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RECOVERY OF VANADIUM PENTOXIDE FROM VANADIUM BEARING TITANIFERROUS MAGNETITES - PROJECTED PILOT PLANT STUDIES (*)

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The treatment of vanadium bearing ores for the recovery of vanadium pentoxide is not new to India. A plant capable of producing 250 lbs. of vanadium pentoxide per day was set up at Jamshedpur during World War II by the Tata Iron & Steel Co. Ltd., but as the demand of ferro-vanadium decreased considerably after the war, the plant had to be shut down. A company was also set up for the extraction of vanadium at Rairangpur during World War II and it is reported that the plant went into production in September, 1945 and stopped work in April 1946 and has since been lying idle. Various reasons, viz., high cost of production, lack of demand etc. have been assigned for closing down the plant. With the country's industrial development and the establishment of the alloy and tool steel industry, as envisaged in the 3rd Five Year Plan, it is anticipated that the demand of ferro-vanadium will increase considerably.

The National Metallurgical Laboratory in its programme for the development of ferro-alloy industry in India has undertaken a systematic study of the vanadium bearing ores for the recovery of vanadium pentoxide and subsequently the production of ferro-vanadium. Based on these laboratory scale studies, a pilot plant for the treatment of vanadium bearing ores is being set up.

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Vanadium deposits:

Vanadium occurs widely distributed in trace amounts. The primary vanadium ores are rare and the element generally occurs as a complex mineral in a primary ore of another metal. Though as many as about 65 vanadium bearing minerals have been identified, only 5 to 6 have been found to be of practical importance. The workable reserves of vanadium ores are rather limited and only U.S.A., Peru, Northern Rhodesia, South-west Africa and Australia are the chief producers.

Vanadium bearing titaniferrous magnetites have been located in Bihar and Orissa and the reserves have been estimated to be about 22 million tons. These deposits owe their importance primarily to the vanadium content that varies between 0.1% to 1.8% and will be studied on the pilot plant scale for the recovery of vanadium pentoxide.

Laboratory scale studies:

A systematic study for the recovery of vanadium pentoxide from Singhbhum District has been recently completed at the National Metallurgical Laboratory. The ore studied analysed as follows:

V	...	1.4%
TiO_2	...	13.12%
Fe	...	57.12%
SiO_2	...	1.2%
Al_2O_3	...	2.21%

The crushed ore was mixed with varying quantities of sodium salts like sodium carbonate, sodium chloride and sodium sulphate and roasted at 950°C. The different factors studied include: (a) roasting with varying proportions of sodium carbonate and sodium chloride, (b) roasting with varying quantities of sodium carbonate, (c) temperature of roasting, (d) time of roasting,

(e) particle size of vanadium bearing ore. It has been observed that sodium carbonate is the best roasting medium for the maximum recovery of vanadium, and 75 to 76% recovery is obtained by roasting the ore crushed to -72 mesh B.S.S. sieve with 20% sodium carbonate at 950°C for 2 hours. The roasted ore was leached with hot water and the effect of agitation, time and temperature of leaching, have been studied. Leaching at 70 to 80°C for 3 hours with vigorous agitation has been found to result in maximum recoveries. The leach liquor is filtered and the vanadium pentoxide precipitated at pH 1.5 to 2 at elevated temperatures. The effect of temperature, pH and concentration of the solution on the recovery of vanadium pentoxide have been studied. It has been observed that a leach liquor containing 20 grams per litre of vanadium vigorously agitated at a temperature of 80 to 90°C at a pH of about 1.5 to 2 will remove about 90 to 95% of vanadium from the solution.

Projected Pilot Plant Studies:

The process for the recovery of the vanadium pentoxide from the magnetite ores consists of the following steps:

1. Crushing and grinding,
2. Roasting of the ore with salts,
3. Leaching of the roasted product,
4. Precipitation of the vanadium pentoxide from the leach liquor,
5. Drying of the vanadium pentoxide.

The Tata Iron and Steel Co.Ltd., have kindly donated their own vanadium plant and efforts have been made to make use of their equipment as far as possible.

1. Crushing, Grinding and Mixing:

The ore is obtained in the size ranging 2 to 4 inches and has to be crushed to pass -72 mesh B.S.S. sieve. The ore should be so crushed as to obtain maximum fraction in the fraction -72+140 mesh B.S.S. sieve. Since the vanadium occurs very finely disseminated in the ore, fine crushing is essential to obtain good recoveries. Preliminary crushing down to 15 mm. is accomplished in a jaw crusher and the crushed ore is fed to a double roll crusher. The crushed product averaging 20 mesh is then fed to a ball mill in closed circuit and the undersize averaging -72 mesh is used for roasting.

No separate crushing unit is being installed for this plant since a central crushing unit will be available for all the pilot plants.

The crushed ore will be mixed with the requisite quantity of sodium salts and about 10% water. Water is added just to moisten the charge and prevent dusting when the mixture is charged in the roasting furnace. A concrete mixer with 4 cu.ft. capacity is being installed and will be used for mixing the charge.

2. Roasting:

The roasting of the vanadium ore with sodium salt will be carried out in an oil fired rotary kiln lined with sillimanite bricks, 30 ft. long and 30 in. in diameter. The kiln is driven by a 25 h.p. motor through variable speed reduction gear to obtain 0.5 to 1 revolution per minute. The kiln is supported on rails and the inclination can be adjusted as desired. For the roasting of vanadium ores, it is proposed to adjust the inclination at 1 in 40. Supply of air and oil are regulated so that a temperature of 950 to 1000°C is attained inside the kiln. The temperature in the different zones is recorded by a multi-point temperature recorder. The rate of drive of the kiln has been so adjusted as to permit a retention time of 2 to 2½ hours in the hot zone at 950°C. The furnace has a capacity of about 1 ton per hour.

The kiln has been designed keeping in view that it should not only be suitable for roasting vanadium ores but should be capable of roast reduction studies for other projects.

The discharge end of the kiln is being provided with a cooler so that the roasted mass may be directly fed into the cooler from the rotary kiln and cooled in an inert atmosphere. This is particularly desirable for roast reduction experiments, as otherwise the reduced mass will be re-oxidised.

The projected studies for the roasting of vanadium ores for maximum recovery will include the following:

1) The effect of keeping the reaction mixture in different parts of the furnace for different periods,

2) The use of briquettes for roasting instead of the powdered mass,

3) The effect of oxidising atmosphere,

4) The use of different sodium salts, particularly the soda ash and Glauber's salt,

5) The attack of sodium salts on the lining material.

3. Leaching:

On roasting the vanadium ore with sodium salt, the vanadium oxide is converted into soluble sodium vanadate, part of alumina and silica are also converted in the soluble aluminate and silicate respectively. The roasted mass is lifted by a bucket elevator for charging to one of the six leaching tanks supported on a platform 10 ft. above the floor level.

The leaching tanks, $5\frac{1}{2}$ ft. high, $2\frac{1}{2}$ ft. in diameter are provided with a conical bottom and are made of mild steel. The tanks can handle 1500 lbs. of charge at a time, and are provided with water inlet, slurry outlet and flushout door. The slurry will be heated through the steam coils and steam at a pressure of 100 p.s.i. will be available from an electrode boiler installed separately. Steam recorders, control valves and steam traps have been provided in the system. The tanks are provided with mechanical agitators operable at various speeds of rotation, and are suitably inter-connected to one another through a centrifugal slurry pumps.

The leaching is carried out at 70 to 80°C using 1:1 ratio of solids and liquids. Ore settles quickly to the bottom and the speed of rotation has to be so controlled as to prevent the settling. The leaching is carried out in 5 steps on the counter-current principle and the enriched solution is pumped from one tank to another. The residue being allowed to remain in the tank and in turn will be digested again with a stronger solution. Thus, the leached liquor from tank No.1 is pumped into tank No.2 and from tank No.2 to 3 and so on and in 5 such steps the concentration of the leach liquor will be about 20 grams per litre of vanadium pentoxide. The tanks have been so connected that only one pump will meet the requirements and the solution from any one of the tanks can be fed to the other. About 250 gallons of enriched leach liquor will be available in one operation. The leach liquor is pumped to an intermediate storage tank where most of the solid particles settle down. The clear supernetant liquid is pumped to a storage tank and led to a filter press.

A plate and frame type of filter press employing 3 plates of $18\frac{3}{4}$ in. square is used for filtration of the vanadium enriched liquor and a residue containing iron and titanium is left behind.

The studies on the leaching of ore will include the minimum number of steps required for maximum recovery, the optimum slurry density, rate of agitation and settling of the residue. It has been observed that a part of aluminium is also dissolved along with the vanadium and this unnecessarily increases the acid consumption during the precipitation of vanadium pentoxide. Studies will be taken to suppress the solubility of sodium aluminate by leaching the roasted mass in the carbon dioxide atmosphere.

4. <u>Precipitation, separation and drying of vanadium pentoxide</u>:

The leach liquor containing 15 to 20 grams of vanadium pentoxide as sodium vanadate is pumped into lead lined precipitation tanks and vanadium pentoxide precipitated at 90 to 95°C by adjusting the pH to 1.5 to 2.

2 3/4 The precipitation tanks consist of two lead lined vessels ~~4~~ ft. dia. x $4\frac{1}{2}$ ft. height and are provided with lead coated steam coils. The tanks are fitted with acid resisting paddle type mechanical agitators.

The enriched liquor containing 15 to 20 grams per litre of vanadium pentoxide is pumped into the precipitation tanks and sulphuric acid is run into the tanks from the acid storage vessel, till the pH reaches 1.5 to 2. The acidified solution is agitated and heated to the desired temperature and within about 2 hours, the vanadium is thrown down as vanadium pentoxide. The precipitate is granular in nature and the particle size is governed by the temperature, concentration of the solution and the rate of agitation.

The acid slurry is pumped to a storage tank and a rotary drum vacuum filter removes the vanadium pentoxide cake.

The cake is dried and packed for use. The vanadium pentoxide so produced contains 85% V_2O_5 and can be used for the production of ferro-vanadium.

<u>By-product</u>:

The recovery of vanadium pentoxide from the vanadium bearing titaniferrous magnetite produces the following by-products and their suitable utilisation is of prime importance for the economic running of the plant:

1. Titania rich sludge
2. Solution containing sodium sulphate and unrecovered vanadium pentoxide.

The titania-rich sludge will contain all the titanium and iron as contained in the ore and studies shall also be undertaken for the production of pig iron and titanium dioxide slag suitable for pigment manufacture.

The liquor left after the removal of vanadium pentoxide will contain about 18 to 20 tons of sodium sulphate per 80 to 100 tons of ore processed and the recovery of Glauber's salt will yield a very useful by-product. Studies will be undertaken for the recovery of $Na_2SO_4 . 10H_2O$ from the spent liquor. The solution left after the recovery of sodium sulphate can then be recycled for treating the roasted ore.

Conclusion:

From the cost estimation carried out, it has been observed that it will be economical to manufacture vanadium pentoxide on a method based on roasting with sodium carbonate. The pilot plant has been planned on the basis of laboratory investigations, to further enrich the data in planning on industrial scale unit. By-product recovery is a major factor in the economic stability of the process. The problem is under investigation and it is hoped that the vanadium pentoxide recovery planned will be an economically sound proposition. The production cost of vanadium pentoxide is expected to compare favourably with the cost prevailing in the foreign countries and it is hoped that it may be possible to build an export market.

It is hoped that the pilot plant will serve a very useful purpose on the recovery of some other metallic values on pilot plant scale.

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