REDOX CHEMISTRY OF VANADIUM IN MOLTEN BINARY SILICATES AND SLAGS

H. CHAUDARY[1], D. M. MILLER[2], M. P. BRUNGS[3]
and G. R. BELTON[4]

1. Post Graduate Student & 3. Associate Professor, School of Chemical Engineering and Industrial Chemistry, 2. Associate Professor, School of Physics; University of New South Wales, Sydney NSW 2052, Australia. Phone. 61 2 385 1000. 4. Chief Scientist, BHP Research Newcastle Laboratories, PO Box 188 Wallsend NSW 2287, Australia. Phone. 61 49 512444.

ABSTRACT

An Electron Spin Resonance technique has been developed in order to overcome inherent difficulties in the conventional analytical methods for vanadium species in slags. A series of redox equilibria experiments have been carried over a range of experimental parameters on sodium silicates to apply the newly developed method. The results are discussed in order to gain an understanding and resolution of paradoxes existing in the redox chemistry of vanadium.

1. INTRODUCTION

The removal of vanadium during iron and steel making has always been a process of interest to metallurgists. However, vanadium redox chemistry is not yet completely understood because of the existence of multiple oxidation states. Previous work[9,12,15,16] has indicated that one of major difficulties in interpretation of the vanadium redox reaction is dependence on conventional analysis which seriously affects the accuracy of the results. It has been found that data on the vanadium slags is limited and unreliable over a range of experimental parameters.

The current study, which is a part of a continuing project , is an attempt to develop a new analytical method based upon a spectroscopic technique coupled with chemical method for analysis of vanadium in slags. Electron spin resonance spectroscopy (ESR) has been used by many workers[1,2,5-8,11,13,14] to examine the co-ordination of vanadium in melts. ESR can also be used as a quantitative tool for determination of V^{4+} species and the first phase of the project was to establish calibration curves over a range of experimental parameters. Employed in conjunction with traditional wet chemical analysis, the ESR results enabled quantitative determination of all three vanadium valance states.

Since vanadium chemistry has been found similar in a range of matrices including sodium[16] and calcium silicates[12] and aluminosilicate[9], sodium silicate was selected as a model system for fundamental studies of slag at different compositions, temperatures and oxygen partial pressures. This system was used to evaluate the new analytical method. The analytical results were interpreted in terms of the vanadium redox chemistry in soda slags.

2. EXPERIMENTAL

2.1 Preparation of samples

50g (1.763oz) of master melts were prepared from analytical grade reagents Na_2CO_3, SiO_2 and V_2O_5. All reagents were dried at 120°C (248°F) for 24 hours , then carefully weighed , mixed and heated to 1000°C (1832°F) to decompose the carbonates. The master melts were melted in a platinum crucible at 1450°C (2642°F), crushed in a tungsten mill and analysed by XRF. Time required to achieve an equilibrium was determined by a series of kinetic studies.

As a requirement for equilibrium study between gas and slag, a range of O_2 partial pressures $1.01*10^{-3}$ $-1.01*10^{-15}$MPa (10^{-2} -10^{-14}atm) was introduced inside the furnace tube using a precalibrated mass flow controller. Ar, CO, CO_2 and Ar-O_2 mixtures were used for various compositions. The data for various compositions of gases to achieve particular O_2 potentials* was calculated using the CSIRO Thermochemistry system[17]. "Hydroperges" and "oxygen traps" supplied by Alltech Australia were used to remove the traces of moisture and oxygen from the gas mixtures. A molybdenum wound electric resistance tube furnace was used for experiments. The temperature of the furnace was controlled by a Eurotherm temperature controller within ±5°C (±7.6°F). A quenching chamber built at the bottom of reaction tube was used to quench the sample under the same environment. 2-3g (0.07-0.1oz) of samples were kept in the alumina crucibles [outer diameter =15 mm (0.59inches), height = 40mm (1.57inches)] and were raised from the bottom of the tube into the hot zone, melted under the required O_2 potential and temperature and finally quenched in the quenching chamber. In the beginning it was assumed that alumina contamination would not affect the results

within the experimental scatter. Later XRF analysis of quenched samples showed that alumina dissolution from crucible was quite high.
*[$pO_2 \sim 1.01*10^{-7}$Mpa (10^{-6}atm) is approximate]

2.2 Analysis

Vanadium can exist as V^{3+}, V^{4+} or V^{5+} depending upon the melt composition and is generally present as either of the redox pairs (V^{3+}/V^{4+} or V^{4+}/V^{5+}), although it is possible over a limited range of oxygen potential for all three vanadium species to be present simultaneously. When this occurs, determination of the various vanadium species via analysis in aqueous solution presents difficulties in that the following reaction takes place.

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

Thus before wet chemical analysis it is necessary to determine accurately the concentration of at least one of the vanadium species to enable the wet chemical results to be corrected for reaction (1). Since V^{4+} is paramagnetic and can thus be determined by ESR, a combined ESR/wet chemical analysis was proposed on the basis of a literature survey and an introductory series of experiments[3,4].

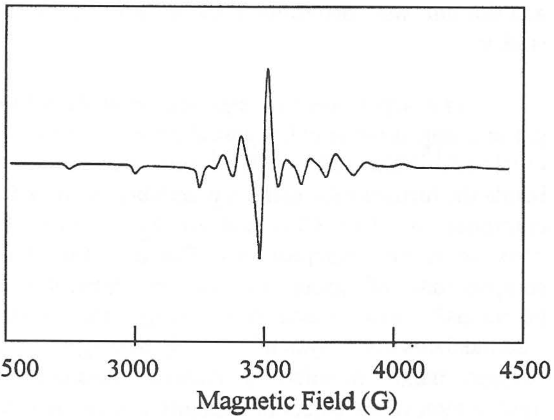

Fig. 1. Characteristic ESR spectrum for V^{4+} in sodium silicate melt scanned over 0.2T (2000 Gauss).

It was found that reaction (1) can occur while grinding the sample in air. Hence a small piece of solid slag, after quenching, was used for ESR analysis. V^{4+} was determined by ESR as follows. A Varian E-line spectrometer operating at 9.48 GHz (G cyc/s) was used. A known quantity of samples (few hundred mgs. in case of powdered sample, few mgs. in case of point sample) was placed in standard quartz tubes, held in the resonance cavity which was continuously flushed with N_2 gas and scanned over 0.2T (2000G). A representative spectrum of V^{4+} in sodium silicate is presented in fig. 1.

It has been found from previous results[3,4] that a change in matrix does not affect ESR signal. No ESR signal was found for V^{5+} or V^{3+} ions. A correction was made for blank absorption and any trapped oxygen from air. The area under the second derivative of absorption curve was found to be directly proportional to the amount of paramagnetic ion present. A computer program was used to integrate and evaluate the relative and absolute number of spins using "strong pitch" as reference material. Manganese was used as a g-value marker. Finely powdered samples were also analysed by a potentiometric method established by Mittelstadt and Schwerdtfeger[12] in order to determine the vanadium species present in aqueous solution. It involved oxidation of reduced species to V^{5+} and then reduction of V^{5+} to V^{4+} to find the total vanadium content.

A calibration curve derived from representative samples containing known amounts of V^{4+}, melted under oxidised or reduced atmosphere where either of two redox pairs are present without interference from a third species, is presented in fig. 2.

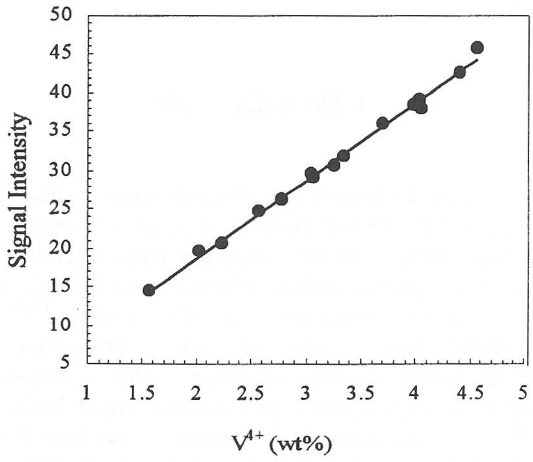

Fig. 2. Correlation between ESR signal intensity and V^{4+} ion determined by chemical analysis (R^2=0.994).

Wet analysis was limited by the difficulty of analysing low (≤1wt%) concentrations of vanadium. However, ESR has been found fairly sensitive for this lower vanadium content. Total vanadium, sodium and alumina content was also determined by XRF analysis.

3. RESULTS AND DISCUSSION

Vanadium can exist as V^{3+}, V^{4+} or V^{5+} ions depending upon the composition of melts. The following equations may be used to describe the equilibria among various V species, assuming activity of O^{2-} is constant and can be incorporated into equilibrium constant,

$$V^{4+} + 1/4O_2 = V^{5+} + 1/2O^{2-} \quad (2)$$

$$V^{3+} + 1/4\ O_2 = V^{4+} + 1/2O^{2-} \quad (3)$$

giving following equilibria (for the reduction reaction).

$$K_1 = (V^{4+} / V^{5+})pO_2^{\ -1/4} \quad (4)$$

$$K_2 = (V^{3+} / V^{4+})pO_2^{\ -1/4} \quad (5)$$

Hence a plot of log $V^{n+}/V^{(n+1)+}$ vs. log pO_2 should give a straight line with a slope of -1/4 for any redox pair if ideal behaviour is followed. An example is presented in fig. 3 for a Na_2O-SiO_2 melt containing 5 mol% V_2O_5, studied over the range of O_2 partial pressure of 10^{-2} - 10^{-12} atm. The -1/4 slope of line is followed until pO_2~$1.01*10^{-11}$Mpa (10^{-10} atm) after which the third species became apparent. Therefore, at pO_2 ~$1.01*10^{-13}$Mpa (10^{-12}atm) significant quantity of V^{3+} was also present along with V^{4+} and V^{5+}, determined by new analytical method. Here the ratios are presented as V^{3+}/V^{4+} and V^{4+}/V^{5+};

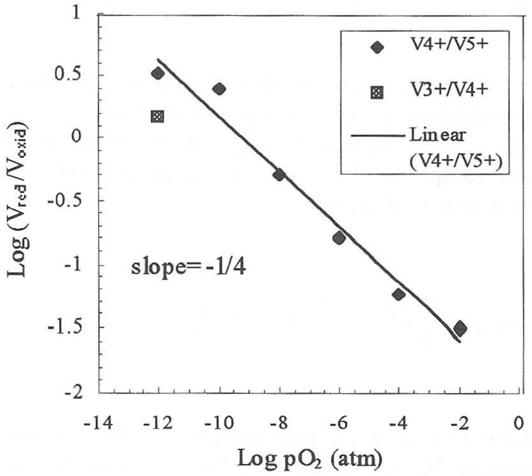

Fig. 3. Change in redox ratio of vanadium with oxygen partial pressure in Na_2O-$2SiO_2$ melt containing 5mol% V_2O_5 at 1225°C (2237°F). (atm=9.87MPa).

Whereas Johnston[10] studied sodium disilicate melts containing ~ 1.3 wt% vanadium in alumina crucibles at 1085°C (1985°F). Two lines were required to express the two equilibria while the valency ratios tend to approach to infinity in the overlapping region (at pO_2 ~10^{-12} atm). It was assumed in previous studies[10,12] that the two equilibria (equation 2 and 3) could explain the oxidised/reduced conditions of the melts. The necessity for such an assumption was the unability to determine the fraction of third species when ever present. There methods were based upon wet chemical analysis which made it impossible to determine the three species together because of reaction(1).

3.1 Redox Chemistry of Vanadium

The over all oxidation state of vanadium could be represented by a function x (in VOx) for three ionic species of vanadium[12].

$$X = \frac{nO}{nV}$$

$$= \frac{1.5(\frac{V^{3+}}{V^{5+}}) + 2.0(\frac{V^{4+}}{V^{5+}}) + 2.5}{\frac{V^{3+}}{V^{5+}} + \frac{V^{4+}}{V^{5+}} + 1.0} \quad (6)$$

The experimentally determined x versus log pO_2 plots presented in fig. 4(a,b,c) are characterised by S-shaped curves confirming Mittelstadt's calculations based on equation (6).

Previous data is limited over a range of experimental conditions. Mittelstadt and Schwerdtfeger[12] have studied Na_2O-V_2O_5 melts at 1000°C (1832°F) with Na_2O/V_2O_5 = 0.5, in platinum crucibles and analysed using thermogravimetric technique. Tsukihashi et al.[15,16] have investigated the distribution of vanadium valencies between Na_2O-SiO_2 and carbon saturated iron at 1200°C (2192°F) in graphite crucibles. The atmosphere inside the furnace was very reducing (pO_2 ~$1.01*10^{-19}$ MPa (10^{-18} atm). They found that at Na_2O/SiO_2 = 0.5, vanadium could exist as V^{2+} or V^{3+} which would change into V^{4+} and V^{5+} when the basicity ratio was increased to 1.0 or 1.5 under the same oxygen partial pressure and temperature. Fig. 5 compares the current results with other available work. It indicates that there is consistency in the behaviour of the vanadium in the different systems and the magnitude of distribution among various valencies is similar in sodium vanadate and sodium alumino disilicates.

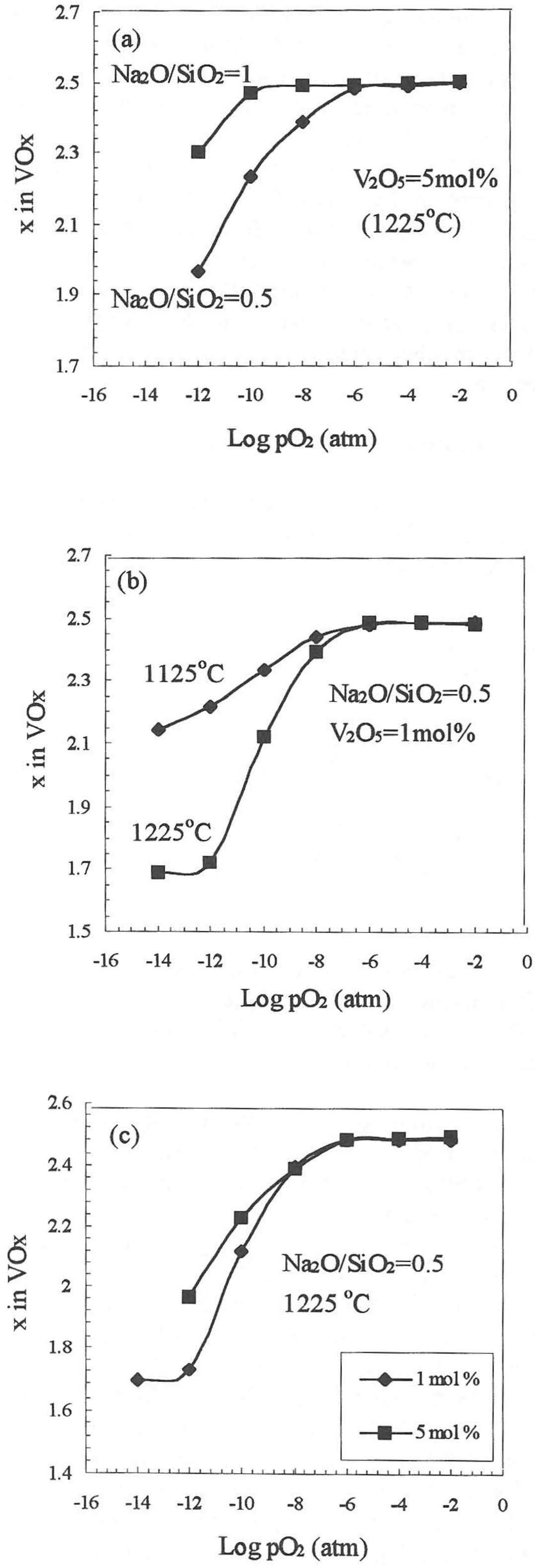

Fig. 4. Variation in x function in Na_2O-SiO_2 melts as a function of oxygen pressure at different (a) basicity ratios (b) temperatures and (c) vanadium content. (atm=9.87MPa)

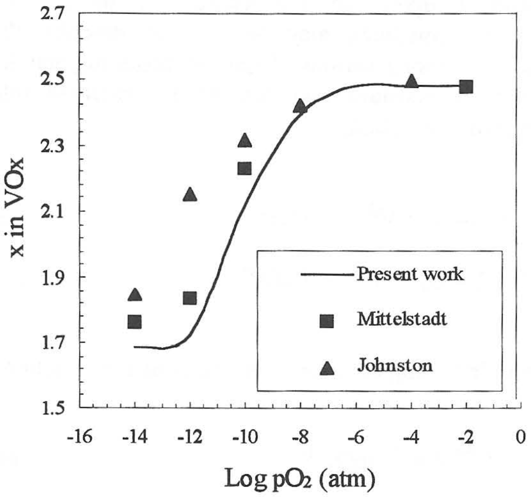

Fig. 5. Comparison of distribution of different valencies of vanadium for Na_2O-$2SiO_2$ melt (1 mol% V_2O_5)at 1225°C with Mittelstadt and Schwerdtfeger[12] [Na_2O-V_2O_5 melts,1000°C] and Johnston[10] [Na_2O-$2SiO_2$ melts,1085°C]. (atm=9.87MPa; °F=9/5°C+32)

Since vanadium can exist in multiple valance states, a general mass expression could be written for a reduction reaction[18]

$$4MO_{(s)}^{(m-2x)} \Leftrightarrow 4M_{(s)}^{(m-n)} + (4x-2n)O^{2-}_{(s)} + nO_{2(g)} \qquad (7)$$

where n is the number of electrons involved in the reduction, m is the charge on the redox species, x is the relative number of oxygen atoms associated with oxidised species. For vanadium, a general expression arises from this relation,

$$VO_{n-1}^{2-n} + \frac{1}{2}O^{2-} + \frac{1}{4}O_2 = VO_n^{1-n} \qquad (8)$$

where n=3 or 4 for two equilibria. This expression accounts for the effect of activity of free O^{2-} ions, which is assumed constant in expression 2 and 3, on the redox ratio.The activity of free O^{2-} is in turn determined by the melt composition.

It is evident from fig. 6 that increase in basicity stabilises the proportion of vanadium in higher oxidation state, hence vanadium follows the O-type redox reaction. Melts with a basicity of 1.0 contain only V^{4+} and V^{5+} species over the whole range of oxygen partial pressure studied, whereas in low basicity (0.5) melt V^{3+} started to appear under reduced atmosphere at 10^{-12} atm. The effect of basicity on vanadium oxidation state is also obvious in fig. 4(a) where this data has been plotted in terms of 'x'.

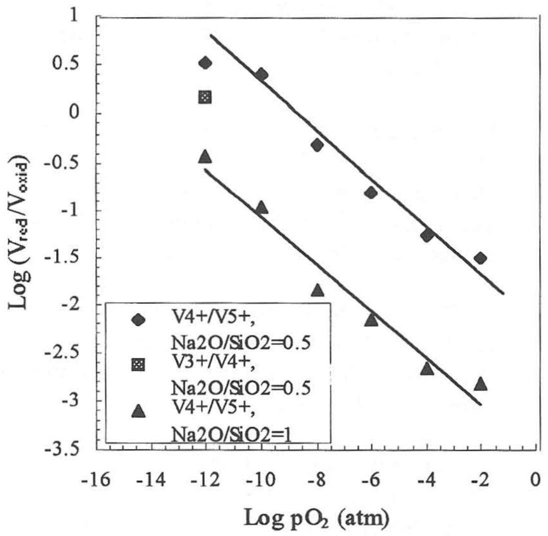

Fig. 6. Relationship between the redox ratios of vanadium and oxygen partial pressure at different basicity ratios for Na_2O-SiO_2 melts containing 5 mol% V_2O_5 at 1225°C (2237°F). (atm=9.87MPa)

From the expression 2 or 3, a relation between redox ratio and oxygen activity or oxygen partial pressure was evaluated by many workers. The slope of lines in fig. 6 follows~-1/4 for different kinds of melts, confirming the relation.

Effect of variation of vanadium content on valency distribution at fixed oxygen potential and temperature is shown in fig. 4(c) where oxidation states remains higher at higher vanadium oxide content indicating stability of VO_4^{3-} or VO_3^{2-} complexes.

The Clausius claperyron equation for a redox ion could be modified as[19],

$$\log\frac{[M^{(m-n)+}]}{[M^{m+}]} = -\frac{\Delta H}{2.303R}\left(\frac{1}{T}\right) + b \tag{9}$$

where R is the gas constant, T is the temperature (°K), ΔH is the enthalpy of reduction, the redox ratio represents the equilibrium constant and b is a term incorporating oxygen fugacity and composition.

Reduction of vanadium species being an endothermic process is favoured at higher temperatures as indicated in fig. 4(b) for valency distribution and also in fig. 7 where redox ratio is plotted against temperature.

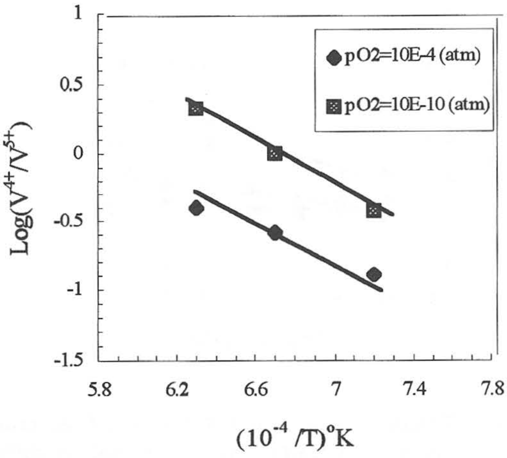

Fig. 7. Dependence of redox ratios of vanadium on reciprocal of temperature for Na_2O-$2SiO_2$ melt containing 1 mol% V_2O_5. (atm=9.87MPa)

3.2 Effect of Alumina Dissolution

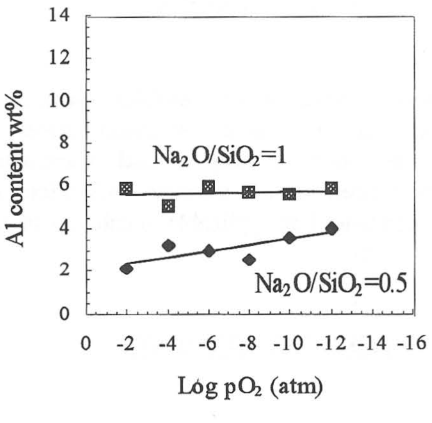

Fig. 8. Trends in aluminium dissolution from crucible material in Na_2O-$2SiO_2$-V_2O_5 melt at 1225°C (2237°F) at different basicities. (atm=9.87MPa)

It has been mentioned in the literature[9] that an alkali silicate melt containing iron could be saturated with~10 wt% Al_2O_3 at 1400°C (2552°F) and 6 wt% at 1100°C (2012°F), without affecting the Fe^{2+}/Fe^{3+} ratio. Johnston[10] also found that melts containing vanadium were not affected by Al_2O_3 contamination. The results of this study confirm Johnston's work in that the slope of lines from expressions 2&3 remained essentially constant in spite of aluminium contamination of up to 8wt%.

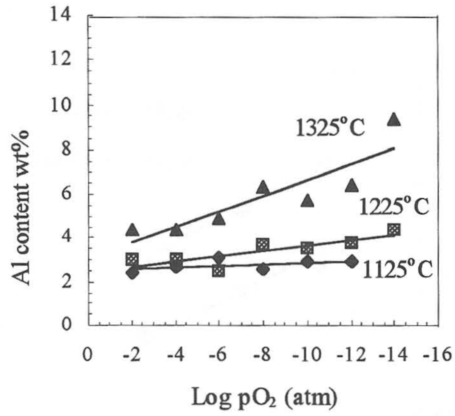

Fig. 9. Trends in aluminium dissolution from crucible material in Na_2O-$2SiO_2$-V_2O_5 melt at different temperatures. (atm=9.87MPa; °F=9/5°C+32)

As would be expected alumina saturation increased with both basicity (fig. 8) and temperature (fig. 9). Of interest is the fact that reducing atmosphere apparently also favoured alumina dissolution (fig. 9).

4. CONCLUSIONS

A new method which enables quantitative determination of the three oxidation states of vanadium has been developed and successfully evaluated on molten sodium silicates. Indications are that the method would be applicable to calcium silicate and complex melts.

ACKNOWLEDGMENTS

This project is a joint venture between UNSW and BHP Central Research laboratories. The financial support provided by BHP Central Research Laboratories, Newcastle, Australia is gratefully acknowledged.

REFERENCES

1. R. V. Anavekar, N. Devraj and J. Ramakrishna, "Direct Current Electrical Resistivity of Zinc Borate Glasses Containing Transition Metal Oxides," Phy. Chem. Glasses, Vol. 32, 1991, pp. 103-108.

2. L. D. Bogomolova, and E. K. Henner, "The Effect of Cluster Formation of The Fe^{3+} ion in Silicate Glasses," J. Mag. Res., Vol. 41, 1980, pp. 422-431.

3. H. Chaudary, M. P. Brungs and G. R. Belton, "Investigation of the Oxidation States of Vanadium in Slags Using Spectroscopic Techniques," Second Australian Melt Chemistry Symposium. Melbourne, Australia, 1995.

4. H. Chaudary, M. P. Brungs, D. M. Miller and G. R. Belton, "Vanadium in Silicate Melts," Third Australian Melt Chemistry Symposium. Melbourne, Australia, 1996.

5. R. Muncaster and S. Parke, " EPR Spectra of Glasses in the System V_2O_5-TeO_2," J. Phy. Chem. Solids, Vol. 24, 1977, pp. 399-412.

6. E. J. Frieable, L. K. Wilson and D. L. Kinser, "Magnetic Behaviour and Microstructure of Vanadium Phosphate Glasses," J. Am. Ceram. Soc., Vol. 55, 1972, pp. 164-168.

7. A. Goldstein, V. Chiriac and D. Becherescu, "On Some d^1 Ions Spectra in Oxide Glasses" J. Non-Cryst. Solids, Vol. 19, 1987, pp. 271-277.

8. S. Gupta, N. Khanijo and A. Mansingh, "The Influence of V^{4+} Ion Concentration on the EPR Spectra of Vanadium Glasses" J. Non-Cryst. Solids, Vol. 181, 1995, pp. 58-63.

9. W. D Johnston, "Oxidation-Reduction Equilibria in Iron-Containing Glass," J. Amer. Ceram. Soc., Vol. 47, 1964, pp 198-201.

10. W. D. Johnston, "Oxidation-Reduction Equilibrium in Molten Na_2O-$2SiO_2$ Glass," J. Amer. Ceram. Soc., Vol. 48, 1965, pp 184-189.

11. L. D. Bogomolova et al., "EPR of V^{4+} Ions in Silica Glass," J. Non-Cryst. Solids., Vol. 103, 1988, pp. 319-323.

12. R. Mittelstadt and K. Schwerdtfeger, "The Dependence of the Oxidation state of Vanadium on the Oxygen Pressure in Melts of VO_x, Na_2O-VO_x, and CaO-SiO_2-VO_x," Met. Trans. B, Vol. 21, 1990, pp. 111-120.

13. A. Paul and F. Assabghy, "Optical and ESR Spectra of Vanadium (IV) in Different Simple Germanate, Phosphate and Borate Glasses," J. Material Science, Vol. 10, 1975, pp. 613-620.

14. R. H. Sands, "Paramagnetic Resonance Absorption in Glass," Phys. Rev., Vol. 99, 1955, pp. 1222.

15. F. Tsukihashi, A. Werme, A. Kasahara, M. Okada and N. Sano, "Vanadium, Niobium and Antimony Distribution Between Carbon-Saturated Iron and Na_2O-$2SiO_2$ Melts," Tetsu-to-Hogane, Vol. 71, 1985, pp. 831-838.

16. F. Tsukihashi, A. Werme, F. Matsumoto, A. Kashara, M. Yukinbu, T. Hyodo, S. Shiomi and N. Sano, "Thermodynamics of the Soda Slag System for Hot Metal Treatment," Metallurgical Slags and Fluxes, 2nd Symp., AIME, New York , 1984, pp. 89-106.

17. A. G. Turnball and M. W. Wadsley, "The CSIRO-Monash Thermochemistry System," CSIRO Divisions of Mineral Products, Australia, 1988.

18. S. B. Holmquist, "Ionic Formulation of Redox Equilibria in Glass Melts," J. Am. Ceram. Soc, Vol. 49, 1965, pp. 228-229.

19. H. D. Schreiber, "Redox Prccesses in Glass-Forming Melts," J. Non-Cryst. Solids, Vol. 84, 1986, pp. 129-141.