Vanadium losses to ferrovanadium smelter slag:
Results from industrial slags

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Abstract

Vanadium losses to the slag in the electro-aluminothermic process include metal droplet entrainment and unreduced vanadium oxide. The effect of slag basicity ($CaO:Al_2O_3$ ratio) on oxidic vanadium loss and metal droplet entrainment was assessed by investigating solidified industrial slag samples. It is shown that the oxidic vanadium losses to the slag are much lower for slags with higher Al_2O_3 contents. The effect of droplet entrainment on vanadium loss could not be fully quantified due to the strong segregation behavior and crowding close to the slag-metal surface, but the indications are that slag basicity does not play a strong role.

1. Introduction

Ferrovanadium is sometimes produced from vanadium trioxide in electric arc furnaces, using aluminium as reductant.[1] CaO fluxes the alumina-rich Al_2O_3-CaO-MgO slag which is formed during the reduction process. The entire MgO content of the slag is a result of refractory wear of the magnesite lining. In addition to vanadium lost as unreduced vanadium oxides in the slag, vanadium yield is also decreased by entrained ferrovanadium droplets, which remain in the slag after solidification.

The influence of slag basicity on incomplete reduction of vanadium oxide was the subject of a previous study.[1] In that work, the effect of slag basicity on oxidic vanadium losses was investigated with high-temperature equilibrium experiments, which showed that these losses should be substantially lower if the Al_2O_3 content of the slag is increased above ca. 65% (because of the strong increase in the vanadium oxide activity coefficient at high Al_2O_3 levels).

While decreasing the oxidic vanadium loss, lower CaO fluxing additions (i.e. maintaining high Al_2O_3 levels) will increase the liquidus temperature of the slag. This may have an adverse effect on metal entrainment. In the work reported here, the effect of slag basicity on metal entrainment was assessed by investigating solidified industrial slag samples. The actual oxidic content of the slag for the industrial slags was also compared with the equilibrium predictions.

2. Slag sampling and analysis procedure

A number of factors such as cooling rate, tap temperature and slag volume influence the amount of entrained metal droplets. The amount of entrained droplets is also influenced by the location of the slag samples taken from the bulk slag (slag closer to the refractory lining solidifies more quickly, resulting in a larger amount of entrained particles). Nevertheless, by taking slag samples at a fixed location within the slag, the effect of slag basicity on droplet entrainment can be assessed semi-quantitatively.

The vertical segregation effect was addressed by investigating the best and worst positions regarding vanadium loss as entrained droplets, by sampling from the top and bottom of the bulk slag sample at a fixed horizontal position (see Figure 1).

The slag temperature was recorded prior to tapping, taking temperature readings (with an infrared pyrometer) of the slag pool near the electrodes seconds after the arc had been extinguished. Temperature readings of the tap stream could not be obtained due to large dust emissions surrounding the metal tap stream during tapping.

The slag samples were impregnated with epoxy resin under vacuum, polished, carbon coated and analysed by energy dispersive X-ray spectrometry (EDX). Parts of the samples were milled into powder for X-ray diffraction (XRD) analysis. EDX microanalyses were performed on polished sections using a Jeol 5800 scanning electron microscope at 20 kV, using a Voyager analysis system. Back-scattered electron imaging was first employed to identify all the possible phases, including metal droplets, before quantitative EDX analysis was performed. Due to the homogeneous nature of the oxide phases, analysing 10 fields per phase was sufficient to obtain average compositions, with small standard deviations.

The average chemical composition of the slag samples was determined by performing EDX analysis at the lowest obtainable magnification of 85x. Metal droplets were inevitably included in the field of analysis, giving an overestimate of the dissolved vanadium levels in the slag. The average oxidic vanadium content (corrected for the contribution of the metal particles) was found by the following procedure: Four elements (V, Al, Ca and Mg) were analysed by EDX and – based on the average compositions of the four major phases as found by EDX – a simple mass balance was used to find the mass percentages of the four major phases (the three major oxide phases as mentioned below, and the metallic phase).

3. Oxidic losses in industrial slags
3.1 Results from EDX analyses

A typical back-scattered electron image of a slag sample is shown in Figure 2. The three major oxide phases which are visible in Figure 2 were identified – based on X-ray diffraction and EDX analysis – as $MgO.Al_2O_3$ (MA), $CaO.Al_2O_3$ (CA), and $CaO.2Al_2O_3$ (CA_2). All three of these phases were present in all the slag samples investigated. A fourth phase, which is a result of impurities (especially Na) introduced by the vanadium starter material, was also identified in some of the slag samples (see Figure 2). In the beneficiation of vanadium oxide, Na_2CO_3 or Na_2SO_4 is used as a roasting reagent to react with V_2O_5 in the magnetite ores to form soluble sodium vanadates; some sodium sometimes remains in the oxide product which is the feed material for the ferrovanadium smelter. The resulting sodium-rich phase in the ferrovanadium smelter slag was usually less than 1 volume % of the slag, and was found not to have a significant effect on vanadium losses.

The ternary $MgO-Al_2O_3-CaO$ phase diagram[2] indicates that for slags without Na_2O contamination, the average slag composition lies within the $CA-CA_2-MA$ alkemade triangle, in the primary phase field of MA. The primary crystals of MA are expected to be relatively large and idiomorphic, as can be seen in Figure 2.

Interestingly, the metal particles occur only on the edges of or within the MA grains (see Figure 2). The metal droplets (containing mainly V, Fe and Al) have a higher liquidus temperature than the slag,[3] resulting in metal solidification while the slag is molten. On subsequent slag solidification, the solid metal particles may serve as nuclei for the MA phase, a possible explanation for the occurrence of metal particles within or on the boundary of the MA grains. Thus location can serve to distinguish between metal particles of different origins: metal particles not associated with the MA phase probably originate from entrainment after primary crystallization of MA. This may occur during slow tapping when molten ferrovanadium is tapped onto semi-solidified slag.

As mentioned earlier, high temperature equilibrium experiments indicated a very strong relationship between the slag composition and the amount of oxidic vanadium in the slag, especially where $CaO:Al_2O_3<0.7$ (molar basis).[1] The results of EDX analyses on the industrial slag samples are summarised in Figure 3, confirming the laboratory results:[1] oxidic vanadium losses are much higher for slags with lower alumina contents. The V_2O_3 content of the slag can be reduced from about 6% to 2% by raising the alumina content from 62% to 67% (mass basis). This confirms the importance of basicity control by limiting CaO additions and MgO refractory wear.

Figure 3 does show a difference in oxidic vanadium content between samples taken from the upper and lower parts of the slag block: the samples taken at the bottom contain up to 1.5% (mass basis) less V_2O_3 than those taken at the top. It is not known whether the differences

indicated by Figure 3 reflect segregation within the furnace or whether these arose during solidification. Nevertheless, vanadium concentration gradients do clearly occur in the solidified slag and sampling of the entire bulk sample would be necessary to fully quantify the oxidic vanadium content of the slag.

3.2 Production slag dip samples

At the ferrovanadium plant for which data were available, slag samples are taken prior to tapping by dipping a steel rod into the slag. After dipping, the rod is withdrawn quickly, solidifying some slag onto the rod. After cooling the slag is removed from the rod, crushed to a fine powder and analysed by X-ray fluorescence (XRF).

Figure 4 gives a back-scattered electron image of such a dipped slag sample, showing the slag to be present as a glass phase, formed as a result of rapid solidification of the thin slag layer. This figure also reveals entrained metal particles in the glass phase; these would contribute significantly to the average vanadium content of the slag as determined by XRF analysis of the milled dip samples.

A number of pieces of the dipped sample were co-mounted in epoxy resin, polished and analysed by EDX. Special care had to be taken to ensure that the metal particles were excluded during analysis. At least 40 fields were analysed to establish a good mean and standard deviation. The results are summarized in Figure 5. As this figure indicates, the dipped sample analysed appreciably higher for V_2O_3 than the two samples taken from the corresponding solidified bulk slag sample. The figure also shows that the alumina content of the dipped sample compares well with the average alumina content of the other two samples. The marked chemical segregation in the slag has clear implications for practical approaches to process refinement: as Figure 5 suggests, the V_2O_3 content of the slag as determined by XRF may be in excess of the average vanadium content of the slag (even without the contaminating effect of metal droplets). Changing the process on the basis of the composition of the dipped sample may thus lead to unreliable results. Ways have to be found to address this problem and to ensure that slag sampling is more representative of the bulk of the slag; further investigation is necessary to address this.

3.3 XRF results from production slag dip samples

Although the vanadium content of the dipped samples is likely to be in excess of that of the average bulk sample, the industrial XRF analyses are of some value (to show trends) as long as the sampling procedure is consistent. Historic industrial data, relating to 3 months of production (more than 550 melts), were collected, grouped and are summarised in Figures 6-8. The large confidence intervals are a result of extensive scattering of the plant data.

Figure 6 shows that high-alumina slags are beneficial for vanadium recovery. The alumina content strongly influences the oxidic amount of vanadium, in agreement with the laboratory results.

Because of strict specifications on the aluminium content of ferrovanadium, the effect of higher alumina contents on the residual aluminium in the ferrovanadium is of concern. However, Figure 7 shows that the aluminium content of the ferrovanadium remains constant for higher-alumina slags.

4. Metallic losses in industrial slag samples

EDX analyses on industrial slag samples and laboratory results indicate that the Al_2O_3 content of the slag has a strong effect on the oxidic vanadium loss to the slag. The decrease of the slag basicity (achieved with lower lime additions) will result in higher liquidus temperatures which may lead to higher metallic losses. It is uncertain which of the oxidic or metallic loss contributes most strongly to the total vanadium loss in the slag. The aim of this section is to quantify the amount of vanadium typically associated with the metallic phase and the extent to which slag basicity influences metal droplet entrainment.

The investigations were carried out on the polished sections previously subjected to oxidic phase analysis, as reported in section 3.1. Polished sections were investigated using an optical microscope and photographs of the entrained droplets were taken with a digital camera. The y coordinate of the polished sections (vertical in the bulk slag sample) was incrementally increased, while photos were taken randomly along the x coordinate. Special care was taken to ensure that the photographs were representative of the entire sample. Using the Imagetool software package, the areas of the individual particles as well as the total droplet area expressed as a fraction of the total area, were estimated. The area fraction of metal droplets (numerically equal to their volume fraction) was recalculated to a mass percentage in the slag; the results are given in Figure 8.

The strong difference between the metal particle concentration close to the bottom surface of the slag and in the upper region of the slag is evident from this figure.

High tap temperatures will reduce the slag viscosity and increase the solidification period of the slag, perhaps resulting in the reduction of metal droplet entrainment. However, Figure 8 reveals that no relation between the amount of droplets entrained and the tap temperature could be observed.

Based on the results in Figures 3 and 8, the contributions of oxidic and metallic vanadium losses are quantified in Figure 9, for respectively "top" and "bottom" positions in the solidified slag block. Figure 9 a) indicates that the contribution of the metal particles to the total vanadium loss is relatively small; the maximum contribution is some 0.5 % vanadium in the slag. As illustrated by this figure, adjustments made to the slag basicity (by decreasing the CaO addition) will increase the metal recoveries: the total vanadium content of the slag can be reduced from ca. 3.5 % to ca. 1.5 % by adjusting the alumina composition from ca. 60 % to ca. 70 %. Figure 9 a) appears to have a minimum at around 67 % alumina, but further sampling would be required to test whether this is a real effect. It is worth noting that the XRF analyses to indicate a similar effect (Figure 6). The higher liquidus temperatures appear not to affect the entrainment of metal particles strongly, for slag samples taken from the top of the industrial bulk slag blocks.

In contrast, Figure 9 b) shows a very strong effect of the slag basicity, with a strong contribution of metallic losses. It is worth mentioning that these slag samples were taken within centimetres of the slag-metal interface, and that the amount of entrained droplets strongly depended on vertical position within the bulk sample. The first few centimetres above the slag-metal interface contained most of the entrained droplets, beyond which the concentration declined strongly. The very high concentration of the droplets close to the interface gives rise to unusually high local losses of vanadium to the entrained metal particles, which are not representative of the entire bulk slag sample. The influence of slag basicity on average metal droplet entrainment is thus better depicted by Figure 9 a) than Figure 9 b).

It can be concluded that metallic vanadium losses could not be fully quantified by analysing samples from the top and bottom of the bulk slag sample. Although the samples taken at the top of the bulk slag sample are expected to be more representative of the entire slag sample, the positional effect on droplet entrainment introduces much uncertainty. In order to quantify metal droplet entrainment as a possible cause of vanadium loss to the slag fully, more exhaustive sampling would be required.

4. Conclusion

The following can be concluded:

- Analyses of industrial slags confirm that slags with higher Al_2O_3 contents clearly have lower vanadium oxide contents, in line with equilibrium predictions.
- The amount of droplets entrained (metallic loss) does not depend strongly on the tap temperature.
- Vanadium losses as entrained metal droplets could not be fully quantified due to the strong segregation behaviour and crowding close to the slag metal interface.

References

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2. Verein Deutscher Eisenhüttenleute (eds.): *Slag atlas*, 2nd edition. Düsseldorf, Verlag Stahleisen (1995).
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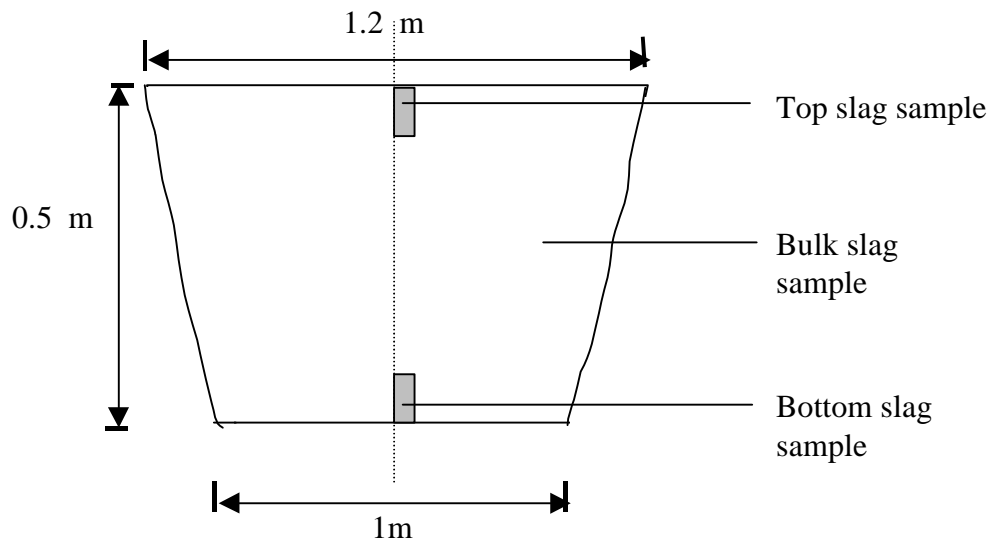
Figure 1: Schematic diagram of a vertical section through the bulk sample showing the location of the samples.
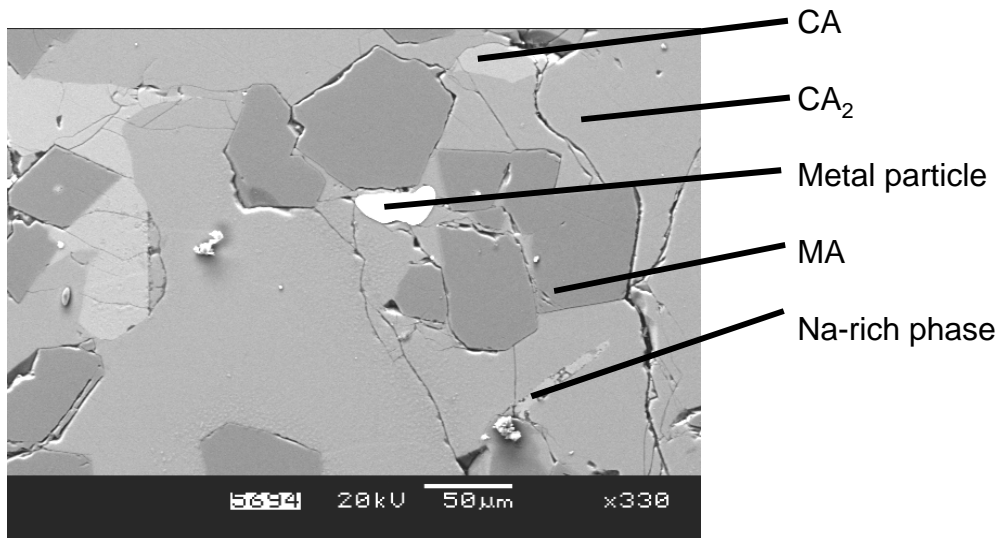

Figure 2: Back-scattered electron image of an industrial slag sample showing the three major oxide phases and the sodium-rich phase.
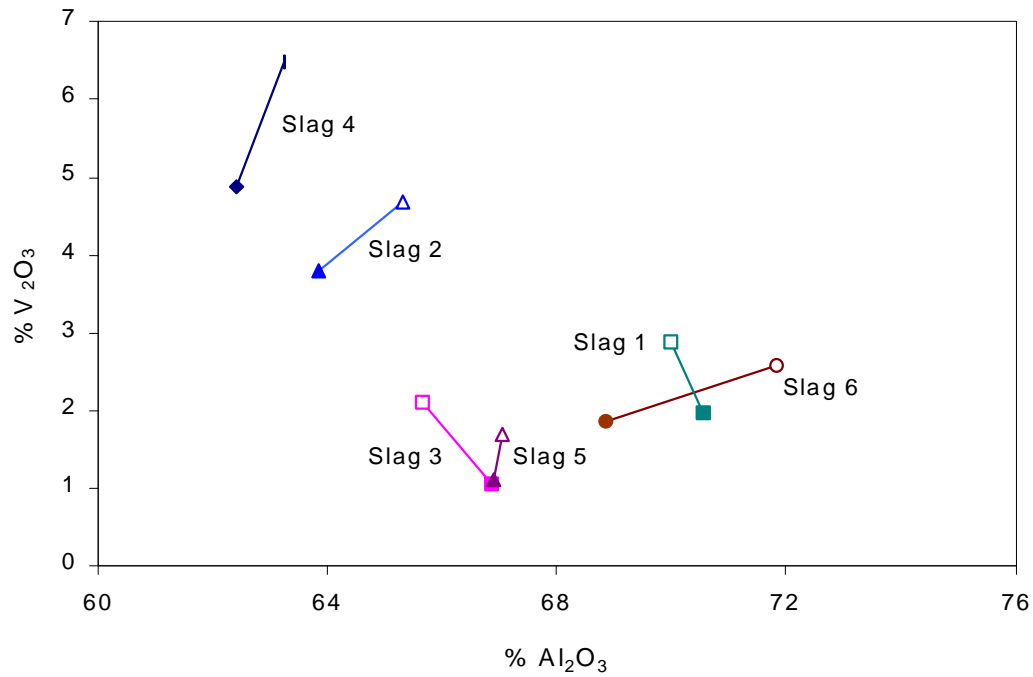
Figure 3: The effect of the alumina content of the industrial slag samples on the oxidic vanadium content, as analysed by EDX. Solid markers present data of samples taken at the top of the bulk sample and open markers samples taken from the bottom (mass percentages).
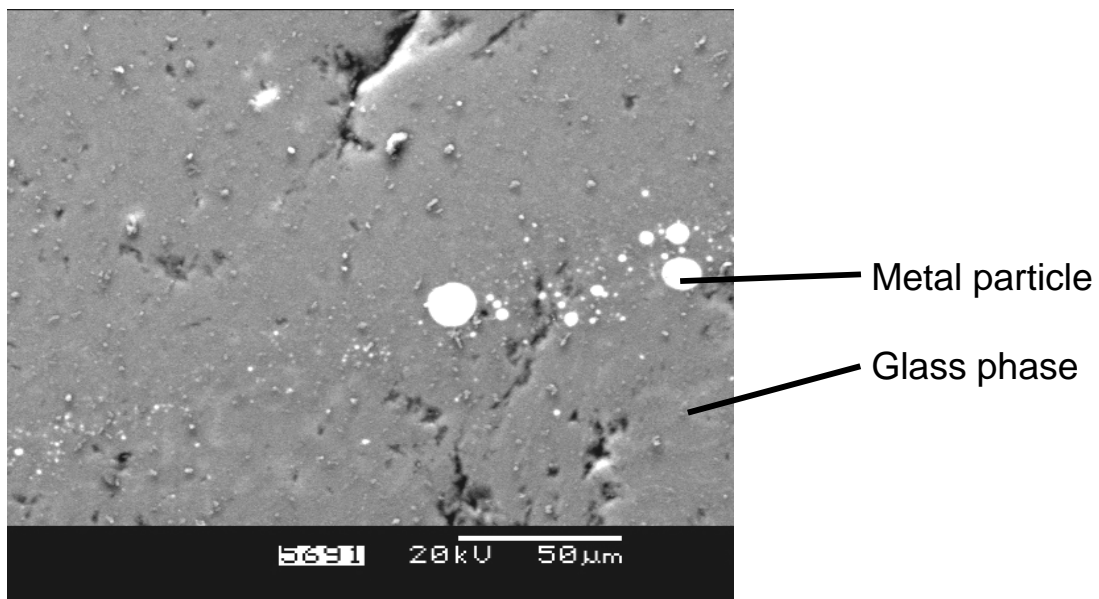
Figure 4: Back-scattered electron image of dipped slag sample with metal particles.
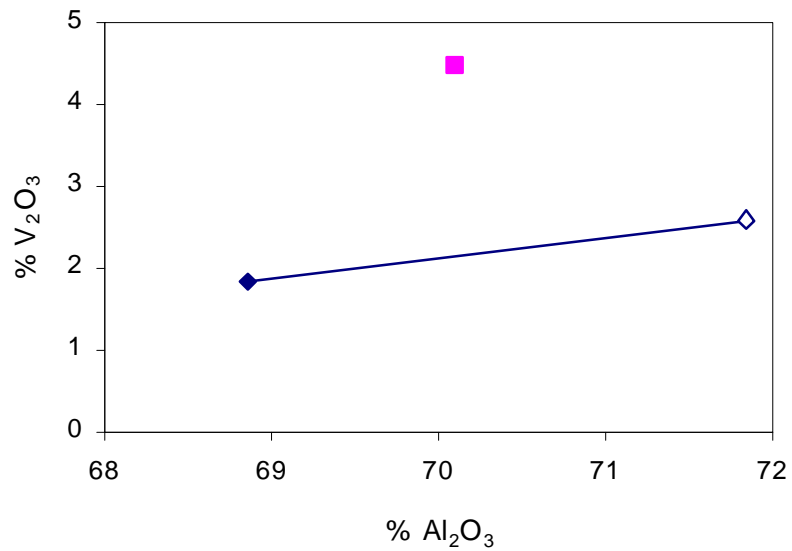
Figure 5: Comparison between vanadium content of a dip sample and samples taken from the bulk solidified sample after tapping. The square data marker is for the dip sample and diamond markers for the bulk slag samples.
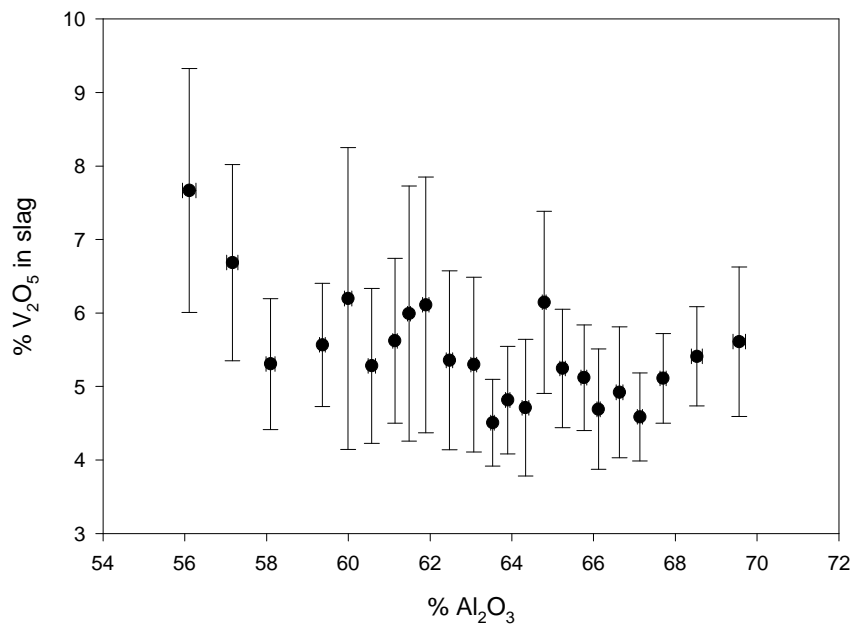
Figure 6: Total vanadium oxide content of the slag (reported as V_2O_5) as a function of the alumina content, based on in-plant XRF analyses of dip samples. Error bars are 95% confidence intervals.
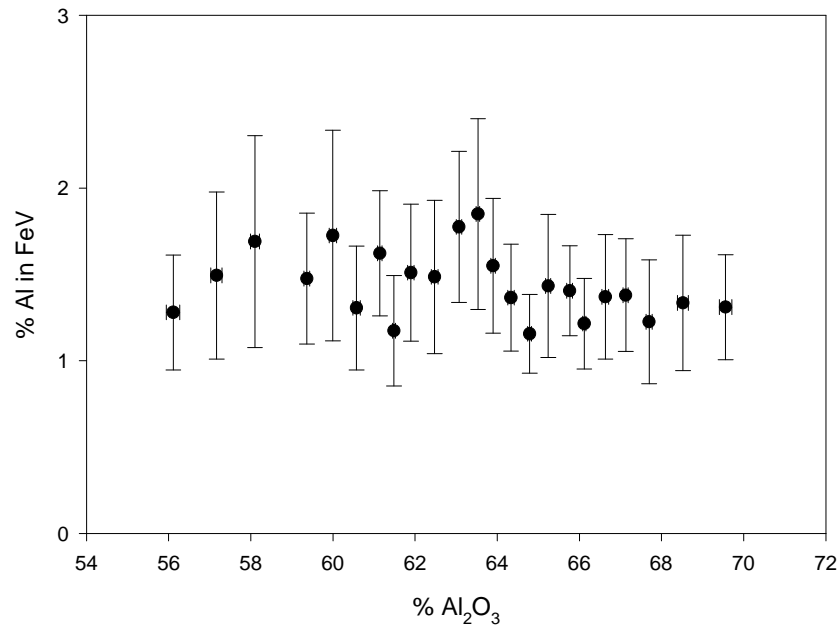
Figure 7: The effect of the slag composition on the aluminium content of the ferrovanadium, based on in-plant XRF analyses of the alumina and aluminium in dip slag and metal chip samples respectively. Error bars are 95% confidence intervals.
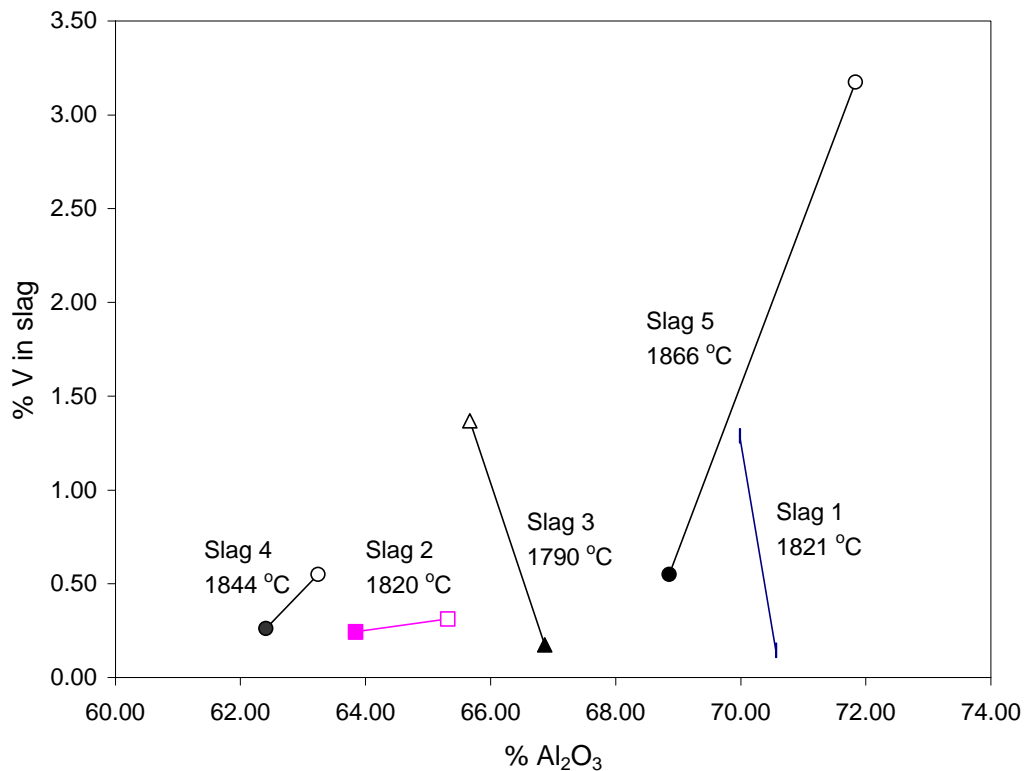

Figure 8: Metallic vanadium losses (based on image analysis), with recorded tap temperatures for different slag samples. The open data markers and solid data markers represent samples taken at the bottom and top of the bulk sample, respectively. The investigations were carried out on the polished slag sections of which the VO_x content was determined previously.
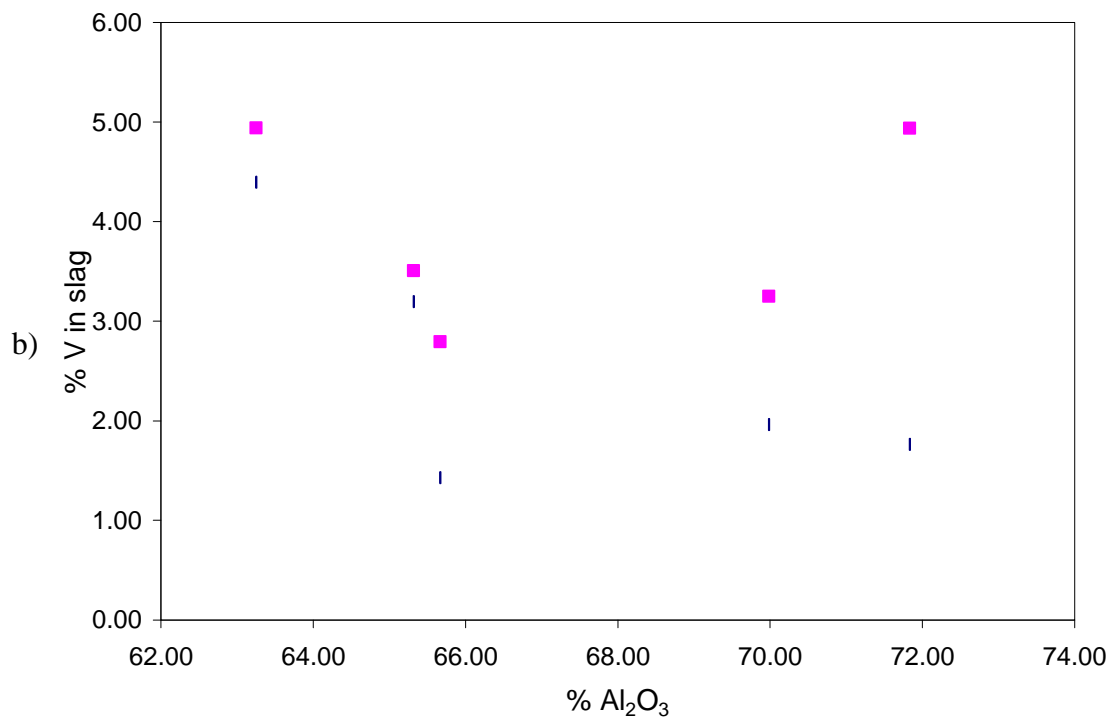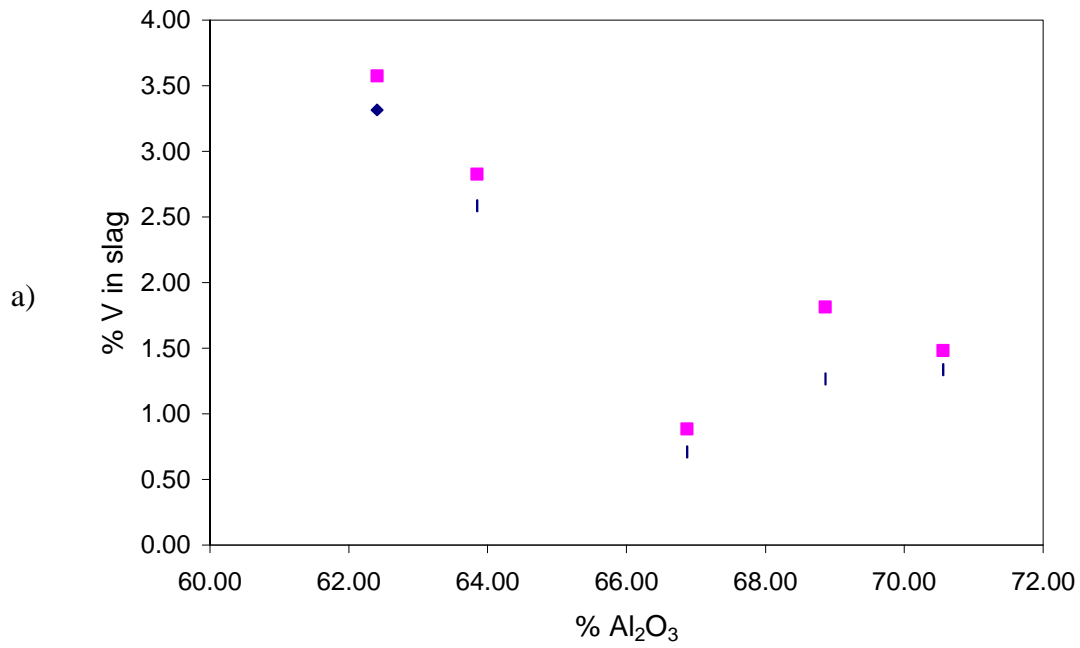
Figure 9: Soluble and total vanadium loss to the slag as function of the slag basicity for the samples from the top of the slag block (a), and at the lower surface of the slag block (b). In this figure the squares show the total vanadium content and the diamonds the oxidic vanadium content of the slag