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W. R. GRACE & CO.

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Process for Breaking Monazite Sands Into Rare Earth and Thorium Compounds

Monazite sands are essentially an orthophosphate of rare earths and thorium. The sands vary in composition according to the locality of origin and method of concentration. The monazite occurs as crystalline occlusions in pegmatites of parent rock, and is normally associated with other heavy minerals such as ilmenite, rutile, zircon and garnet.

A chemical separation process is used to break the monazite and produce rare earth fractions relatively free from thorium, and a thorium fraction relatively free of rare earths.

FIRST OPERATION Digestion of the Monazite (Sulfonation Reaction)

The first operation of the process involves digestion of the finely ground monazite sands with hot concentrated sulphuric acid. The rate of the reaction of the monazite sand with the sulfuric acid, or sulfonation, increases with finer particle size of the monazite sand and higher reaction temperatures. The reaction starts as a fluid mixture of the two components. As the reaction proceeds it gradually becomes more viscous and finally putty-like due to the formation of voluminous anhydrous rare earth sulfate crystals. The phosphate content of the monazite goes into solution as phosphoric acid. Further agitation will cause sufficient thinning of the mixture to allow discharge from the cast iron reactor. The reaction may be considered complete at the end of four to six hours.

SECOND OPERATION

The second operation involves the crude separation of the thorium sulfate from the rare earth sulfate. At the end of the sulfonation reactio.. the hot charge is quenched in a tank containing water and wash streams from subsequent process steps. The wash streams contain sufficient water to dilute the free acid in the sulfonation and also provide water hydration for rare earth sulfates from the sulfonation.

The hydrated rare earth sulfates are pumped through a filter press to remove the sulfuric acid.

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Process...(Continued)

THIRD OPERATION Rare Earth Removal from Acid Streams

The thorium-rich acid liquors, or top acid, contain a small quantity of the original rare earths contained in the monazite. These rare earths are stripped from the acid by the addition of sodium sulfate which forms insoluble acid rare earth double salt. This double salt contains some occluded thorium and, therefore, must be processed to properly distribute the rare earth and thorium values. The double salt is separated from the acid liquor, then called stripped acid, by means of a drum filter. The acid rare earth double salt is converted to water insoluble rare earth hydroxide by treating it with boiling caustic soda. The caustic soda and soluble salts are removed by hot water washes and the thickened rare earth hydroxide is then mixed with the filtered rare earth sulfate in operation isx.

FOURTH OPERATION Thorium Separation from the Acid Stream

The thorium is removed from the stripped acid by addition of either sodium fluoride or hydrofluoric acid which causes insoluble thorium fluoride to precipitate from the acid. The thorium fluoride is separated from the acid and the acid is saved for disposal. The thorium fluoride is then water washed in the Shriver thickener. The washed product is then dried and packed as thorium fluoride product.

FIFTH OPERATION

The hydrated rare earth sulfates (Operation 2) are filtered and counter-concurrently washed with the rare earth process wash liquors before these liquors are sent to the quench tank. This operation serves to remove the bulk of the phosphoric acid and sulphuric acid from the rare earth sulfates so that in operation six they contain a minimum acid contamination, since acid interferes with the thorium separation.

SIX OPERATION Removal of Thorium from Rare Earths

The thickened rare earth hydroxide from operation 3 is mixed with the soluble rare earth sulfates from operation 5 and filtrate from operation 8. The rare earth values go into solution as neutral rare earth sulfates and the gangue and thorium remain soluble as thorium phosphate. Complete removal of thorium from the rare earths is accomplished by maintaining the pH of this solution at 5.5. The phosphate cake is removed by filtration and the polished rare earth liquors are sent to the second precipitation tank (operation 8).

Process...(Continued)

SEVENTH OPERATION Recovery of Thorium and Rare Earths from Gangue

The thorium phosphate cake in operation six is combined with the gangue from the precoat drum filter in operation two and is countercurrently treated with a dilute sulphuric acid solution to solubilize the rare earth and thorium values leaving insoluble residues. These residues are of two types; one consisting of heavy minerals and unreacted monazite; the other consisting of finely divided silica, calcium sulfate, filter-aid, etc. The heavy minerals and monazite are recovered as the underflow of a cyclone classifier and the finely divided material is removed by filtration and after washing is sent to the dump. The acidified rare earth and thorium liquors are recycled as washes through the crude rare earth filter to the sulfonator quench tanks.

EIGHTH OPERATION Formation of Rare Earth Double Sulfate

In the double sulfate precipitation tank, neutral rare earth sulfate liquors from operation six are treated with sodium sulfate to form rare earth double sulfates. This salt forms as a dense precipitate and is removed from the slurry by settling and filtration. The filtrate is collected and treated with soda ash to pH eight, which causes the soluble yttrium earths to precipitate. The yttrium earths are filtered and stored, the filtrate from the operation goes to the plant waste.

Exposure Evaluation

Since this is a batch type operation, the maximum amount of source material present at any step in the process is determined by the percentage of naturallyoccuring thorium in the monazite sand. Because of the low percentage of radioactive material to the total mass of the batch and the nature of this material, the maximum radiation levels are such that an employee would not receive an exposure in excess of the limits set forth in Title 10, Part 20, par. 20.101 during the regular course of his work activity.