

Pyrometallurgical Processing of Vanadiferous Slag Using Plasma/Induction Heating

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A direct pyrometallurgical route for the production of ferrovanadium from slag was investigated. The conventional process route to ferrovanadium usually involves the aluminothermic reduction of vanadium pentoxide (V_2O_5) in the presence of iron scrap. A large cost component in the manufacture of ferrovanadium resides in the production of the V_2O_5 feedstock. A direct route involving the pyrometallurgical reduction of a modified vanadiferous slag therefore offers the potential of considerable cost savings.

In order to produce a ferroalloy grade acceptable for use in most steelmaking applications, a vanadium content in excess of 45 per cent vanadium is desirable. Pyrometallurgical processing of available slag therefore requires the removal of excess FeO prior to a final reduction operation. The degree of control that could be exercised over iron–vanadium partitioning in molten systems was investigated. Information on the amount of vanadium oxide remaining in the slag after final reduction, together with the levels of residual reductant in the metal phase, indicated the likely composition of ferrovanadium produced by this process route.

The effect of slag basicity on the distribution of vanadium and iron was determined at various degrees of reduction by carbon, silicon, and aluminium. The smelting conditions during the various slag-reduction reactions was assessed with respect to the design of d.c. transferred plasma-arc furnaces.

The results showed that the extent of iron–vanadium partitioning was dependent upon the lime/silica ratio in the slag. Greater partitioning of vanadium and iron was achieved at high lime/silica ratios.

The remnant V_2O_3 concentration after final reduction of the slag was found to be 0.8 per cent. This level was attained by silicothermic reduction and by aluminothermic reduction over ferrovanadium containing 12 per cent Si and 0.1 per cent Al respectively.

The heat-distribution characteristics produced under the various reduction regimes need to be accommodated in the furnace design. The use of a combined plasma–induction furnace at the 20 kg scale provided a solution to the problem of the variability of slag–metal heat distribution encountered in these laboratory smelting trials.

Introduction

High-vanadium slags are generated as a co-product in steelmaking operations using titanomagnetite ores. In this process, vanadium-containing hot metal is treated using a controlled oxygen blow to oxidize vanadium into a slag. Vanadiferous slags are an internationally traded commodity, most of which is produced in South Africa¹. In 1986 the scale of New Zealand Steel's titanomagnetite smelting was increased significantly. The expansion of the South Auckland plant included the installation of two vanadium-recovery units (VRUs), which for the first time permitted the

production of commercial quantities of slag. In anticipation of this output, the options for the on-site pyrometallurgical production of ferrovanadium from slag were investigated.

The composition of vanadiferous slags appears to vary considerably depending on source, but generally ranges from 15 to 20 per cent V_2O_3 , 25 to 45 per cent FeO, and 10 to 20 per cent SiO_2 , with up to around 6 per cent metallic iron. These slags are used in the production of vanadium pentoxide (V_2O_5) by salt-roasting and leaching. To achieve efficient vanadium recovery in this process, the CaO and MgO contents of the feedstock must be kept to a

minimum². Vanadiferous slags are therefore acid in nature, and are produced in VRU vessels with alumina-silica refractory linings³.

The majority of the world's V₂O₅ output is used in the manufacture of ferrovanadium⁴, usually by aluminothermic reduction. In combination with steel punchings, ground aluminium, lime, and V₂O₅ are smelted to produce ferrovanadium containing typically 80 per cent vanadium.

An alternative and more direct route to ferrovanadium involves pyrometallurgical processing of the slag itself. A patent⁵ filed by the Norwegian company Christiania Spigerverk in 1968 describes a two-stage silicothermic process using an arc furnace and shaking ladle. Another patent⁶, filed by the Foote Mineral Co, USA, also describes a process based on the intermediate formation of vanadium silicide. In general, pyrometallurgical processing of slag appears to result in a lower-grade ferroalloy containing up to 45 per cent vanadium.

The critical process step in the pyrometallurgical route is to establish a low Fe-V ratio in the slag. This requires control over the partitioning of iron and vanadium between the molten slag and metal phases. The reduction characteristics of vanadium and iron oxides in various slag compositions were therefore investigated. The objective was to demonstrate a low-cost process for producing ferrovanadium from conventional VRU slag, and to determine the composition of the product. The plant requirements for pyrometallurgical processing were also investigated, with particular reference to the benefits cited for d.c. transferred plasma-arc smelting⁷⁻⁹. Laboratory plasma-smelting facilities were designed for a programme of smelting trials using carbon, silicon, and aluminium as reductant. Slag basicity was varied over a wide range to determine its influence on vanadium and iron distribution between the slag and metal phases.

Experimental Method

The compositions of the slags used in this work are shown in Table I.

The experimental programme was carried out in two stages.

Prereduction tests were carried out to determine the effect of slag basicity on Fe-V partitioning over molten iron. An objective was to measure the level to which FeO could be reduced from the slag before an arbitrary 2 per cent vanadium metallization was reached.

The final reduction of prereduced slag was then investigated. These smelts were carried out over molten ferrovanadium so that the efficiency of vanadium recovery under process conditions could be determined. Both aluminothermic and silicothermic reduction was carried out.

Preliminary Trials Using d.c. Transferred-arc Smelting

Initial smelting trials were carried out in a laboratory plasma-arc furnace, as shown in cross-section in Figure 1. A mixture of crushed slag, lime, and reductant was fed onto a molten-iron heel. After being held for 20 minutes, the furnace contents were poured into chill moulds. The slag and metal phases were separated mechanically, and samples of each were analysed for iron and vanadium.

During carbothermic reduction, the heat distribution in the crucible, and the associated metal and slag fluidity, were favourable. However, during silicothermic smelting, limited heat transfer to the lower regions of the furnace resulted in poor metal recovery. An attempt to correct this by increasing the arc current caused excessive refractory dissolution without achieving full metal recovery. The use of this design of furnace was therefore discontinued.

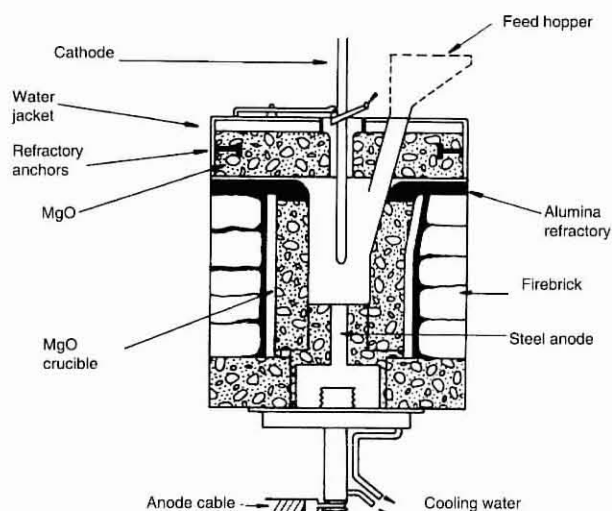


FIGURE 1. The laboratory transferred plasma-arc furnace with drilled graphite cathode. Initial crucible diameter 150 mm

Plasma-Induction Smelting

The use of plasma induction (PI) heating in the refining of steel has been reported previously^{10,11}. Based on these design principles, a 60 kW induction melting furnace was modified to accept a d.c. transferred arc as shown in Figure 2. This required the installation of a steel anode in the base of the furnace and the addition of a lid and cathode support system. The management of the furnace and plasma-arc supply cables is shown in Figure 3.

The dual heating system provided a solution to the poor heat distribution encountered in the previous furnace. With up to 32 kW of plasma-arc power and 5 to 15 kW of induction power, depending on the reductant used, a bath temperature chosen within the range 1550 to 1670 °C could

TABLE I
COMPOSITION OF FEED SLAGS, % BY MASS

Slag	Al ₂ O ₃	CaO	Cr ₂ O ₃	FeO	MgO	MnO	SiO ₂	TiO ₂	V ₂ O ₃	FeO	Total
VRU	8,0	1,5	1,1	41,0	1,0	5,1	21,5	4,7	13,5	0,6	98,0
P-R	6,1	27,5	1,4	7,0	10,2	8,0	19,4	7,6	12,9	0	100,1

VRU Vanadiferous slag
P-R Prereduced slag

be maintained uniformly over an extended holding period. The incremental addition of reductant enabled a series of steady-state conditions to be established and a corresponding sequence of paired slag and metal samples to be taken. An argon-purged silica tube was used to sample the molten slag and metal 15 minutes after each addition of reductant. From previously determined reaction rates¹², it was estimated that the reaction would be about 90 per cent completed after this period. The metal samples were analysed using emission spectrometry and the slag samples using atomic absorption (AA) spectroscopy. The distribution of iron and vanadium was determined over a wide range of reduction potential.

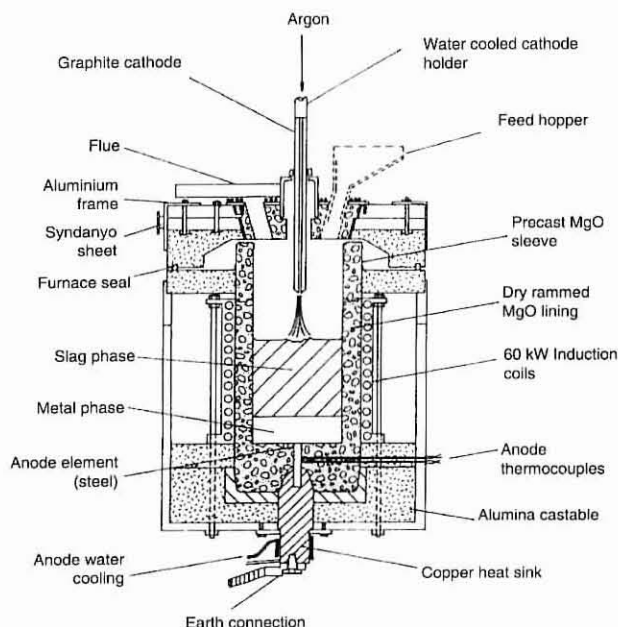


FIGURE 2. The laboratory plasma induction furnace operated at 320 A maximum arc and up to 25 kW induction power

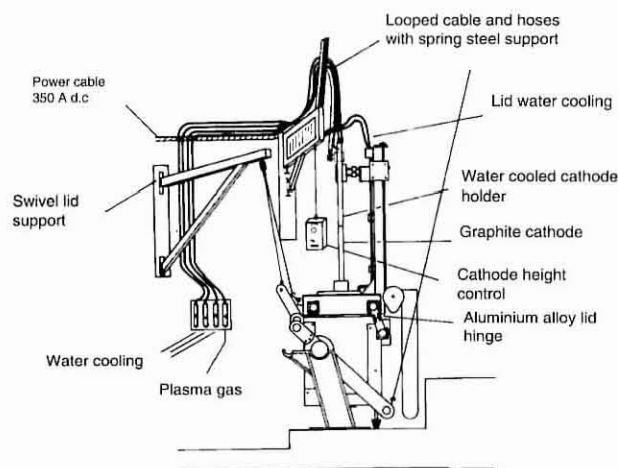
Distribution of Vanadium in Prereduction

A mixture of crushed VRU slag and CaO (when added) was fed onto a heel of 4 kg of molten iron. Reductant in the form of either crushed coke or ferrosilicon was added in increments of between 50 and 200 g until the desired stoichiometric target was reached. Smelting runs were made at CaO/SiO₂ ratios ranging from 0.07 to 1.5 for silicothermic reactions and 1.8 to 2.7 for carbothermic reactions. CaO was also added with each packet of ferrosilicon reductant in order to maintain a constant lime/silica ratio. A summary of charge details, reductant stoichiometry, and slag basicity for smelting runs made over molten iron is shown in Table II.

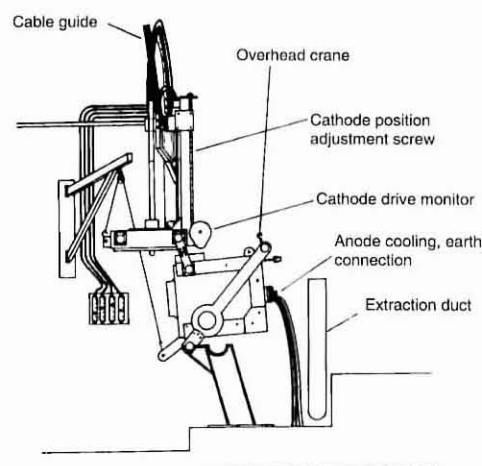
Vanadium Distribution in Final Reduction

The limit to which FeO could be reduced prior to vanadium metallization was established from the results of carbothermic trials. Using these conditions, a series of runs was carried out, each producing up to 20 kg of prereduced slag. The composition of the final blend of these slags is shown in Table I.

A molten heel containing 40 per cent vanadium was prepared from iron and commercial ferrovandium, and



OPERATING POSITION



POURING POSITION

FIGURE 3. Management of the lid and cathode assembly of the plasma induction furnace during pouring

crushed prereduced slag was fed onto the molten bath maintained at around 1600 °C. After initial bath samples had been taken, the changes in vanadium distribution resulting from additions of ferrosilicon and aluminium were determined. Details of the reductant stoichiometry and slag basicity are shown in Table III.

Results

Although the majority of smelting trials were carried out on slags containing CaO in the range 30 to 45 per cent, dissolution of the crucible resulted in a gradual increase in the MgO concentration during each smelting run, particularly in the prereduction trials where the VRU feedstock was used. The fluidity of all the slags was excellent.

Partitioning of Iron and Vanadium

The vanadium distribution between molten iron and slag was calculated from the proportion of vanadium present in the iron phase relative to the total vanadium introduced in the slag feed. Changes in the vanadium distribution at various levels of slag FeO content for the silicothermic trials are shown in Figure 4. In a slag with a CaO/SiO₂ ratio

TABLE II
CHARGE DETAILS AND CONDITIONS FOR SLAG PREREDUCTION MELTS OVER 40 kg OF IRON

Details of total charge						Slag conditions		
Run no.	VRU slag kg	CaO (total) kg	Reductant*	Total reductant kg	Stoich. [†] reductant kg	Pouring temperature °C	Basicity [‡]	CaO/SiO ₂ (mole ratio)
1	4,0	2,7	FeSi	0,5	0,59	1 600	1,80	1,50
2	6,0	2,4	FeSi	0,6	0,87	1 600	1,80	1,40
3	6,0	2,4	FeSi	0,6	0,94	1 550	2,04	1,15
4	6,0	0,0	FeSi	0,9	0,74	1 630	0,77	0,14
5	6,0	0,0	FeSi	0,7	0,77	1 630	0,23	0,07
6	4,0	1,6	Coke	0,8	0,37	1 670	2,70	1,80
7	4,0	1,6	Coke	0,9	0,44	1 560	2,40	1,90
8	6,0	5,0	Coke	1,2	0,83	1 600	3,20	2,70

* Reductants contained 70 per cent Si and 85 per cent C

† Stoichiometric quantity of reductant required to react with reducible oxides present in the slag bath

‡ Basicity calculated as (MgO + CaO)/SiO₂ mole ratio

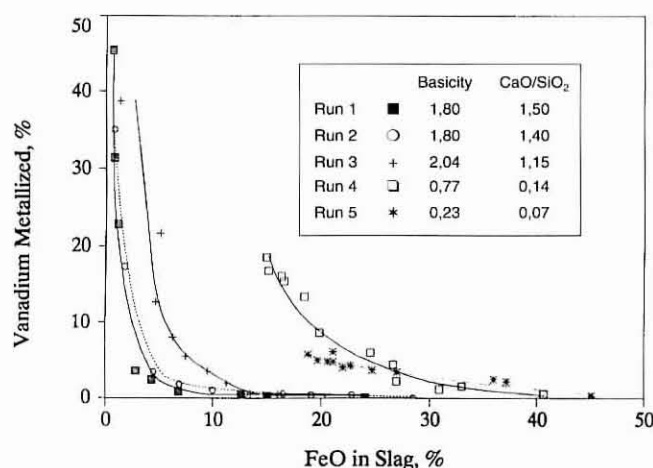


FIGURE 4. The effect of CaO/SiO₂ mole ratio on vanadium distribution during silicothermic reduction of VRU slag

adjusted to 1,5, the effect of ferrosilicon additions was to reduce the FeO content to around 7 per cent before any significant metallization of vanadium occurred. The extent of preferential FeO reduction was diminished as the CaO/SiO₂ ratio was lowered to 1,15. In highly acid slags (runs 4 and 5), both vanadium and iron oxides were reduced simultaneously.

The trend towards more efficient iron–vanadium partitioning at CaO/SiO₂ ratios in excess of 2,0 was evident from the results of the carbothermic trials (Figure 5). The onset of vanadium metallization at 7 to 10 per cent FeO was observed at a CaO/SiO₂ ratio of 1,8 to 1,9. However, at the highest ratio (2,7), the FeO content at which 2 per cent vanadium metallization occurred was lowered to 3,5 per cent. The composition of bath samples taken after the onset of vanadium metallization is shown in Table IV.

Final Slag Reduction

The results of the final-stage silicothermic reduction of prerduced slag are shown in Figure 6, and those for aluminothermic reduction in Figure 7. The progress of the reactions is described in terms of V₂O₃ concentrations in the slag at the various levels of residual reductant in the metal phase.

TABLE III
FEED DETAILS AND SLAG CONDITIONS FOR THE FINAL REDUCTION OF PREREDUCED SLAG OVER FERROVANADIUM

Details of total charge							Final slag conditions		
Run no.	Prerduced slag kg	CaO kg	FeV heel kg	Type of reductant*	Total reductant kg	Stoich. [†] reductant kg	Pouring temperature °C	Basicity (MgO + CaO)/SiO ₂	CaO/SiO ₂ (mole ratio)
9	6,0	1,8	3,2	Al	1,0	0,66	1 660	5,4	3,5
10	6,0	1,5	3,2	Al	0,9	0,45	1 650	3,4	2,2
11	6,0	2,28	3,2	FeSi	1,0	0,56	1 620	2,5	1,7

* Reductant consisted of 99,5 per cent Al or 70 per cent Si

† Stoichiometric quantity of reductant required to react with reducible oxides present in the slag bath

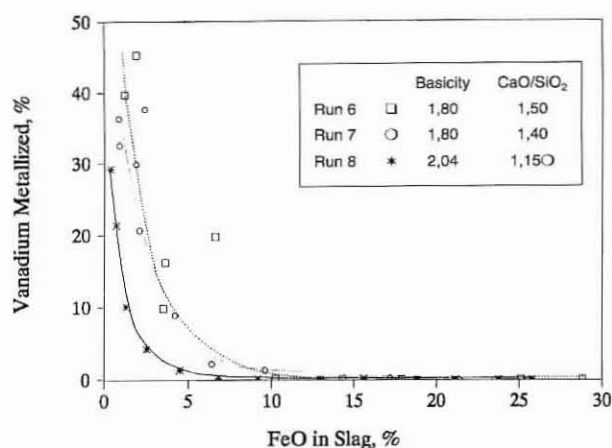


FIGURE 5. The effect of high CaO/SiO₂ ratio on vanadium distribution during carbothermic reduction of VRU slag

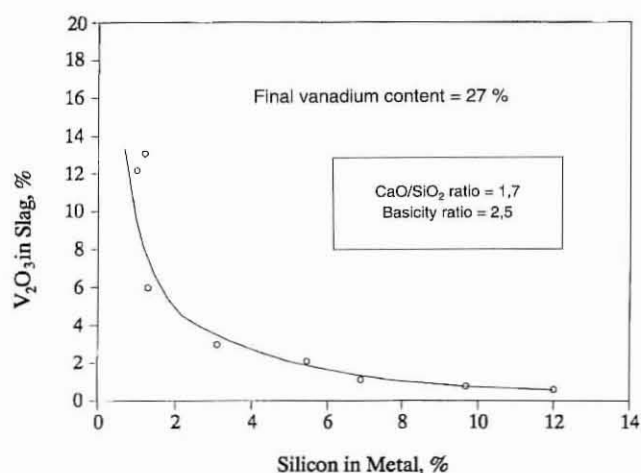


FIGURE 6. Final silicothermic reduction of prerduced slag over ferrovanadium

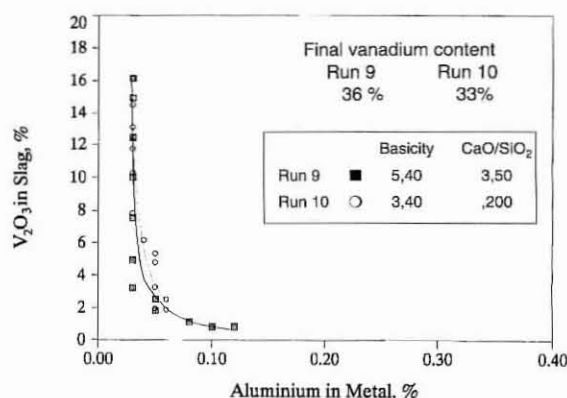


FIGURE 7. Final-stage aluminothermic reduction of prerduced slag over ferrovanadium

In these trials, reduction by aluminium was seen to be more effective, lowering the V₂O₃ content to 0,8 per cent at an aluminium concentration of 0,12 per cent. The same level of V₂O₃ reduction using silicon was achieved over a metal phase containing 9,7 per cent silicon. A summary of the slag and metal phase compositions at the start and finish of each final reduction run is shown in Table V.

Discussion

Partitioning of Iron and Vanadium

The degree to which FeO could be preferentially reduced from VRU slag was related to the CaO/SiO₂ ratio, and appeared to be unaffected by the choice of reductant. During silicothermic reduction, the partitioning of iron and vanadium increased with increasing CaO/SiO₂ ratio up to a value of 1,5. Higher ratios were not investigated owing to the excessive levels of CaO addition required. A comparison of runs 1, 2, and 3 indicated that the increase in slag basicity due to MgO pick-up had little additive effect on partitioning in slags containing CaO.

The preferential reduction of FeO in the presence of vanadium oxide in the form of either V₂O₃ or VO was consistent with the favourable free-energy change for this reaction. The improved partitioning at higher CaO levels is attributed to a relative increase in the activity of FeO compared with that of vanadium oxide. This tendency was reversed in acid slags (runs 4 and 5), where FeO displayed a lower relative activity. The increase in FeO activity with increasing lime/silica ratio was consistent with published data on the CaO-FeO-SiO₂ system¹³.

TABLE IV
COMPOSITION OF SLAG AND METAL-BATH SAMPLES FOLLOWING THE ONSET OF VANADIUM METALLIZATION, % BY MASS

Run no.	Slag								Metal			
	Al ₂ O ₃	CaO	FeO	MgO	MnO	SiO ₂	TiO ₂	V ₂ O ₃	C	Mn	Si	V
1	3,5	35,0	4,3	10,3	7,1	25,5	6,6	7,1	0,02	0,06	0,04	0,15
2	4,7	33,1	6,9	7,0	6,3	25,2	7,6	9,2	0,0	0,07	0,02	0,16
3	6,1	27,3	11,3	14,2	4,2	24,8	3,6	7,9	0,0	0,05	0,03	0,18
4	8,1	3,5	30,9	7,1	4,3	26,1	4,8	10,4	0,0	0,02	0,05	0,19
5	8,1	2,1	37,2	3,4	6,0	31,8	4,8	8,9	0,0	0,0	0,07	0,25
6	4,6	34,5	6,4	6,4	8,7	19,3	8,1	10,7	0,32	0,20	0,0	0,16
7	4,3	32,3	3,5	14,1	7,3	20,0	7,8	8,6	0,53	0,73	0,03	0,59
8	6,4	46,1	4,5	6,9	3,6	18,0	3,4	9,6	0,42	0,26	0,0	0,13

TABLE V
COMPOSITION OF START AND FINISH BATH SAMPLES DURING FINAL REDUCTION BY ALUMINIUM (RUNS 9 AND 10) AND SILICON (RUN 11), % BY MASS

Run no.	Sample	Slag								Metal			
		Al ₂ O ₃	CaO	FeO	MgO	MnO	SiO ₂	TiO ₂	V ₂ O ₃	Al	Mn	Si	V
9	Start	4,5	42,5	0,6	8,1	4,1	17,9	5,9	16,1	0,03	4,4	0,22	22,3
	Finish	28,4	39,2	0,1	14,9	0,4	11,9	5,2	0,8	0,12	6,6	4,00	38,0
10	Start	5,12	44,4	0,22	7,9	4,1	18,5	7,1	16,1	0,03	3,9	0,30	23,6
	Finish	24,4	35,8	0,08	13,8	1,4	16,3	6,6	1,9	0,05	6,8	2,5	33,0
11	Start	5,4	35,7	3,8	9,5	5,9	19,2	6,7	13,1	0,0	0,83	1,2	22,0
	Finish	7,0	43,5	0,04	15,3	0,4	27,5	4,9	0,6	0,07	5,4	12,0	27,0

Processing Implications

A high degree of control of vanadium distribution has been demonstrated using pyrometallurgical processing. The desired decrease in the Fe/V ratio in molten VRU slags can be achieved by additions of lime and coke. At higher CaO/SiO₂ ratios (i.e. greater than 2,0), a slag containing 3,5 per cent FeO and 9,5 per cent V₂O₃ can be produced. The final reduction to this material would yield ferrovanadium containing an Fe/V ratio around 0,4.

Aluminium is the preferred final reductant. Although the reaction is exothermic, the heat generated would be insufficient to produce a self-sustaining reaction. However, the sensible heat from molten prereduced slag may be sufficient to allow complete reaction during a ladle treatment. From the metal distributions determined in this work, a mass balance for a pyrometallurgical process and the probable composition of the product were calculated. The process assumes as its starting material a crushed feedstock of VRU slag of the composition shown in

Table I. The process details are shown in the flow chart in Figure 8, based on the following assumptions.

1. The heat content of the prereduced slag is sufficient to sustain a ladle treatment.
2. No material losses have been included.
3. The composition of the prereduced slag is based on the mid-range of CaO/SiO₂ levels studied.
4. Carbon pre-reductant is added at 125 per cent of the stoichiometric requirement.
5. Aluminium is added at 133 per cent of the stoichiometric requirement.
6. Vanadium in the spent slag is 0,8 per cent V₂O₃.

The composition of the ferrovanadium product was calculated to be 47 per cent vanadium, 18 per cent manganese, 4 per cent silicon, and 31 per cent iron. The efficiency of vanadium recovery based on 0,8 per cent V₂O₃ in the discard slag was 93 per cent.

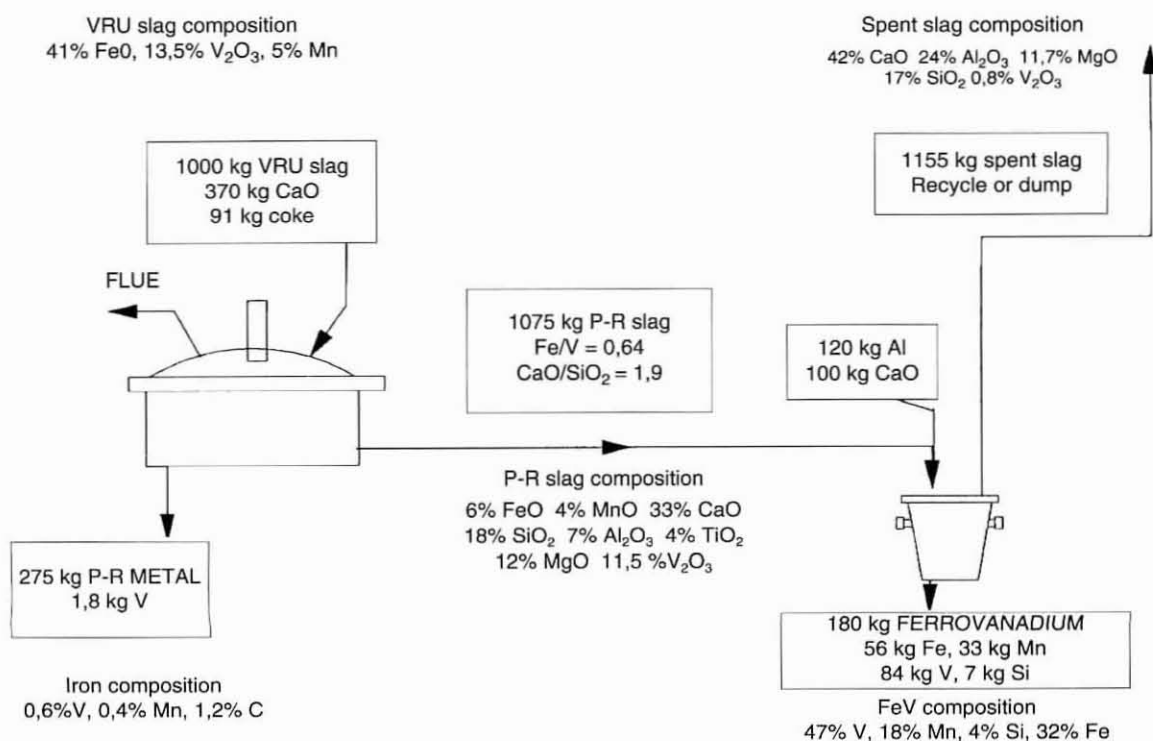


FIGURE 8. Flow diagram for the aluminothermic reduction of carbon-prereduced slag (P-R = Prereduced)

Plasma-smelting Considerations

The flexibility provided by plasma-induction heating enabled the furnace heat distribution to be adjusted to accommodate a wide range of smelting conditions. However, considerable refractory dissolution was observed. The extent to which this occurred depended on the slag temperature and the extent of arc radiation and impingement on the refractory lining. This is an indication of the importance of selecting the correct ratio of hearth diameter to arc power during furnace design.

These laboratory observations indicated the parameters that deserve particular attention in the design of a commercial-scale plasma-smelting unit. The important ratios of arc power, hearth diameter, and maximum bath depths should be established by pilot-plant trials. This would enable a heat distribution to be established in which the required fluidity of the bath could be established without incurring either excessive wall heating or accretion due to 'cold wall' conditions, which may also affect tapping. The method of furnace tapping considered here would be compatible with a non-tilting furnace arrangement. The retention of a stationary metal heel would then promote more reliable operation by preventing contact of the anode region with molten slag.

Laboratory-scale smelting has demonstrated the favourable operating characteristics of plasma heating using the d.c. transferred-arc system. The highly directional arc was extremely quiet and stable under all feeding and melting conditions. It is believed that, with adequate pilot-plant testing of such a system, the environmental and control advantages of plasma smelting would make it the preferred method of ferrovanadium production in association with the VRU-ironmaking process.

Conclusions

The control that can be exercised over the partitioning of vanadium and iron from vanadiferous slag has been examined. The effect of slag basicity (in terms of the CaO/SiO₂ ratio) has been determined using silicothermic reduction. The following conclusions can be drawn.

- (1) The degree to which FeO could be preferentially reduced was highly dependent on the CaO/SiO₂ ratio.
- (2) The preferential reduction of FeO was promoted as the CaO/SiO₂ ratio was increased. MgO from refractory dissolution did not improve iron-vanadium partitioning in slags to which CaO had been added.
- (3) The improvement in partitioning due to increasing CaO/SiO₂ ratio has been attributed to an increase in FeO activity. In slags containing low CaO levels, the activity of FeO was suppressed, allowing vanadium oxide to be reduced when the FeO content of the slag was greater than 30 per cent.
- From the results of the investigation of slag reduction by carbon, the following can be concluded.
- (4) Iron-vanadium partitioning characteristics did not differ significantly from those observed during silicothermic reduction.
- (5) The lowest Fe/V ratio in slag was achieved at a CaO/SiO₂ ratio of 2.7.

The direct pyrometallurgical process route to

ferrovanadium appears to offer many potential cost-saving advantages. The prereduction of FeO from slag adjusted to a CaO/SiO₂ ratio in the range 2.0 to 3.0 could produce a slag with an Fe/V ratio of around 0.4. Using the residual heat of the prereduced slag, a final aluminothermic reaction carried out by ladle metallurgy should be feasible. A ferrovanadium suitable for most applications could therefore be produced on site using existing services and the traditional work-force skills associated with the steelmaking industry.

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