4. Results and discussion.

4.1. Activity coefficient relations.

Table 16 gives a summary of all the experiments conducted, containing the H_2O/H_2 ratio, sample composition, equilibration temperature and vanadium cation mole fraction as well as the respective 95% confidence intervals. (for analyzed vanadium mole fraction and calculated basicity).

The activity of vanadium oxide in the slag, shown in Table 16, was calculated from the equation 41 shown below.

$$K_2 = \frac{a_{VO_{1.5}} p_{H_2}^{1.5}}{a_V \, p_{H_2O}^{1.5}} \qquad (41)$$

After completion of the experimental runs the crucibles were analyzed by EDX, and was found to be pure, with no measurable aluminium pick-up. Hence, the activity of vanadium in equation 41 was taken to be 1. The activity of water and hydrogen was fixed by the gas mixture. After analysing the the mole fraction of vanadium oxide in the slag, the activity coefficient of $VO_{1.5}$ was calculated from equation 42

$$\gamma_{VO_{1.5}} = \frac{a_{VO_{1.5}}}{X_{VO_{1.5}}} \qquad (42)$$

In this calculation, the mole fraction of vanadium oxide in the slag ($X_{VO_{1.5}}$) was determined from EDX analysis of the amounts of Ca^{2+}, Al^{3+} and V^{3+} in the slag, by taking species which make up the slag to be CaO, $AlO_{1.5}$ and $VO_{1.5}$. Hence the experimentally determined activity coefficients ($\gamma_{VO_{1.5}}$) also refer to this convention.

Experiment	Temp K	moisture (g/h)	X_{H2O}	P_{H2O} (atm)	K	$a_{VO1.5}$	$\frac{N}{X_{VO1.5}}$	95% Confidence limit	$\gamma_{VO1.5}$	Basicity	95% Confidence limit
1	1973	1.70E-02	1.97E-03	1.72E-03	8264.77	0.721	6.24E-02	0.214	11.54	0.90	0.009
2	1973	1.70E-02	1.97E-03	1.73E-03	8264.77	0.724	7.74E-03	0.129	93.52	0.64	0.013
3	1973	1.76E-02	2.04E-03	1.79E-03	8264.77	0.762	5.79E-02	0.208	13.17	1.01	0.014
4	1973	1.72E-02	1.99E-03	1.75E-03	8264.77	0.735	8.69E-02	0.975	8.46	1.70	0.021
5	1973	1.69E-02	1.96E-03	1.71E-03	8264.77	0.715	7.28E-02	0.397	9.82	1.13	0.015
6	1973	1.68E-02	1.95E-03	1.71E-03	8264.77	0.712	6.23E-03	0.067	114.24	0.62	0.004
7	1973	1.68E-02	1.95E-03	1.71E-03	8264.77	0.712	2.21E-02	0.096	32.17	0.63	0.004
8	1973	3.03E-02	3.51E-03	3.08E-03	8264.77	1.717	1.69E-02	0.158	101.83	0.70	0.015
9	1923	0.0156	1.81E-03	1.58E-03	11656.17	0.895	7.42E-02	0.128	12.07	1.00	0.044
10	1923	0.0151	1.75E-03	1.53E-03	11656.17	0.853	9.37E-02	0.699	9.10	1.47	0.009

Table 16: Summary of experiments performed

Before any activity-composition calculations could be performed, the oxidation state of vanadium should first be determined. For a first approximation, the oxidation state of vanadium can be estimated by plotting the oxygen activity as a function of temperature for different vanadium metal and oxide equilibria. (Unit activities of oxide species are assumed). In this case, the equilibrium constant for the different vanadium metal and oxide equilibria was calculated using the correlations of Kubaschewski et al (1992) for the free energy values. At this stage, it should be noted that there appears to be a serious discrepancy between the literature values for the free energies of the vanadium oxide species. For example, the. Kubaschewski et al correlations predict the free energy of solid V_2O_3 to be -1649 244 J/mole, whereas the F.A.C.T. database yields a value of -1673 483 J/mole. This substantial difference - largely due to the difference in the entropy values - changes the equilibrium constant K_2 (see table 17) by a factor 2.1 (being larger if the F.A.C.T. values are used).

$H_2O = H_2 + 0.5O_2$ $K_1 = \dfrac{p_{H_2}\, p_{O_2}^{0.5}}{p_{H_2O}}$; $\log K_1 = 3.0456 - 13170/T$
$V + 1.5H_2O = VO_{1.5} + 1.5H_2$ $K_2 = \dfrac{a_{VO_{1.5}}\, p_{H_2}^{1.5}}{a_V\, p_{H_2O}^{1.5}}$; $\log K_2 = -1.8258 + 11331/T$
$2Al + 2VO_{1.5} = Al_2O_3 + 2V$ $K_3 = \dfrac{a_{Al_2O_3}\, a_V^2}{a_{Al}^2\, a_{VO_{1.5}}^2}$; $\log K_3 = 4.0365 - 25570/T$

Table 17. Equilibrium constants germane to this work

(Correlations fitted for the temperature range 1600°C to 1850°C; temperature in Kelvin for the correlations; reference states are pure solid V, V_2O_3 and Al_2O_3, pure gaseous H_2 and H_2O, and pure liquid Al)

The data point shown in figure 46 indicates the average oxygen activities and the equilibration temperature used to determine the influence of slag composition on the activity coefficient of vanadium oxide. As indicated, the divalent oxidation state of vanadium was expected to be stable for unit activities.
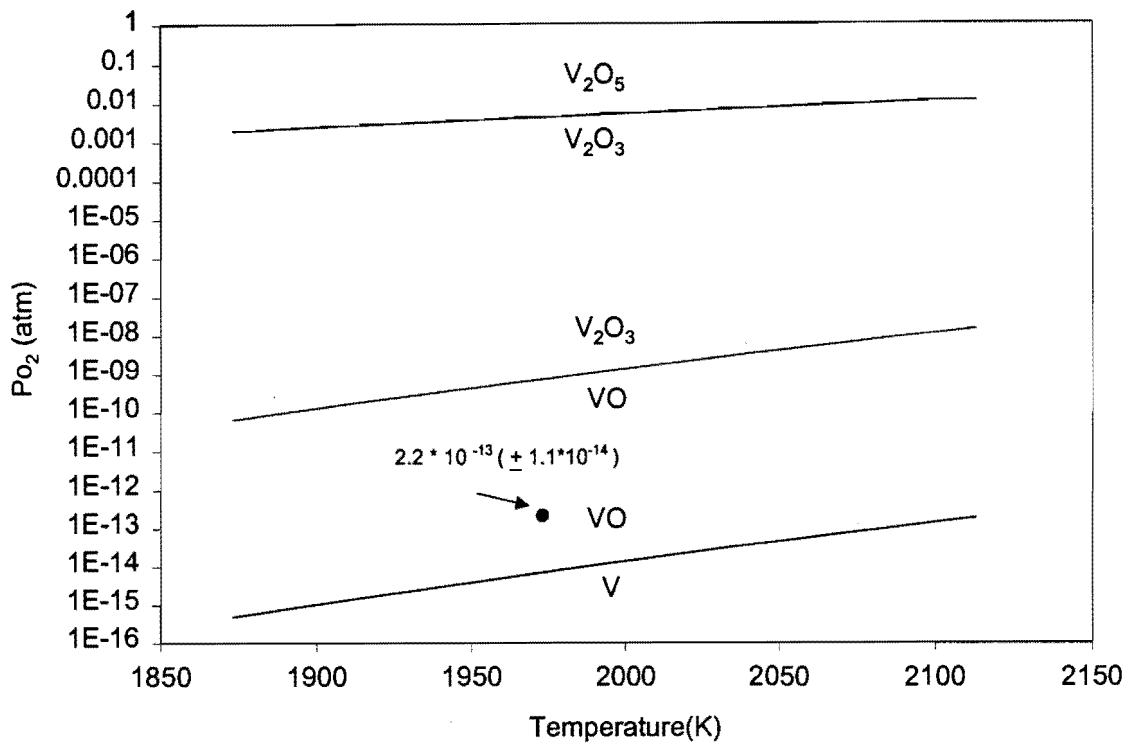
Po$_2$ (atm)

1
0.1
0.01
0.001
0.0001
1E-05
1E-06
1E-07
1E-08
1E-09
1E-10
1E-11
1E-12
1E-13
1E-14
1E-15
1E-16

1850   1900   1950   2000   2050   2100   2150

Temperature(K)

V$_2$O$_5$

V$_2$O$_3$

V$_2$O$_3$

VO

$2.2 * 10^{-13} (\pm 1.1*10^{-14})$

VO

V

Figure 46: Predicted oxidation state of vanadium. Reference states were pure solid V,VO,V$_2$O$_3$ and pure liquid V$_2$O$_5$ and the correlations of Kubaschewski et al (1992) were used. Data point indicates experimental conditions.

By conducting an experiment at a higher oxygen activity and at constant basicity and temperature the vanadium oxidation state can be determined more accurately. This was done by changing the water content of the gas mixture to 0.0035 mole fraction water. These results are presented by figure 47, which shows the predicted relative change of the mole fraction of VO$_x$ in the slag as function of the relative change in the oxygen activity for the different equilibria. (Po$_2$ = 2.0 × 10^{-13} atm at 1700°C.) The initial water vapour content of 0.0020 yielded an initial mole fraction of VO$_x$ in the slag of 0.0077 (See experiment 2 and 8 in Table 16). The data points on the graph present actual measurements - indicating the best agreement between predicted and measured effects of the change in the oxygen activity to be for the trivalent state.
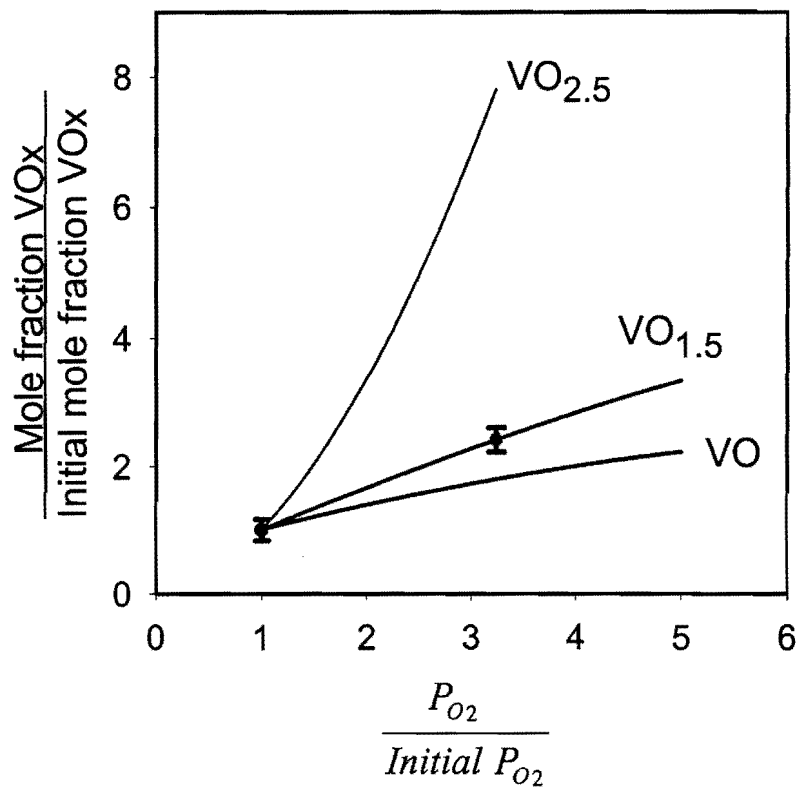
Figure 47: Expected and real vanadium oxide contents of the slag.

The actual mole fraction VO_x as function of the $CaO:Al_2O_3$ ratio is given in figure 48 for experimental conditions as listed in table 16. The effect of the varying of the Po_2 was taken into account during further analysis.
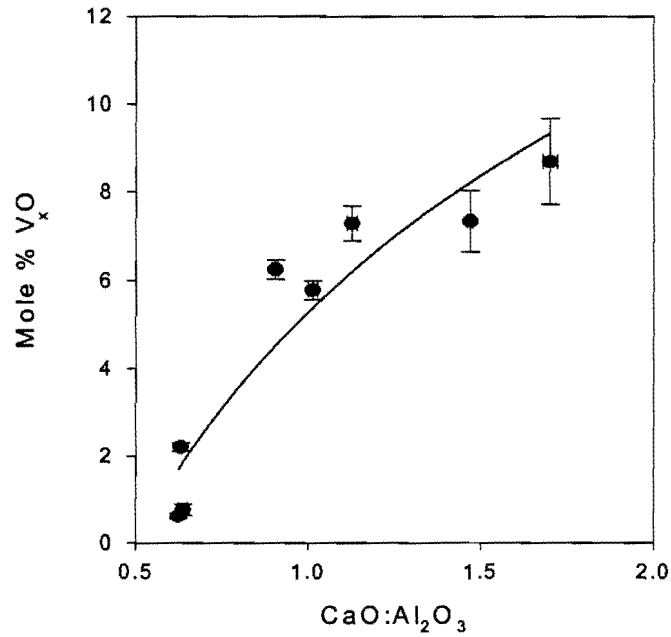
Figure 48: Effect of slag basicity on VO_x content for experimental conditions as listed in Table 16.

Nevertheless, Figure 48 demonstrated the actual amount of soluble vanadium to be strongly dependent on the slag basicity. It is clear, that in order to minimize vanadium loses to the oxide phases the slag basicity should be as low as possible, yielding at best 0.6 mole $\%VO_x$ at a basicity of 0.6 (for the Po_2 values used here).

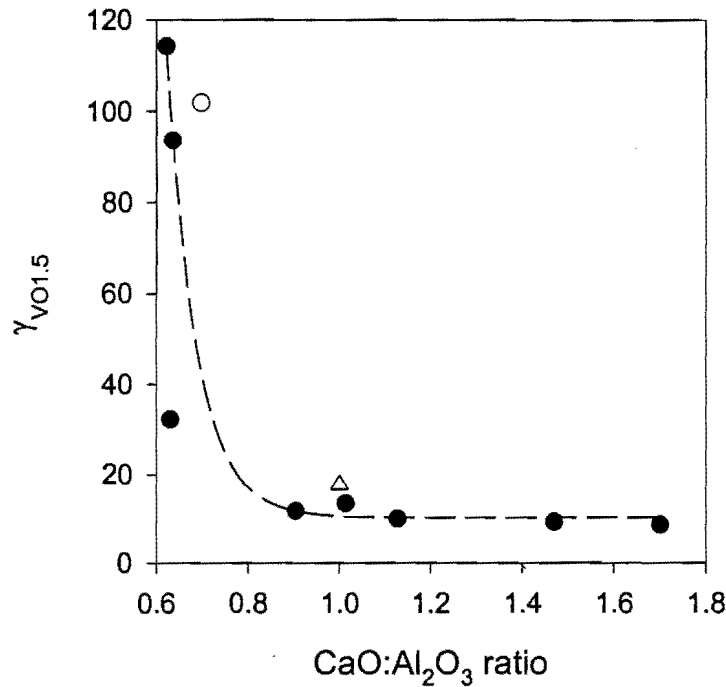The determined activity coefficient values of $VO_{1.5}$ are illustrated in figure 49.

Figure 49. Calculated value of the activity coefficient of $VO_{1.5}$ in $CaO-Al_2O_3$, based on equilibration runs at 1700°C under a hydrogen-water mixture, with a water mole fraction of 0.002 (filled circles). The open circle (See experiment 8) is for a hydrogen-water mixture (at 1700°C) with a water mole fraction of 0.0035, and the triangle(See experiment 9) for 1650°C.

Figure 49 demonstrates the activity coefficient of $VO_{1.5}$ to be strongly dependent on the slag basicity, with a sharp decrease in the activity coefficient at higher basicities. The measurement of the vanadium oxidation state is indicated by open circle in the figure. Furthermore, the data point shown as a triangle indicates an experiment conducted at 1650°C. As expected, the activity coefficient is not strongly dependent on temperature. This indicates that the laboratory data - conducted at 1700°C - can be used to calculate approximate equilibrium compositions at the furnace tapping temperature of 1840°C.

The reliability of the measured activity coefficients depends on the reliability of the equilibrium constant (which was discussed earlier), and of the gas composition and the chemical analyses. As far as the latter two are concerned, the variation of ±2.5% in the

H_2O content of the gas (as mentioned earlier) yields an uncertainty of ±4% in the activity coefficient (since $a_{VO_{1.5}}$ is proportional to $p_{H_2O}{}^{1.5}$). The largest 95% confidence interval on the vanadium oxide content, expressed relative to the average vanadium oxide content, amounted to 17% for the lower-basicity slags (with the lowest vanadium contents), and 11% for the slags with basicities higher than 0.7. This means that the maximum estimated variability in the activity coefficients (assuming no systematic errors) is ±21% for the lower-basicity slags, and ±15% for the higher-basicity slags. The largest 95% confidence interval on the analysed $CaO:Al_2O_3$ molar ratio was 0.04. See Appendix 2 for the 95 % confidence limits of the experimental results.

From the viewpoint of the ferrovanadium producer, it is clear that efficient recovery of vanadium from the slag is favored by low basicity. This can be achieved by lowering the amount of CaO added to the furnace as burned time.