Development of the process for production of vanadium rich slag and low silicon pig iron from vanadium bearing titaniferous magnetites of Masanikere at VISL, Bhadravati

By

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ABSTRACT

The paper describes the smelting trials carried out for utilisation of vanadium bearing magnetites of Masanikere in collaborative efforts by NML and VISL. The trials were carried out in a 1500 KVA submerged arc furnace by smelting vanadium bearing titaniferous magnetites with nut coke and lime stone as flux to produce vanadium bearing pig iron which was subsequently blown in a converter to obtain a vanadium rich slag and low silicon pig iron.

The commercial feasibility of the process was established by carrying out smelting trials in 13.2 MVA furnace followed by blowing the hot metal in 15 ton capacity converter.

Introduction

The titaniferous magnetite occurs in many parts of the world and is a potential source of vanadium. These are igneous in orgin and principally found in South Africa, Norway, Finland, Canada, Australia and India. In India most of the reserves are located in Bihar, Orissa, Karnataka and Maharashtra States. The deposits in Karnataka are mostly found in magnetite ore bodies in Masanike e area of Shimoga district at a distance of about 60 km. from VISL Bhadravati. The major reserve of this ore containing vanadium is estimated at around 4.5 million tonnes according to the exploration conducted by G. S. I. Karnataka Circle, with an average of 0.8 to 0.9% V_2C_5.

Various ore samples from different parts of India containing vanadium have been petrologically examined and chemically analysed at the NML. Their Chemical analysis differ with respect to the titania and vanadium contents. In general, they contain Fe ranging from 45 to 57%, TiO_2 8 to 14% and V_2O_5 0.4 to 1.8%.

The proposal to take up the utilization of vanadium bearing titaniferous magnetites of Masanikere, was envisaged first during the discussion between the Officers of NML and VISL on the basis of the on the spot studies of the ore bodies in the presence of Officers G.S.I. Karnataka Circle. It was suggested that the ferro alloy furnace of 1500 KVA rating at VISL, which was used periodically for internal require-

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ments of ferro manganese and ferro chrome would be suitable for inplant trials of smelting vanadium bearing iron ores. Modifications required for using the furnace for iron production and lancing were worked out in details and executed. Two campaigns first in July-August '75 and the second in Jan. - Feb. '76 were conducted.

Treatment of vanadium containing ores :

The titaniferous magnetites throughout the world are treated in different ways depending under local conditions. Generally the V or Fe or both are recovered, it has however not proved economical to recover TiO_2. Several processes are in use and in general the process depends upon number of factors, in particular the cost of power, the cost of chemicals such as the salt used, sulfuric or hydrochloric acid and ammonium compounds, the cost of fuel and the labour. If the ore is relatively cheaply mined and the cost of fuel and chemicals is reasonable, direct extraction is resorted to provided the V_2O_5 content is above about 1.3%. This is the practice followed by the Transval Vanadium Co. in the South Africa. The iron is discarded in the tailings. On the other hand, if the V_2O_5 content is relatively low say in the region of 0.8 to 1% V_2O_5 and electric power is cheaply available, then it is profitable to resort to electric smelting to recover vanadium in pig iron which is then selectively oxidised by blowing with oxygen. The pig iron is then processed further for steel making, while the vanadium is recovered in enriched slag. The vanadium rich slag can then be processed preferably for chemical extraction of V_2O_5 and then to FeV although sometimes direct silico-thermic reduction is carried out to produce medium grade ferro vanadium.

Theoretical Considerations :

In the electric smelting of vanadium bearing titano magnetites, apart from the iron oxide reduction, the reduction of vanadium and titanium oxides also takes place. The reducing medium is carbon and due to the fact that the electric smelting process is carried out in absence of nitrogen, no trouble from the formation of titanium nitrides is experienced as in case of blast furnace smelting. In slags, TiO_2 behaves as an acid, forming titanates. For successful smelting low liquidus temp., acid slag (low CaO/SiO_2 ratio of the slag) are essential.

Looking to the phase diagrams Fig. 1, 2 & 3 of lime titania-alumina-silica system it may be noted that the smelting slag is primarily of sphene regions. If charcoal is used as reductant instead of coke then the slag in composed of CaO, SiO_2 and TiO_2 of slightly varying composition and has the lowest M. pt. of 1318-1380°C. In the ternary system of $CaO-SiO_2-TiO_2$ (Fig. 1) the Sphene region lies almost in the middle of ternary diagram. The region has the composition of 30 to 50% SiO_2. 20 to 50% TiO_2 and 35 to 45% CaO. The operating conditions and charge composition should be so regulated as to produce a slag of 'Sphene' composition when a good separation of slag and metal results. If however coke is used instead of charcoal as a reducing agent, wherein alumina is introduced into the slag to the extent of 10 to 20%, the quartenary systems (Fig. 2 and 3) of segments 10% and 20% Al_2O_3 level[2] may be followed as

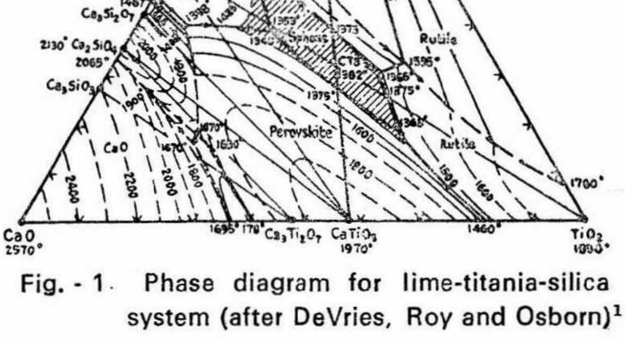

Fig. - 1. Phase diagram for lime-titania-silica system (after DeVries, Roy and Osborn)[1]

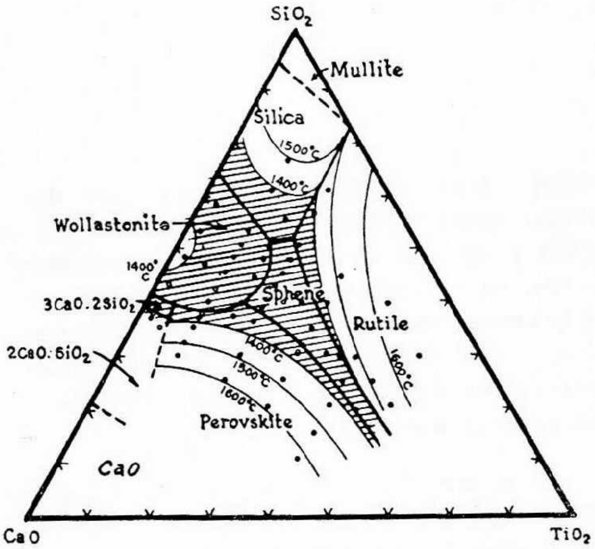

Fig. - 2. Liquidus diagram of lime-titania-alumina-silica system with 10 per cent alumina.

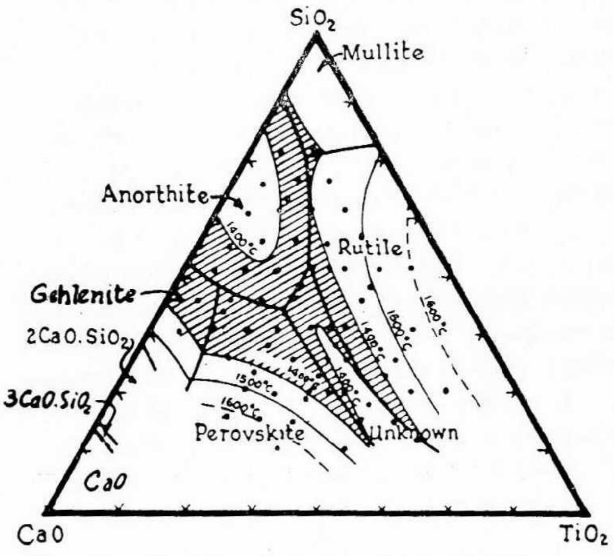

Fig. - 3. Liquidus diagram of lime-titania-alumina-silica system with 20 per cent alumina.

the guide to the smelter operation. These figures also point out that with increase of Al_2O_3 in CaO-SiO_2-TiO_2 the low melting 'Sphene' region shifts more towards the silica rich side and narrows towards the titania rich side. Thus slags of lower CaO/SiO_2 ratio (0.8 to 0.9) and appreciable Al_2O_3 are favourable. Thus acid condition provides a low melting and fluid slag.

The level of FeO content in the smelter slag also gives an indication of reduction of SiO_2 and TiO_2 in the furnace. 2 to 5% FeO content in the slag prevents silica and titania reduction. When the FeO in the slag falls to less than 1%, the slag and metal are tapped at higher tem. viz. 1450°C or higher. If the Ti in the metal exceeds 0.5% then there is a danger of titanium carbide formation which can accumulate in the furnace.

The oxidation of vanadium containing hot metal is carried out in the converter. Vanadium oxide has high heat of formation and therefore vanadium is oxidised simultaneously with silicon at the commencement of the blow. It forms a spinel and therefore floats on the surface of the molten iron. The essential factor in getting good recovery of vanadium in slag is the temperature control. The temperature is kept low by addition of scrap to make sure that vanadium is oxidised ahead of manganese and carbon.

Process development at VISL, Bhadravati

The test trials were carried out at VISL, in 1500 KVA ferro alloy furnace using titaniferous magnetites, lime stone and pearl coke. The magnetite analysed as : V_2O_5 1.01%, FeO 7.14%, Total Fe 53.80%, TiO_2 8.76%, Al_2O_3 1.64%, SiO_2 5.40%, S 0.01%, P 0.011%. The experiments could be divided into two phases.

1) Electric smelting trials of Masanikere vanadium bearing titaniferous magnetites to produce a vanadium containing pig iron low in silicon.

2) Oxidation of vanadium containing pig iron to produce a vanadium rich slag by oxygen blowing.

The 1500 KVA furnace at VISL is of open top stationary type with effective internal dia of 3.45 meters, and can be operated at any desired voltage between 80 and 105. Three graphite electrodes 40 cm dia placed at the verticles of an equilateral triangle carry the heavy current required by the furnace. The smelting trials were carried out to standardise conditions to produce pig iron containing 0.75-0.8% vanadium and .5-.8% silicon. The vanadium recovery in pig iron was 80 to 85%.

The blowing experiments were carried out with oxygen in ladle by maintaining propper temperature control. Maximum recoveries of vanadium were obtained when the temperature of the blow was kept below 1350°C. The slag produced contained about 10 to 15% V_2O_5. These proved that the process of production of vanadium rich slag and low silicon iron from the Masanikere ores is commercially feasible.

Scale up trial in 13.2 MVA furnace

It was then felt necessary to scale up these trials further to a level of the targetted production of 100 t/year of FeV at least for a shorter duration of about a week by using the 100 tonnes electric pig iron furnace. However, in absence of a shaking ladle to produce vanadium rich slag, it was proposed to carry-out oxygen blowing to the level of 12 to 15 tonnes per heat in LD converter at VISL. The campaigns carried out in 1979 had the following distinct objectives.

1) To standardise the operational parameters for the smelting of vanadium bearing ores in 13.2 MVA furnace to produce a vanadium bearing pig iron of consistant quality and maximise the vanadium recovery in order to establish process parameters earlier evolved.

2) To establish whether LD converter could be used in place of a shaking ladle reported to be in operation in the similar plants abroad. This would help VISL in carrying out the operation on commercial scale without much investment by either using its own LD or alternately establishment of a converter nearer to the 100 tonnes EPIF to oxidise vanadium. The smelting trials in 100 tonnes old EPIF and blowing in LD converter also proved successful, but the availability of LD was not always regular and that no space provision existed in LD shop to add one more LD unit. It was therefore decided to design & install a converter near 100 tonnes old EPIF.

Commissioning trial was conducted with the establishment of a 15 tonnes converter in July 1982. The main aim of these operations was to standardise the production of vanadium bearing pig iron with low silicon content and to train the staff to the process operations involved in regular oxygen blowing in converter. The blowing operation was initially carried out in one shift and slowly taken to 2 & 3 shifts. During the campaign totally about 627 tonnes of vanadium containing pig iron was produced with fluid slag of basicity CaO/SiO_2 in the range of 0.9—1.0. The average power consumption was in the range of 3200 KWH per tonne Oxidation was carried out starting with iron containing 0.7 to 0.8% V, a slag containing 17 to 20% V_2O_5 and blown iron with V—0.05—0.06%, C—3—3.1%, Si — 0.1—0 3% was obtained.

The general trial performance is summarised in the following details :

1. Electric smelting produces hot metal of the average composition C—4.1%, V—0.7 to 0.8%, Si—0 4 to 0.7%.
2. Average vanadium recovery is 80-85% in smelting and 90-92% in the blowing.
3. Vanadium slag analysed as : V_2O_5—17 to 20%.
4. Blowing capacity 12 - 15 tonnes in LD type converter.
5. Blown metal analysis : V—0.05 to 0.06%, Si—0.1 to 0.3%, C—3 to 3.1%.
6. Coke/tonne of metal 0 5 to .6 tonnes.
7. Blowing time—12 - 17 minutes.
8. Electric consumption / tonne of hot metal 2700-3200 KWh.
9. Average O_2 pressure 4—6 Kg/cm^2.

Acknowledgement

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Discussions

A. S. Venkatadri, RDCIS, SAIL, Ranchi

Q. What is the V content of Ferrovanadium so produced ? Normally Ferrovanadium of vandium content of 50% is desired for steel making because it is the eutectic alloy; use of Fe-V with vanadium content less than 50% is undesirable.

A. The V_2O_5 slag is produced by oxidation of vanadium containing pig iron. This gives an 18 to 20% V_2O_5 slag. After removing the slag, it is processed by a chemical extraction process to yield V_2O_5 of 95 to 98% purity. This is subjected to aluminothermic process to yield an alloy containing 50% vanadium.

N. N. Jha, RDCIS, SAIL, Ranchi

Q. During your trial, what was the tonnage production of vanadium rich slag and what is the commercial feasibility of prccess ?

A. Vanadium rich slag containing 18-20% V_2O_5 was produced on tonnages of say 10 to 15 tonnes as and when it was required for production of FeV.

The process has been proved to be commercially feasible, since not only the vanadium rich slag suitable for production of V_2O_5 and Fe-V is produced on large scale, but also a main product viz. low silicon pig iron is produced regularly for steel making. In fact, the vanadium bearing titaniferous ores are primarity smelted for recovery of pig iron as main product and vanadium rich slag as a by-product since the ore contains about 50% Fe in addition to about 0.5 to 0.6% V.