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Oxidation-reduction equilibria of vanadium in CaO-SiO_2, CaO-Al_2O_3-SiO_2 and CaO-MgO-SiO_2 melts

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A series of redox studies of vanadium have been carried out in CaO-SiO_2, CaO-MgO-SiO_2 and CaO-Al_2O_3-SiO_2 melts/slags equilibrated over oxygen partial pressures (pO_2) range 10^{-2}–10^{-9} atm at 1600°C. V_2O_5 level was varied from 1–5 mol%. Three different melt basicities and alumina contents were investigated. Magnesia content was varied between 3.5 and 4.9 wt%. A newly developed analytical technique based upon electron paramagnetic resonance (EPR) spectroscopy was successfully applied to these melts. Two redox equilibria corresponding to V^{3+}/V^{4+} and V^{4+}/V^{5+} pairs followed the O-type redox reaction over the oxygen partial pressure range investigated. Higher oxidation states of vanadium were stabilized with increasing basicity of slags. Two redox pairs coexisted within oxygen pressure region 10^{-4}–10^{-6} atm. However, redox ratios did not indicate clear trends with increasing V_2O_5 content in CaO-SiO_2-V_2O_5 system. In CaO-SiO_2-Al_2O_3-V_2O_5 slags, a slight increase in redox ratios (V^{3+}/V^{4+}) was obvious when alumina quantity was changed from 3.22 to 5.44% at a basicity ratio ~1.3, indicating an increase in slag acidity. CaO-MgO-SiO_2-V_2O_5 slags showed a sharp decrease in redox ratios (V^{4+}/V^{5+}) between 10^{-2}–10^{-6} atm with addition of 3.5 wt% MgO, due to increasing free oxygen ions in slags.

1. Introduction

In our previous study [1, 2], vanadium redox equilibrium has been described in quenched sodium silicates. However the fundamental redox data of vanadium in iron free and iron bearing calcium silicates is unavailable and/or limited. As stated earlier in our work [1–3], vanadium redox chemistry is not yet completely understood because of the existence of the multiple oxidation states. Previous work [4–6] has indicated that one of the major difficulties in interpretation of the vanadium redox rection in melts is the dependence on conventional analysis, which seriously affects the accuracy of the results. Vanadium can exit either as V^{3+}/V^{4+} or V^{4+}/V^{5+} redox pair depending on slag composition, although it is possible that over a certain range of oxygen potential, they could coexist at the experimental temperature in these slags. When this occurs, determination of various vanadium species via analysis in aqueous solution presents difficulties in that the following reaction occurs:

$$V^{3+}_{(s)} + V^{5+}_{(s)} \Leftrightarrow 2V^{4+}_{(soln)} \tag{1}$$

In addition, the iron in the slags could interfere with vanadium analysis by the following reaction [7, 8]:

$$V^{5+} + Fe^{2+} \Leftrightarrow V^{4+} + Fe^{3+} \tag{2}$$

Thus before wet chemical analysis, it is essential to determine accurately the concentration of at least one of vanadium species to enable wet chemical results to be corrected for reaction 1 or 2. The details have been discussed in our work elsewhere [1–3, 9, 10].

Mittelstadt and Schwerdtfeger [4] studied calcium silicates with different basicity ratios at 1600°C over a range of pO_2 (10^{-1}–10^{-8} atm) and 10 mol% V_2O_5 content. However vanadium volatilization was reported under reduced oxygen pressures, which was compensated by reoxidising the sample after equilibration;

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nevertheless this approach could have affected the accuracy of the results. The authors commented that the three vanadium valencies couldn't be analysed in aqueous solution together, owing to the reaction (1).

The CaO-MgO-FeO$_x$-SiO$_2$ steelmaking slags studied by Inoue and Suito [11] were equilibrated with liquid iron at 1550–1650°C and were then chemically analysed in aqueous solution, assuming that the Fe^{3+}/Fe^{2+} ratio is same in these slags, as in the slags without vanadium at a fixed composition. These factors contributed to the error in determination of the true valency of vanadium. The author also admits that the assumption, that only two vanadium species can coexist, could affect the actual vanadium valency. Vanadium distribution between the slag and metal increased as the CaO/SiO$_2$ ratio was raised, as expected.

Fig. 1 presents a comparison of the valency ratios (V^{4+}/V^{5+}) versus (CaO + MgO)/SiO$_2$ molar ratios at different temperatures (1550–1650°C) using tabulated data from Inoue and Suito's work. The presence of the V^{4+}/V^{5+} pair at this reduced pressure disagrees with that of Mittelstadt and Schwerdtfeger [4] who determined an overall valance of 1.8, corresponding to a (V^{3+}/V^{4+}) redox pair under oxygen potential $\leq 10^{-8}$ atm. However Inoue and Suito admit that it is possible that iron free CaO-SiO$_2$ slag would contain V^{3+} ion at this oxygen pressure since V^{3+} ion is evident at 10^{-8}–10^{-9} atm in V-O system. Therefore it is likely that iron has affected the true vanadium valency in these slags. An effect of increasing temperature on the redox ratios is also not evident.

While determining the phosphorous distribution between magnesia saturated steelmaking slag (CaO-MgO-FeO$_x$-SiO$_2$) and liquid iron at 1600°C, Selin [12, 13] found the overall composition of the melt corresponded to oxidation state V^{4+}. Since the vanadium valance states were not determined, this finding cannot indicate the true redox pair of vanadium present at the reduced oxygen partial pressure.

In another study made by Tsukihashi *et al.* [5], vanadium valencies were measured in CaO-CaF$_2$-Na$_2$O-SiO$_2$ at 1300°C. V^{4+} and V^{5+} ions were found dominant in these slags and the valency increased with an increase in sodium oxide content from 0–3 wt%. Werme and Astron [14–16] studied the fundamentals of the vanadium redox ions during the distribution experiments between carbon saturated iron and CaO-Na$_2$O-SiO$_2$ (TiO$_2$, Al$_2$O$_3$, MgO) and FeO(satd)-SiO$_2$ slags at 1300°C with ~1.7% vanadium. Vanadium was found as monomer V^{3+} and VO^{+} ions in silica saturated slags and as VO_2^{-} ion in FeO rich slags. Since wet chemical analysis was used, the prediction of the true vanadium valency was affected and in addition the iron in the slags could have interfered with the vanadium analysis.

Contradictory behavior regarding the vanadium distribution was also reported by Werme [14, 15] when he examined the addition of CaO, MgO, Na$_2$O, Al$_2$O$_3$ and TiO$_2$, to iron and silica saturated FeO-SiO$_2$ melts and found that distribution ratio of vanadium between slag and iron decreased with increasing addition of CaO, MgO, Na$_2$O and Al$_2$O$_3$ under SiO$_2$ saturation, which is in contrast to his previous findings.

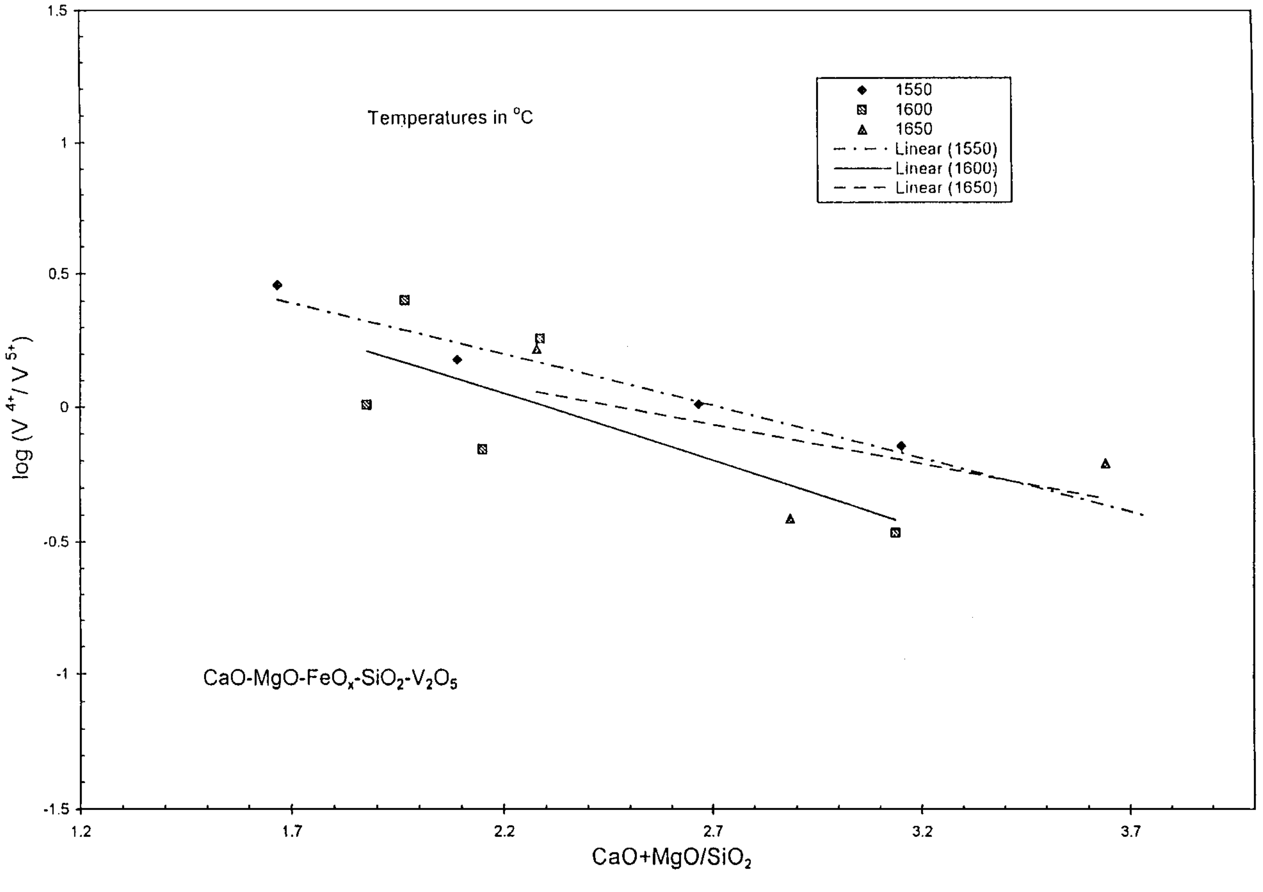


Figure 1 Variation of (V^{4+}/V^{5+}) ratios with (CaO + MgO)/SiO$_2$ molar ratios for CaO-MgO-FeO$_x$-SiO$_2$-V$_2$O$_5$ slags at 1550–1650°C, Tabulated data from Inoue & Suito [11].

Free oxygen ions (O^{2-}) present in the slag led to the concept of slag basicity, which can be defined based upon ionic theory, as the activity of the free oxygen ions, a_O^{2-} [17] assuming basic components produce O^{2-} ions while acid components consume them. Redox equilibrium of an element with multiple oxidation states upon introduction into a melt can be representd by a mass expression named an O-type reaction [4, 18–20].

$$M^{a+} + \frac{(2x-1)}{2}O^{2-} + \frac{1}{4}O_2 \Leftrightarrow MO_x^{(a-2x+1)} \tag{3}$$

for one electron change between the valencies, where x is the number of oxygen atoms associated with the oxidized redox ion in the melt to form an oxo-anion. This expression accounts for the activity of free oxygen ion, a_O^{2-} and describe the equilibria of the redox ions forming oxo ions e.g., CrO_4^{2-}, VO_3^-. A second type of redox expression named as a R-type redox reaction [19] has been used to describe the redox equilibria of a number of ions i.e., Co^{2+}/Co^{3+}, Mn^{2+}/Mn^{3+}. The practical difference between O and R-type redox expressions is that they predict the opposite effect of melt basicity upon the concentration redox ratio [21]. That is, from expression 3, an increase in melt basicity moves the equilibrium in favour of formation of the lower oxidation state, whereas the opposite effect is predicted by R-type reaction. Wright and Jahanshahi [19] reviewed the vanadium redox behavior in various melts and concluded that the vanadium follows an O-type redox reaction. However in some studies, either or both O and R-type equations have been used to describe the vanadium redox reaction, which is misleading and contradictory [4, 6, 11, 24].

In previous studies, the redox data of vanadium is mostly generated using chemical analysis and is available over a limited range of oxygen potential, temperature and melt composition. The aim of this present work was to utilize the newly developed analytical technique based on Electron Paramagnetic Resonance spectroscopy (EPR) in order to remove: (1) one of the major difficulties in interpretation of the vanadium redox reaction, that is dependence on conventional analysis, which often seriously affects the accuracy of the results, (2) the contradictions observed, and also to produce reliable fundamental data for a variety of calcium silica based vanadium melts. This data is applicable to understanding of vanadium behavior in iron and steel making slags.

2. Experimental procedure

50 g of master melts were prepared from analytical grade CaO, MgO, Al_2O_3, SiO_2 and V_2O_5. All reagents were dried at 120°C for 24 hrs, then carefully weighed and mixed. These were melted in a platinum crucible at 1600°C, crushed in a tungsten mill and analysed by XRF. Compositions and identifications of slags are given in Table I. The time to approach equilibration time was determined in a separate kinetic study.

A molybdenum wound electric resistance tube furnace was used for the equilibrium experiments (Fig. 2).

TABLE I Composition of slag samples

S. no.	CaO/SiO_2 (molar ratio)	V_2O_5 (mol%)	Al_2O_3 (wt%)	MgO (wt%)
A	0.7	5	–	–
B	0.9	5	–	–
C	1.23	5	–	–
D	0.7	1	–	–
E	0.9	1	–	–
F	1.21	3	–	–
G	1.23	5	3.22	–
H	1.22	5	5.44	–
I	1.22	5	7.87	–
J	1.57	5	–	3.50
K	1.51	5	–	4.87

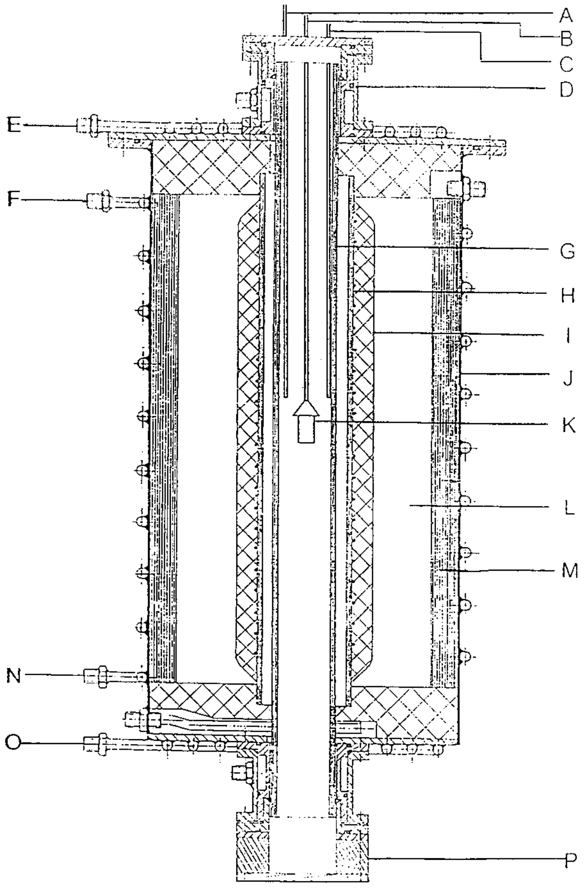


Figure 2 Vertical section of the molybdenum wound electric furance: (A) To control thermocouple, (B) gas delivery tube, (C) to second thermocouple, (D) brass fittings, (E) water outlet, (F) gas outlet, (G) alumina reaction tube, (H) alumina outer tube, (I) heating element, (J) copper drum, (K) crucible, (L) alumina filling, (M) insulating wool, (N) gas inlet, (O) water inlet, and (P) quenching chamber.

Temperature of the furnace was controlled by an Eurotherm temperature controller (±5°C). 1–2 g of samples were placed in platinum crucible and equilibrated at 1600°C in air and over a range of oxygen partial pressures (10^{-2}–10^{-9} atm.). The samples were then quenched in the bottom water-cooled quenching chamber in the same gaseous atmosphere. Ar, CO, CO_2 and Ar-O_2 gas mixtures were used for the preparation of various compositions using precalibrated mass flow controllers. The equilibrium studies were carried out for series of master slags (A-K in Table I) at 1600°C in platinum crucibles. The composition variables investigated were alumina and magnesia content and basicity ratios over the above mentioned range of oxygen partial pressures.

The combined EPR/chemical analysis method detailed elsewhere [3] was employed for all slags. A Varian E-line spectrometer operating in X band at 9.48 GHz was used for the analysis of vanadium (IV). All spectra were recorded over 2000G at room temperature on quenched slags. Details of EPR analysis are also given earlier [2, 3].

3. Results and discussion

3.1. Vanadium redox reaction and oxygen partial pressures

The two redox equilibria corresponding to V^{3+}/V^{4+} and V^{4+}/V^{5+} pairs followed the O-type redox reaction [3] over the experimental oxygen partial pressures and temperature (10^{-2}–10^{-9} atm, 1600°C) with V_2O_5 (5 mol%), alumina (3–8 wt%) and magnesia (3–5 wt%) contents investigated. The redox ratios decreased with increase in oxygen pressure, which is in accordance with limited previous work on sodium and calcium vanadium silicates [4, 6]; since data on the iron free CaO-SiO_2-V_2O_5, CaO-SiO_2-Al_2O_3-V_2O_5 and CaO-MgO-SiO_2-V_2O_5 slags are not available from the literature under the experimental conditions investigated here. Our previous work on soda slags [2, 3], is also in accordance with the findings for calcium silicate based slags, although the soda slags were mostly acidic (Na_2O/SiO_2: 0.5).

Generally the two redox pairs coexisted at oxygen potentials, 10^{-4}–10^{-6} atm. This region is readily observed in Fig. 3a and b where the fractions of the three vanadium species are plotted at different oxygen pressures for CaO-SiO_2-V_2O_5 system (slags B and C, Table I). The oxygen pressure region for coexistence of two redox pairs was expanded with an increase in basicity (B: 0.9 to C: 1.23), as presented elsewhere [6].

3.2. Effect of basicity on vanadium redox equilibria

To find the effect of change in slag basicity, redox ratios (V^{3+}/V^{4+}) of slags B and C (CaO-SiO_2-V_2O_5 system) are compared in Fig. 4a, which reveals that the ratios decreased with increasing basicity (0.9 to 1.23). These plots indicate a good linearity. The section of oxygen partial pressures where V^{4+} and V^{5+} ions exist, was also extended from 10^{-4} atm at a basicity: 0.9, to 10^{-6} atm, by increasing the basicity to 1.23 [10].

Fig. 4b presents a plot of (V^{4+}/V^{5+}) ratios versus CaO/SiO_2 (molar ratio) at pO_2 10^{-2} atm for slags B, C and F-K (Table I). It indicates a decrease in the redox ratios with increasing CaO/SiO_2 ratio and following linear equation was obtained incorporating all these slags.

$$\log\frac{V^{4+}}{V^{5+}} = -1.413\frac{CaO}{SiO_2} - 1.386 \quad R^2 = 0.718 \quad (4)$$

It is evident from the results that an increase in basicity stabilizes the proportion of vanadium in higher oxidation states in the slags investigated, hence vanadium follows an O-type redox reaction [18–20], which agrees with our previous conclusions on sodium silicates [2].

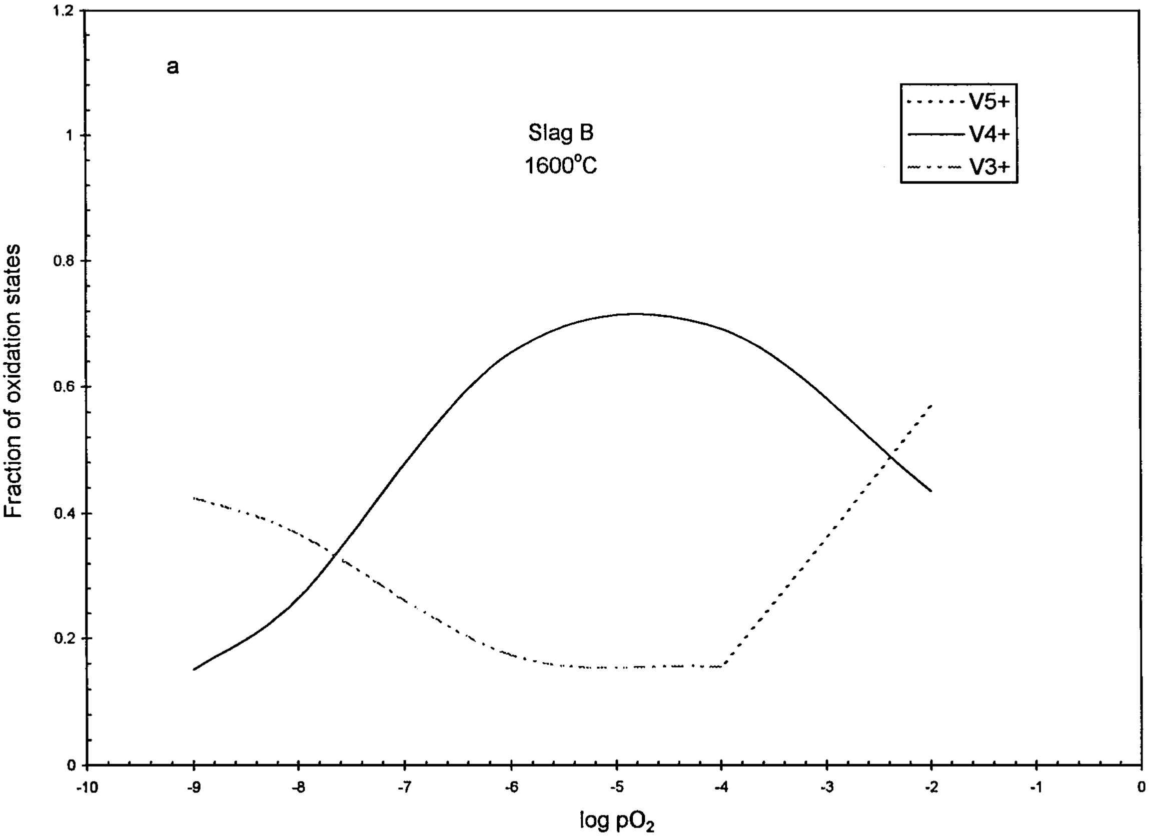
A study made by Tsukihashi *et al.* [5] on CaO-CaF_2-SiO_2 slag (VO_x 3%) at 1300°C to determine the effect of addition of Na_2O addition on vanadium valencies during the hot metal treatment reveals that at a pO_2: 10^{-18} atm, the V^{4+}/V^{5+} pair was present in the melt whereas none of the present slags (A-K, Table I) contains this pair even at a higher oxygen pressure (i.e., 10^{-9} atm) at 1600°C. Their observation may be attributed to the presence of the several transition metals and traces of iron metal, affecting the true valency of vanadium in their slags.

Also, the addition of soda increased the valency of vanadium in the CaF_2 slags which supports the present findings, despite the difference in melt composition, that an increase in the oxygen ion activity (a_{O}^{2-}) increased the vanadium oxidation states. In addition, the increase in the vanadium distribution ratio between the slag and the hot metal increased by an order of magnitude on adding 2 wt% soda in the CaF_2 slag investigated by Tsukihashi *et al.* which supports the earlier observations indicating the effect of increasig basicity in soda slags [1, 2, 9, 10].

A comparison of x, the non stoichiometry of vanadium oxide, between slags B and C (V_2O_5: 5 mol%, basicity: 0.9, 1.23 respectively) and CaO-SiO_2-V_2O_5 slags melted at 1600°C over pO_2 range: 10^{-1}–10^{-8} atm from Mittelstadt and Schwerdtfeger [4] is presented in Fig. 5. Here the tabulated data at basicity ratios: 1.0 and 1.36 (V_2O_5 ~10 mol%) obtained from chemical analysis [4] is plotted. It indicates that the "x" remained lower for slags B and C, compared to those of Mittelstadt and Schwerdtfeger, particularly at higher oxygen partial pressures ($\geq 10^{-5}$ atm). Though this may be attributed to the experimental error and difference in analytical techniques used, as our results show less uncertainties by employment of newly developed analytical technique. Nevertheless low basicity (0.9, 1.23) reduces the 'x" to smaller values compared to that of 1.0 and 1.36 respectively, as expected.

3.3. Dependence of valance states of vanadium on alumina content

Although the alumina contents investigated produced a slight increase in the redox ratios (V^{3+}/V^{4+}) by enhancing the acidity of the melts, clear trends have not been observed. This is illustrated in Fig. 6 where log (V^{3+}/V^{4+}) is plotted against log pO_2 at different alumina levels for the slags G-I (CaO-SiO_2-Al_2O_3-V_2O_5 system) and the alumina free slag C (CaO-SiO_2-V_2O_5 system) (Table I). A slight increase in the redox ratios is obvious when the alumina concentration was changed from 3.22 to 5.44% at a basicity ratio ~1.3. Alumina is generally considered amphoteric. Since the concentration of alumina investigated was low, it may be insufficient to produce a significant change in the redox ratios. The authors have also previously observed



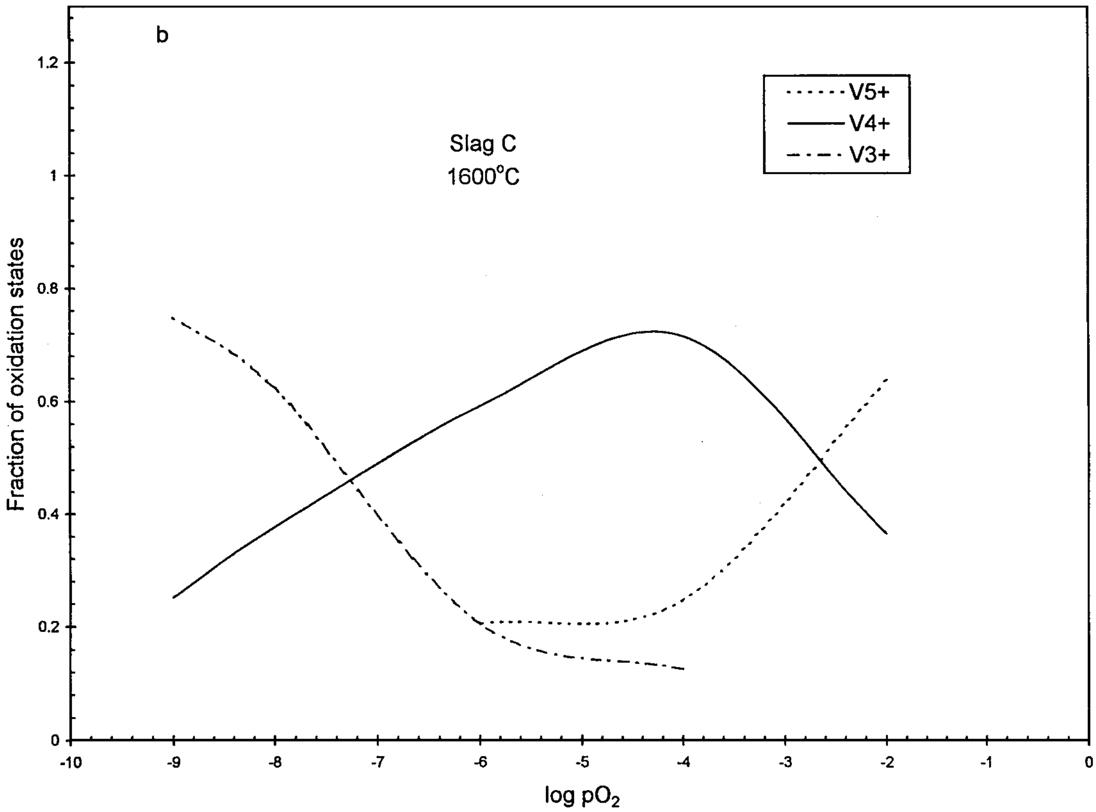


Figure 3 Dependence of fraction of redox species of vanadium (CaO-SiO_2-V_2O_5 system, 1600°C) on oxygen partial pressures at CaO/SiO_2: (a) 0.9 (slag B) and (b) 1.23 (slag C) See Table I for details.

that the addition of different alumina contents had no effect on the oxygen partial pressure region where two redox pairs coexist at measurable concentrations [3].

3.4. Effect of magnesia on vanadium oxidation states

Magnesia, a basic oxide, acts as a network modifer and increases the activity of free O^{2-} ions in

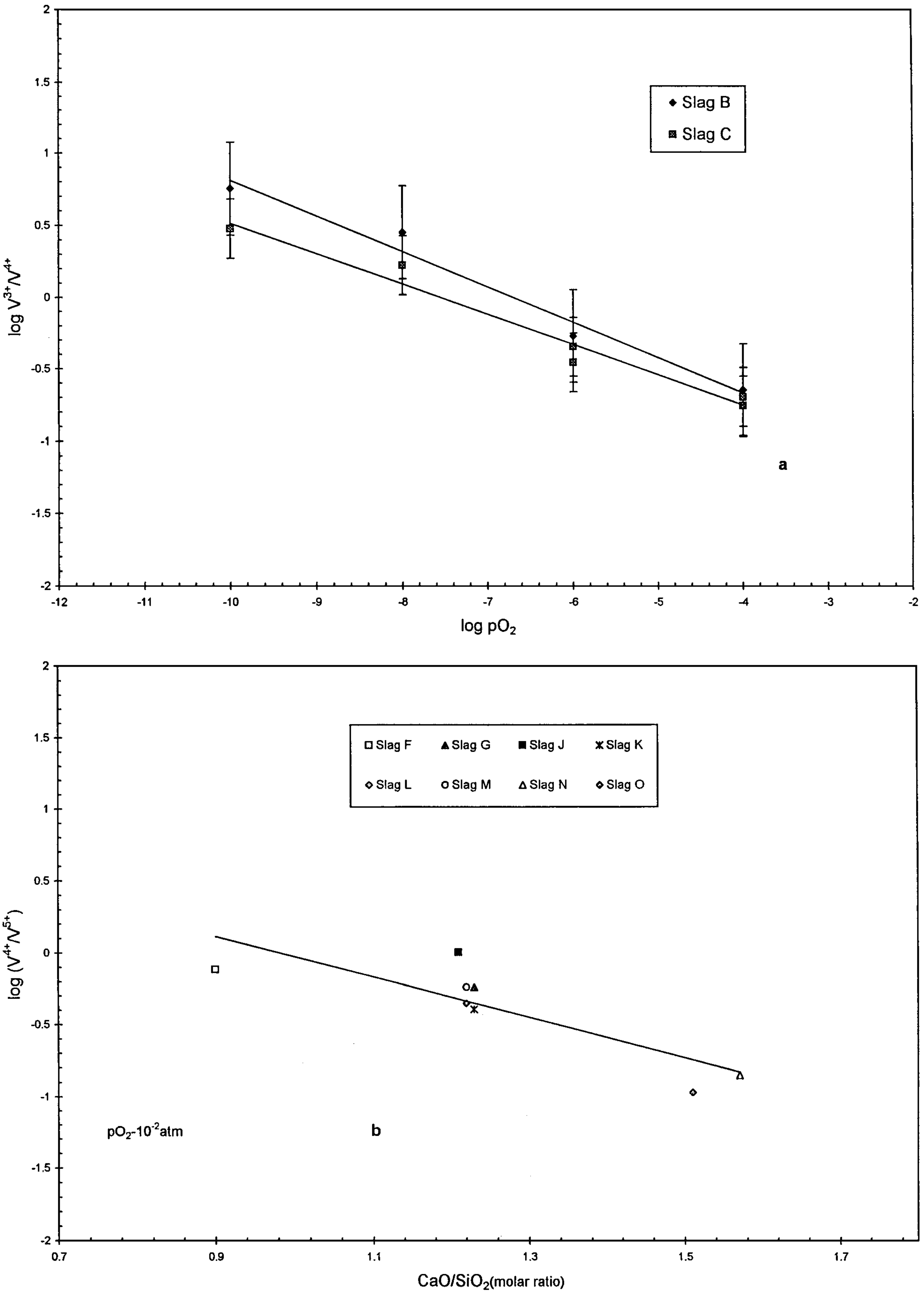


Figure 4 (a) Change in V^{3+}/V^{4+} ratios (CaO-SiO_2-V_2O_5 system, 1600°C) with log pO_2 at different basicity ratios (slag B: 0.9 & slag C: 1.23) and (b) Change in V^{4+}/V^{5+} ratios as a function of CaO/SiO_2 ratio for slags B,C, E-K, See Table I for details.

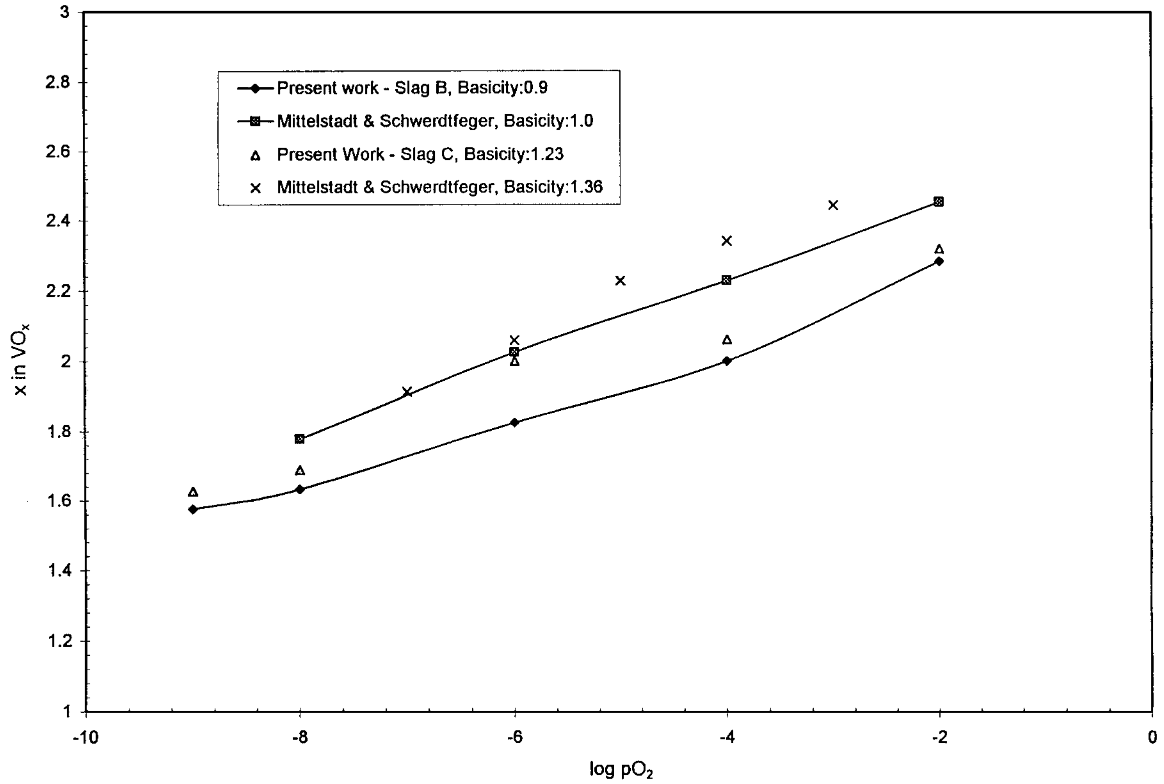


Figure 5 Comparison of overall oxidation state, x in VO_x, in $CaO\text{-}SiO_2\text{-}V_2O_5$ system as a function of oxygen partial pressures at basicity 0.9 & 1.23 ($V_2O_5 = 5$ mol%) with those of Mittelstadt and Schwerdtfeger [4] at basicity 1.0 & 1.36 ($V_2O_5 = 10$ mol%) at 1600°C.

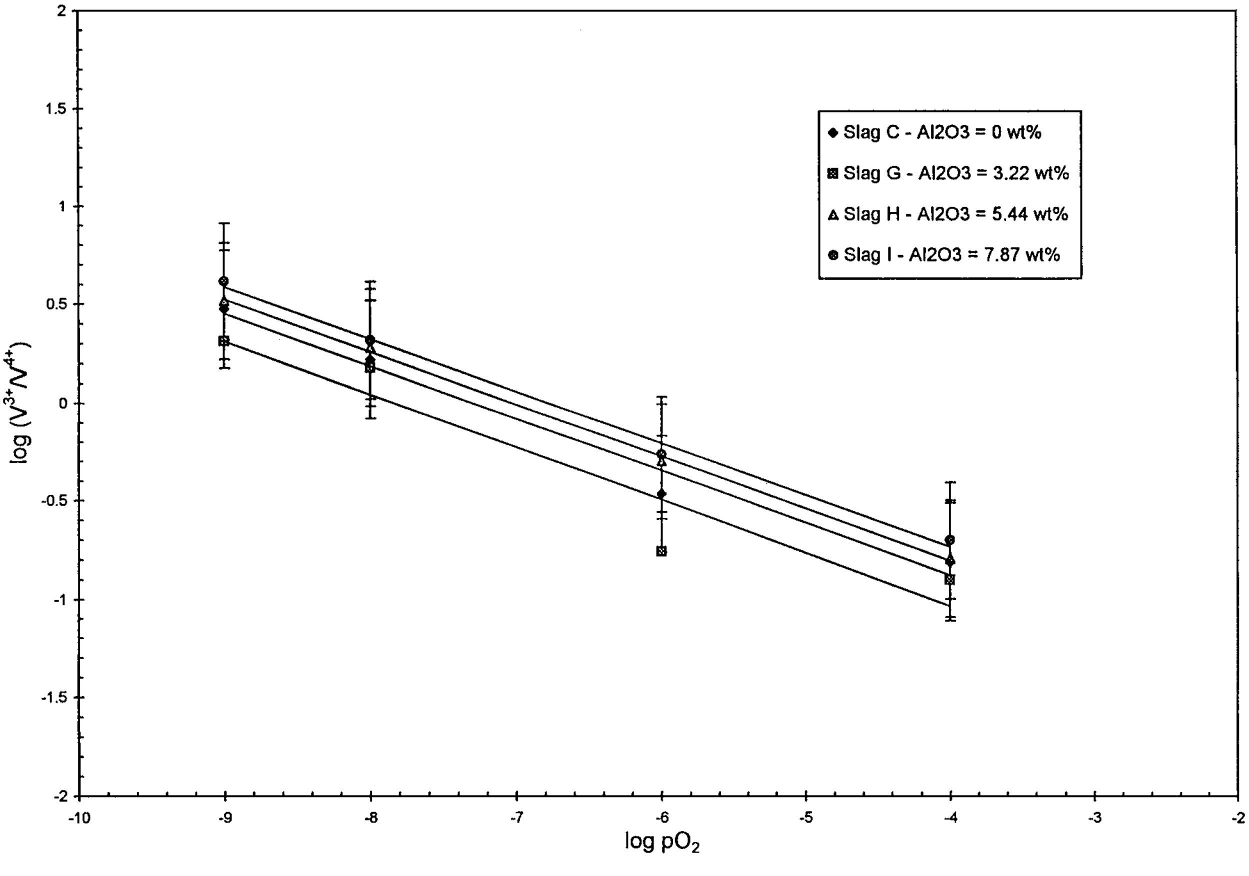


Figure 6 Change in redox ratios (V^{3+}/V^{4+}) ($CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}V_2O_5$ system) with respect to oxygen pressures at different alumina levels (1600°C).

the melt. As expected, the ratio of the redox species (V^{4+}/V^{5+}) between 10^{-2}–10^{-6} atm decreased sharply with the 3.5 wt% addition of MgO ($CaO\text{-}MgO\text{-}SiO_2\text{-}V_2O_5$ system) (Fig. 7). The reduction in the valency ratio was less with a further addition of MgO to 4.87 wt%. This trend generally agrees with previous work [11]. However it is surprising that addition of magnesia caused the overlapping region of the three valance states to diminish. Within the experimental error, there was no oxygen potential

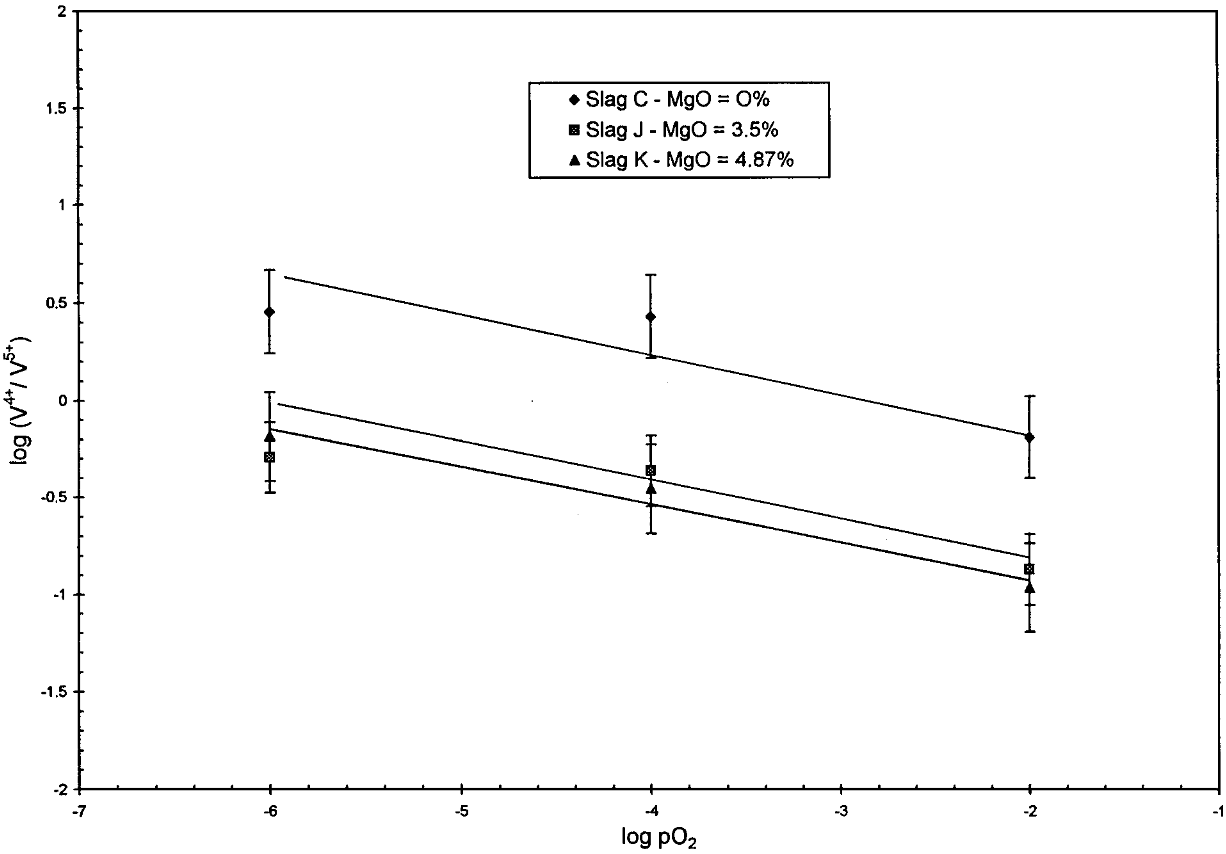


Figure 7 Effect of MgO addition on redox ratios (V^{4+}/V^{5+}) over different oxygen pressures (CaO-MgO-SiO_2-V_2O_5 system) (1600°C).

at which all the valencies coexisted in these slags [3].

Fig. 8 presents variation of vanadium valency ratios (V^{4+}/V^{5+}) versus (CaO + MgO)/SiO_2 molar ratios for slag C (CaO-SiO_2-V_2O_5 system), J and K (CaO-MgO-SiO_2-V_2O_5 system) at an oxygen potential of 10^{-4} atm. and those of CaO-MgO-FeO-SiO_2 slags studied by Inoue and Suito [11] equilibrated with liquid iron (V ~1.5 wt%). The data points are taken from the tables, at an oxygen pressure of 10^{-9} atm at 1600°C. It is difficult to compare these iron bearing slags with the present work due to the difference in composition and unavailability of the data over various oxygen potentials. However the both sets of data show a decrease in the V^{4+}/V^{5+} ratio with increasing MgO content and/or the basicity ratio. In Inoue and Suito's work, FeO has acted as a basic oxide and contributed towards stabilization of V^{5+}; although the presence of V^{4+}/V^{5+} pair at the reduced pressure (10^{-9} atm) disagrees with the current work, where none of the slags contained this redox pair at this oxygen potential.

Other magnesia bearing iron silicate slags with vanadium (wt%) ~ 1.7–2.3 at 1300°C have been studied by Werme [15, 16] and an overall valency as V^{3+} was present at pO_2 ~10^{-12}–10^{-15} atm. It supports the current results where the V^{4+}/V^{4+} pair was present under lower oxygen potentials (at 10^{-8} and 10^{-9} atm). However other experimental data is unavailable over the present oxygen pressure range for comparison. It should be noted that addition of basic oxides (CaO, MgO, Na_2O) changed the activity of FeO and the equilibrium oxygen potential in Werme's iron bearing melts, therefore vanadium valency did not increase with an increase in basicity.

3.5. Effect of V_2O_5 content on vandium valencies

The redox ratios V^{3+}/V^{4+} and V^{4+}/V^{5+} for slags F and C which have almost identical basicity (CaO-SiO_2-V_2O_5 system) containing 3 and 5 mol% V_2O_5 respectively are plotted in Fig. 9. From a close examination, it appears that the redox ratios V^{4+}/V^{5+} did not indicate clear trends. The ratios V^{3+}/V^{4+} are slightly lower for slag F. Therefore the redox equilibria are independent of the change in V_2O_5 content studied.

It has been found earlier in glasses [22, 23] that the redox ratios V^{5+}/V^{4+} increased with the addition of this oxide, which indicates its basic character or network breaking or depolymerising ability. In contrast, Mittelstadt and Schwerdtfeger [4] have reported a decrease in vanadium oxidation state with a decrease in Na_2O/V_2O_5 molar ratios (1.0 to 0.2) in Na_2O-V_2O_5 melts, indicating V_2O_5 as a network former. The discrepancy may be attributed to the differences in the oxygen pressure and possibly the glass composition studied, since all glass investigations reported in the literature were carried out under highly oxidized conditions i.e., in oxygen or air, while those of Mittelstadt and Schwerdtfeger were over the oxygen pressures range of 10^{-3} and 10^{-9}–10^{-16} atm. The overall oxidation state in Mittelstadt and Schwerdtfeger's work corresponded to V^{5+} at 10^{-3} atm at different V_2O_5

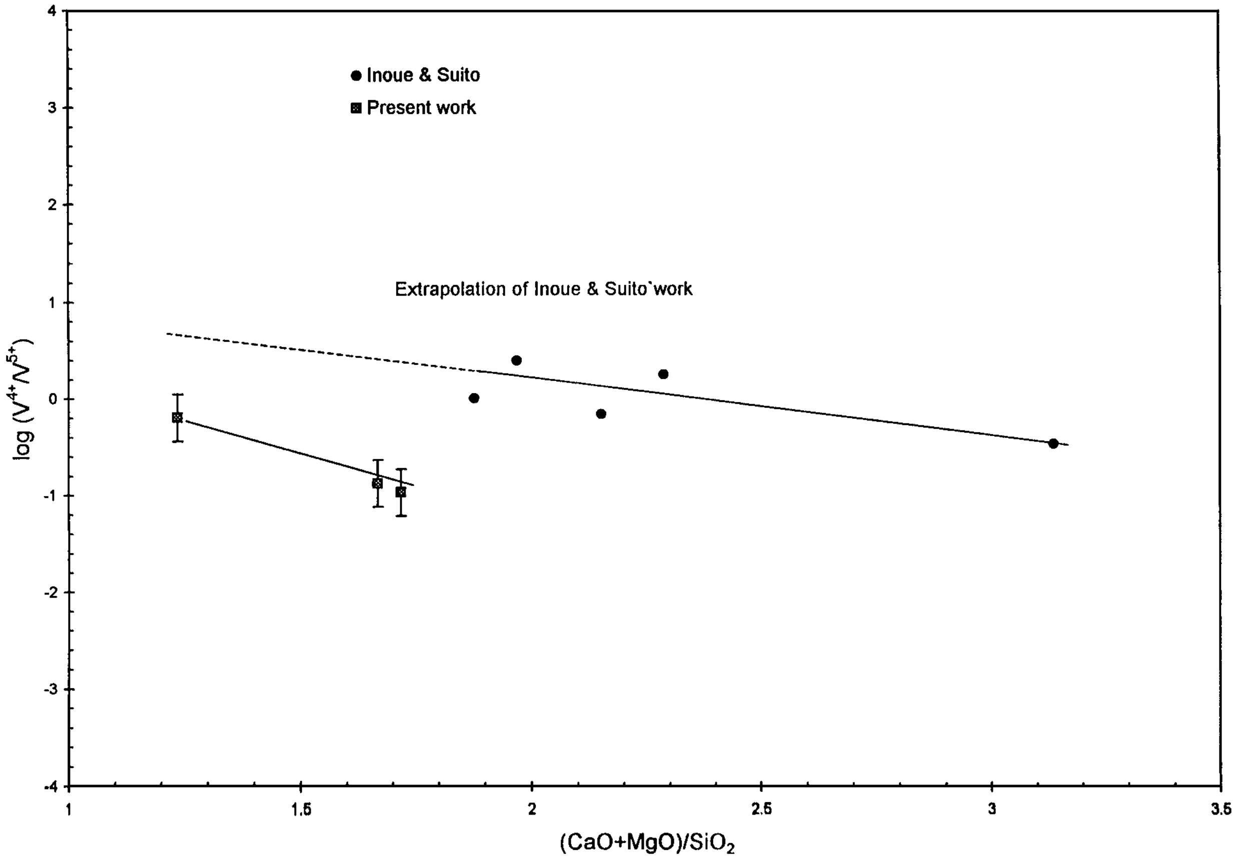


Figure 8 Comparison of redox ratios of vanadium between present work (slags C (CaO-SiO_2-V_2O_5), J & K (CaO-MgO-SiO_2-V_2O_5 system) and those of Inoue & Suito [11] (1600°C). See Table I for details.

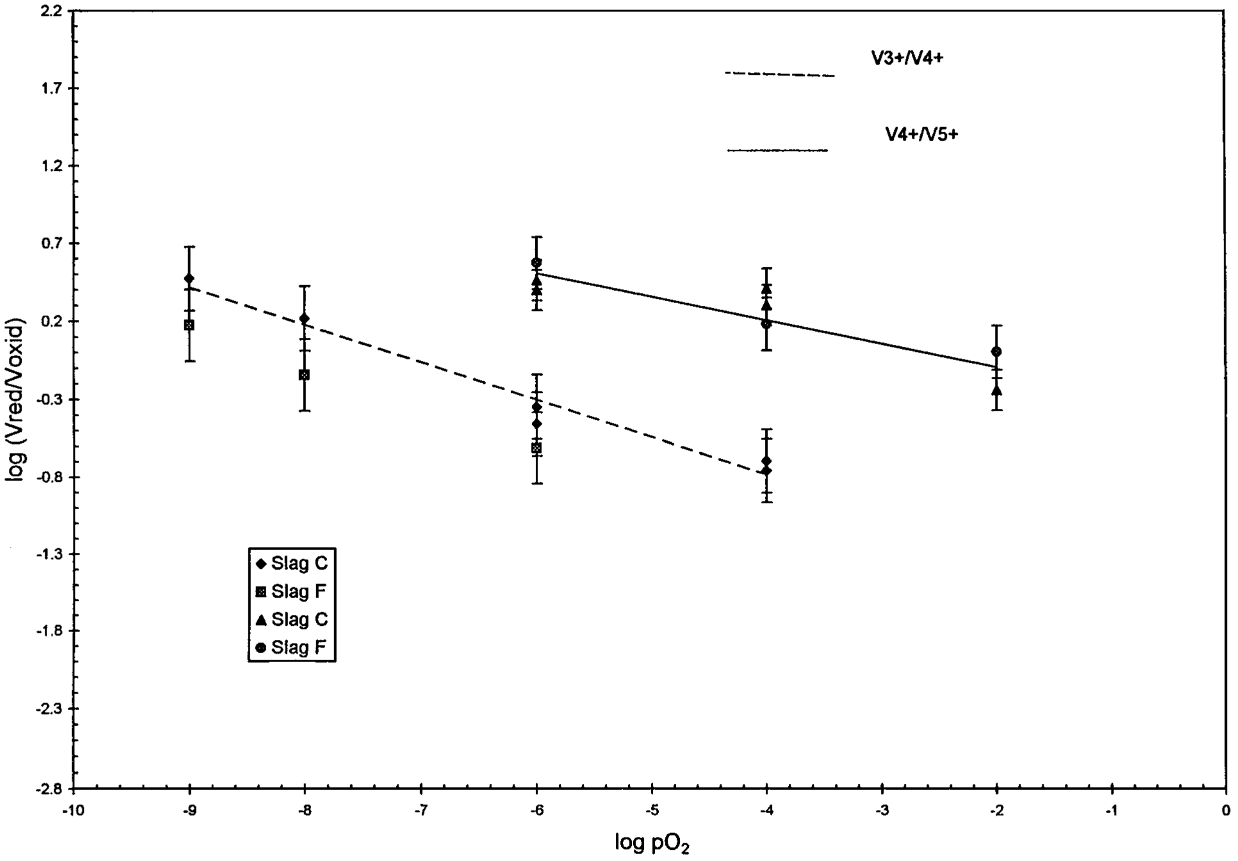


Figure 9 Effect of variation of total vanadium content on vanadium redox ratios in CaO-SiO_2-V_2O_5 system ($V_2O_5 = 3$ mol% for slag F & 5 mol% for slag C). See Table I for details.

contents. Below 10^{-9} atm, it decreased with an increase in V_2O_5 content. Hence the effect of reduced oxygen pressure on the oxidation state, cannot be disregarded. Therefore this oxide acts as a network former. In the present investigation, with a maximum of 5 mol% investigated, V_2O_5 acted as a neutral oxide, when compared to the concentrations >10 mol% as found in other investigations.

4. Conclusions

The newly developed method, which enables quantitative determination of the three oxidation states of vanadium, was successfully evaluated and applied to calcium silicates and complex melts. In calcium silicates, the two redox equilibria corresponding to the V^{3+}/V^{4+} and the V^{4+}/V^{5+} pairs followed O-type redox reaction over oxygen partial pressures 10^{-2}–10^{-9} atm at 1600°C with V_2O_5 (1–5 mol%), alumina (3–8 wt%) and magnesia (3–5 wt%) contents investigated. This result contradicts of previous workers [11, 24] who used both O and R-type redox expressions to describe the vanadium behavior. Generally the two redox pairs coexisted in measurable concentration over oxygen potentials 10^{-4}–10^{-6} atm.

In Al_2O_3-CaO-SiO_2-V_2O_5 slags, there was a slight increase in the redox ratios, when alumina quantity was changed from 3.22 to 5.44% at a basicity ratio ~1.3. However overall, there is no obvious change in the average vanadium valency for melts containing between 3 and 8 wt% alumina.

In CaO-MgO-SiO_2-V_2O_5 melts, the ratio of redox species (V^{4+}/V^{5+}) decreased sharply with the addition of 3.5 wt% MgO over the oxygen partial pressure range 10^{-2}–10^{-6} atm at 1600°C. Although the same trend was observed when the MgO content was further increased to ~5%, the reduction in the valency ratio was small. This trend generally agrees with previous work [4]. Within the experimental error, there was no oxygen potential at which all the valencies coexisted in these slags.

The redox ratios V^{3+}/V^{4+} and V^{4+}/V^{5+} (CaO-SiO_2-V_2O_5 system) did not indicate clear trends with a change in V_2O_5 content from 3 to 5 mol%. Therefore the redox equilibria and the overall valency of vanadium are independent of the change in V_2O_5 content studied.

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