slag composition range. A constant mass of Al_2O_3 of 800kg was assumed.
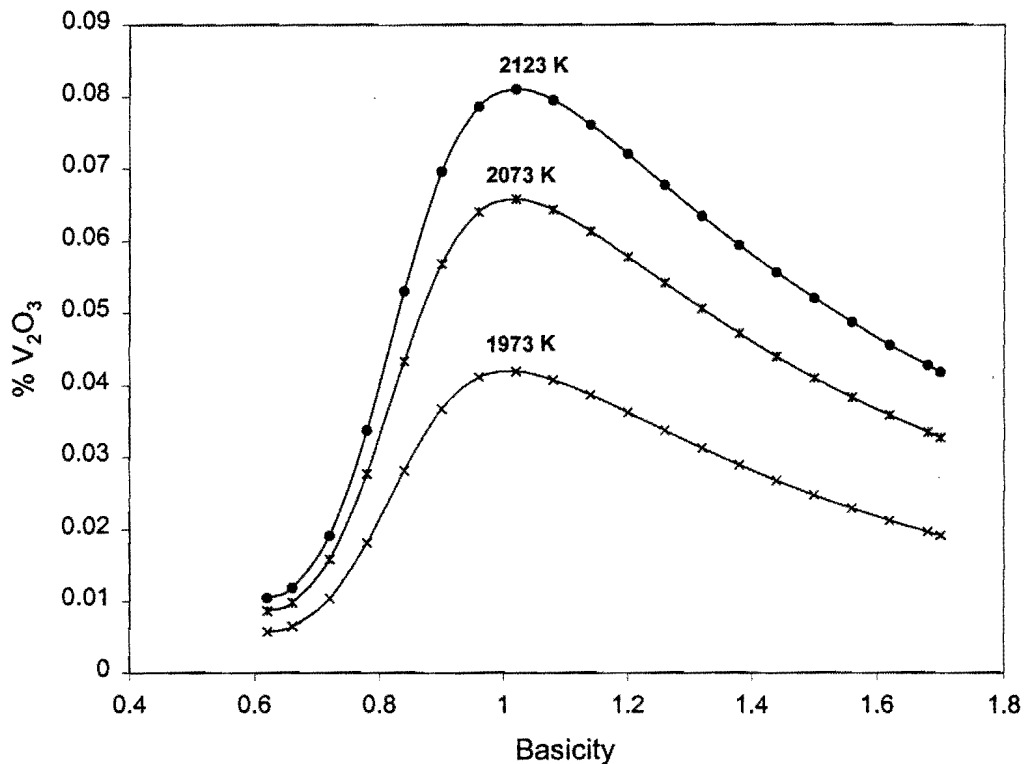

Figure 76: Predicted effect of temperature on oxidic vanadium losses to the slag, assuming a constant ferrovanadium composition of 80% V, 1.5% Al and the balance Fe. See Appendices 11 and 13 for the activities of vanadium and aluminum as a function of temperature utilized to perform the calculations. A total Al_2O_3 mass of 800kg per tonne of ferrovanadium was assumed. Appendix 11 contains the activities of Al_2O_3-CaO-MgO system as a function of temperature.

The predicted relationship of Figure 76 shows the strong effect of temperature on the vanadium losses to the slag. Tapping temperatures of the South African smelter is, as measured by means of an infrared pyrometer, on average around 1820°C.

It is thus expected that a lowering of the tap temperature will increase the vanadium recovery substantially. But from an entrained droplet point of view, lower tap temperatures might be detrimental. At this stage the effect of temperature on droplet entrainment is not fully quantified but the slag samples did not show did not show any strong effect of temperature, this includes temperatures as low as 1740°C, on the amount of droplets entrained. In the meantime it might be worthwhile for the industrial operation to control the tap temperatures around 1750°C and to monitor the effect of temperature on the total vanadium loss over an extended period.

The strong dependence of vanadium losses on the slag composition has clear implications for the operation of the industrial furnace. If it is assumed that the effect of MgO is similar to that of CaO (on a molar basis), the current operation uses the equivalent of a CaO: Al_2O_3 molar ratio of 1.0 (based on the composition shown in Table 3). Figures 73, 75 and 76 indicate that the maximum effects of MgO, Al and temperature, are expected at a CaO: Al_2O_3 molar ratio of 1.0. In addition to the vanadium losses which are expected to be close to the maximum (see figures 73, 75 and 76), the effects of MgO, Al and temperature amplify the maximum vanadium loss at a CaO: Al_2O_3 molar ratio of 1.0 even more. Small decreases in the slag basicity from the current level are expected to cause a large decrease in vanadium oxide loss, as well as to decrease the MgO, Al and temperature effect on soluble vanadium loss. This prediction is supported by analyses of industrial slags (see Figure 57); the slags clearly have lower vanadium oxide contents where the Al_2O_3 contents are higher (lower basicity). In addition to this, lower MgO contents in the slag, higher Al contents in ferrovanadium and lower tap temperature will likely yield lower vanadium oxide losses.