PROPOSED PILOT PLANT FOR PRODUCTION OF SINTERED BERYLLIUM OXIDE FROM BERYL ORE (*)

N. Srinivasan &
G. S. Tendolkar,
Atomic Energy Establishment,
Bombay.

Beryllium metal and beryllium oxide have attracted considerable attention as possible nuclear reactor materials on account of their low neutron absorption cross section and low atomic weight and the consequent moderating properties, i.e., ability to reduce the velocity of fast neutron to thermal level. The inert nature and high melting point of beryllium oxide make it suitable for high temperature gas cooled nuclear reactors. There is some doubt about its stability under extended irradiation by fast neutrons. However, beryllium oxide holds promise as a future power reactor material. The cost of nuclear grade beryllium oxide sintered shapes tends to be high on account of the great degree of purity required and the initial high cost of the ore.

India is one of the principal producers of beryl ore. It appears essential to make a beginning in the exploitation of this ore to produce sintered beryllium oxide or beryllium metal of nuclear grade especially since calculations show that the cost of production can be lower in India compared to other countries for comparable scales of operation. The present paper outlines a scheme for a pilot plant to treat beryl ore to produce sintered beryllium oxide bricks 100 mm x 500 mm x 50 mm. This pilot plant will mainly help in the evaluation of process design, equipment performance, operational problems and economics of production. Further, beryllium and its compounds are extremely toxic materials from the point of view of inhalation and ingestion. The permissible atmospheric contamination is 2 micrograms of beryllium per cubic metre of air. The pilot plant will provide the necessary experience in operating a chemical plant under such strict control as is necessitated by the above conditions.

Choice of the Process:

The production of sintered bricks of nuclear grade beryllium oxide from beryl ore can be divided into three stages:-

(1) Production of beryllium hydroxide (technical purity) from beryl ore.

(*) Paper for presentation at the Symposium on Pilot Plants in Metallurgical Research and Development - 15th to 18th February, 1960, Jamshedpur.

(2) Purification and calcination of the hydroxide to produce beryllium oxide of nuclear grade.

and

(3) Pressing, sintering and finishing the beryllium oxide bricks to accurate dimensions.

For stage (1) the processes used are the sulphate route as practised by Brush Beryllium Co., of U.S.A. and the different modifications of the fluoride process as carried out by Pechiney of France, and Beryllium Corporation of America. In the sulphate process of converting beryl ore to hydroxide, the beryl ore is melted, quenched, heat treated and digested with sulphuric acid and the sulphated mass is extracted with water. Aluminium is removed as alum and separation of iron is achieved by chelation of the impurities while precipitating the hydroxide of beryllium.

In the fluoride route the ore is ground and sintered with a mixture of fluorides when the beryllium is selectively converted into water soluble fluoride which can be leached out and beryllium hydroxide is precipitated from the solution.

The fluoride process has the advantages that it is suitable for any grade of ore and that the solutions involved are essentially non-corrosive and as such is better suited for Indian conditions. Inquiries with the local superphosphate manufacturers showed that their waste gases contain all the fluoride from the original rock phosphate (3% CaF_2) and this can be converted to sodium silico-fluoride necessary for the pilot plant. Among the many variations of the fluoride route the one using a 60-40 mixture of Na_2SiF_6 and Na_3FeF_6 is recommended for its conservation of the fluoride content.

For the second stage, among the different processes for purification of the hydroxide, namely chlorination, distillation of beryllium acetate, solvent extraction of beryllium acetate and recrystallisation of beryllium sulphate the last is favoured on account of its technological simplicity.

<u>Process:</u>

Beryl ore is crushed in a jaw crusher and further ground (70% - 200 mesh) in a wet ball mill. The slurry is de-watered in a vacuum filter and the cake of wet beryl is mixed with sodium ferric fluoride (recovered at a later stage of the process) and sodium silico-fluoride in a kneader type mixer. The mixture is dried in a tray drier and briquetted and then fired in a tunnel kiln of the car bottom type. The temperature of the hottest zone is 780°C and efficient control of temperature is essential for maximum conversion.

The fired briquettes are crushed in a jaw crusher and ground (50% -200 mesh) in a continuous wet ball mill. Considerable extraction of the highly soluble beryllium fluoride takes place during the milling. Further leaching is effected in filter bottom type leach tanks. Short contact between the water and the roast is essential for selective leaching. Hydroxide is then precipitated from the leach liquor. Controlled addition of just the requisite quantity of caustic soda results in granular easily filtrable form of beryllium hydroxide which is filtered in a filter press. The filtrate contains 60% of the fluoride added for the roasting and is precipitated as $Na_3 FeF_6$ by addition of ferric sulphate solution and the ferric fluoride is reused for roasting. A typical analysis of the hydroxide at this stage is 0.1% Fe_2O_3, 0.2% Al_2O_3 and 1.5% silica. Iron is objectionable both for the preparation of bricks of beryllia and for chlorination and electrolysis of metal. This is removed by redissolving the hydroxide in caustic soda solution in a stainless steel tank and heating the solution to 50°C. The iron is left behind as granular ferric hydroxide and is filtered off. The sodium beryllate in the filtrate is then decomposed by boiling in steam jacketted boiling pans of stainless steel and the hydroxide is washed by decantation. The solution containing most of the caustic soda employed for the redissolution is reused for precipitation of the hydroxide from the leach liquor. The hydroxide now contains 0.3% silica and about 1% sodium fluoride and is pure enough for chlorination leading to the preparation of the metal by electrolysis.

For production of the oxide bricks the hydroxide is purified further. It is redissolved in sulphuric acid in a lead lined tank and the solution heated to 105°C to render the silica granular. The solution is diluted and hydrogen sulphide gas passed through it to precipitate copper etc., as sulphides. The solution is filtered and from the filtrate the hydroxide is precipitated with ammonia. The slurry is filtered in polythene lined wooden filter press. Impurities like calcium are removed with the filtrate. The hydroxide is redissolved in sulphuric acid in a steam jacketted enamelled vessel and evaporated to a boiling point of 110°C. The solution is allowed to cool in enamelled crystallisers. The crystals of $BeSO_4$, $4H_2O$ are removed and the mother liquor is recycled to the first dissolution stage. The crystals of sulphate are redissolved in water and beryllium hydroxide is precipitated from the sulphate solution by passing ammonia and is filtered off in a polythene lined filter press. The cake is dried in a tray drier and the dried product calcined in a muffle at 1050°C. The calcined beryllia contains less than 100 ppm each of iron oxide, aluminium and silica, and less than 0.5 ppm of boron.

The calcined beryllia is hot pressed at 1850°C in graphite moulds using induction heating and the bricks after cooling are finished to dimensions (100 mm x 100 mm x 50 mm ± 0.1 mm) with the help of diamond cut off wheels and grinding machines.

Equipment:

The equipment for the first stage of the process are standard in chemical engineering practice and are of conventional materials of construction. These consist of jaw crushers, ball mills, tanks for leaching the sintered reaction mixture and for precipitation of the hydrooxide. Most of these can be fabricated locally except that the stainless steel where required should be imported. The tunnel kiln required will be similar to those used in refractory practice and is best suited for the controlled heating cycle required for firing the briquettes of the mixture. For the purification stage, however, on account of the rigid specifications for the purity of the product the expensive materials of construction like rubber lining or enamel lining are required. The lining material should be boron free and may have to be imported. The lining operation can probably be carried out locally under efficient supervision. The sintering section again makes use of equipment standard in refractory practice, but some of the equipment like high frequency generator, hydraulic press, diamond cut off wheel, etc. are not manufactured in India. Thus on the chemical plant side the foreign exchange requirements are not high, whereas for sintering some equipment has to be imported. The pilot plant will help in assessing effectiveness of the materials of construction chosen and the performance of equipment. Any relaxation in the choice of the materials of construction and changes in design can be made after sufficient experience with the pilot plant.

Capacity of the pilot plant:

In arriving at a capacity two factors have to be optimised viz., the pilot plant should not be excessively costly and at the same time the capacity of the plant should be such that it gives the required operational experience simulating plant level operation. A convenient basis can be the use of one sintering furnace using hot pressing technique. From reported data the daily output of one such furnace is about 9 kilos of finished bricks 100 x 100 x 50 mm. On this basis the plant will treat about 150 kilos of beryl (11% BeO) per day producing crude hydroxide containing about 14 kilos BeO which yield about 12 kilos of calcined nuclear pure beryllium oxide to give the final output of 9 kilos of finished bricks.

Choice and design of equipment:

Equipment required upto the stage of briquetting the feed for the tunnel kiln should be batch type as the capacity is very small. The firing of the briquette should be done in a tunnel kiln though the capacity is small, as the product is sensitive to the heating cycle and further, experience in the design and operating can be gained that way. As a first approximation the following criteria are recommended for the design of the kiln:

Lengths of preheating, firing and cooling zones in the ratio 3:2:2
Material enters at room temperature with 5% moisture
Fired briquettes go out of the kiln at 150°C

Average specific heat of briquette 0.4
Light fuel oil of L.H.V. 18350 BTU/lb is used with 20% excess air, air preheated to 200°C.

The briquettes are stacked on small cars which move through the kiln. Approximate internal dimensions of the kiln will be 2' x 1-1/2' x 35' for output of 300 - 600 kilos of briquettes per day.

The jaw crusher and ball mill for grinding the fired material should be arranged continuous though of small capacity as batch handling of the toxic materials is undesirable. These can be manufactured locally.

The tanks for leaching, precipitation, dissolution etc. will range in capacity from 50 to 250 gallons. The filter presses required will have 1' x 1' plates and frames.

The pilot plant will thus have batch and continuous equipment interlinked to provide maximum data and experience. The type of equipment needed is listed below:

Hydroxide plant:	Size reduction equipment such as jaw crusher, ball mill and pebble mill; Mild steel tanks of various capacities upto [illegible]50 gals., Stainless steel tanks of capacities upto 50 gals., Filtration equipment such as cast iron filter presses. PVC lined wooden filter press, vacuum filter, leaf filter; briquetting machine, drier, tunnel kiln.
Purification Plant:	Stainless steel tanks, provided with agitator Filter press (PVC liner wood; Mixer lined with boron free enamel); tray drier, demineraliser; muffler.
Sintering Plant:	Alternator (60 Kw) Hydraulic press (30 tons) sintering units; cut off wheels; grinding machines.

Building:

Normally in large scale operation a plant of this type would be housed in a reasonably air-tight building with elaborate provision for ventilation. Since however, this is intended as a pilot plant it can be house in industrial type building but care shall be taken that all equipment where there is a possibility of generation of dust of beryllium compounds will be exhausted by ventilation system and the air filtered for removal of toxic beryllium compounds. The space required for the pilot plant is estimated at about 8000 sq.ft.

Power:

The sintering operation is a major consumer of power and the ventilation facilities require considerable quantity of power also. Total power requirements for the pilot plant are estimated at 300 Kilowatts.

Costs:

The building with all the facilities for power ventilation of equipment and provision of services like water, power etc. is estimated to cost approximately Rs.4.25 lakhs and the equipment estimated to cost about Rs. 5.8 lakhs. The total installed cost of the plant inclusive of the building will be approximately Rs. 11 lakhs.

The cost of the consumables including ore, bulk and laboratory chemicals and consumable furnace parts is expected to be about 2 lakhs per year.

CONCLUSION:

The proposed pilot plant will treat about 150 kilos of beryl ore and will produce 9 kilos of bricks per day. The total installed cost of the plant including the building would be about Rs. 1.1 million. The plant will help in the evaluation of the equipment performance and operation from the point of view of producing a nuclear pure material and will give valuable experience of handling toxic materials.

/SKB.