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BOX 468
POMPTON PLAINS, NEW JERSEY

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RARE EARTHS, INC. PROCESS FOR BREAKING MONAZITE SANDS INTO RARE EARTH AND THORIUM COMPONENTS

Monazite sands are essentially an orthophosphate of rare earths and thorium. The sands vary in composition according to 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.

Through the ages these pegmatites have weathered and the monazite sands and other heavy minerals have concentrated in stream beds or beach sands. The monazite sands are rarely present in excess of a few percent and are recovered by dredging or tabling or as a by product of other heavy mineral separations. The concentrates are presently further enriched in electromagnetic and electrostatic separators to yield 90-98% monazite. Non-monazite minerals present in the concentrates after concentration may include silica, rutile, ilmenite, quartz, zircon and magnetite.

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

FIRST OPERATION - Digestion of the Monazite (Sulfonation Reactor)

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 monazite sand with sulphuric 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 4 to 6 hours.

SECOND OPERATION - Crystallization (Tank 1, Centrifuge & Press 3)

The second operation involves the crude separation of the thorium sulfate from the rare earth sulfate. At the end of the sulfonation reaction, the hot charge is quenched in a tank containing recycled acid and wash streams from subsequent process steps. The wash streams contain sufficient water to dilute the free acid in the sulfonation to approximately 50% total acidity, and also provide water hydration for rare earth sulfates from sulfonation.

The hydrated rare earth sulfates form as a dense crystalline salt in a slurry of approximately 50% phosphoric sulphuric acid liquor. The thorium sulfate produced in the sulfonation is more soluble in this acid than the rare earth sulfates which permits a crude separation of thorium and rare earths.

The hydrated rare earth sulfates from the crystallization are pumped to a classifier to remove the finely ground non-monazite gangue and acids from the rare earth sulfates. The overflow from the classifier is filtered through a precoat drum filter to separate the gangue from the thorium-rich acid liquors. A portion of this filtered acid is removed for thorium separation and the remainder is recycled to the crystallizer tanks.

Process for breaking monazite sands into rare earth and thorium components (cont'd.)

THIRD OPERATION - Rare Earth Removal from Acid Stream (Tank 24, Press 5A, Tank 1)

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 an 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 its acid liquor, 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 washed rare earth sulfate crystals in operation 6.

FOURTH OPERATION - Thorium Separation from Acid Stream (Tank 25, Press 5B, Tank 1, Filter 3)

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 on a drum filter and the spent acid is sent to an acid dilution boot for the Superphosphate Plant. The thorium fluoride is then treated with caustic soda to convert the thorium fluoride to hydroxide. Sodium fluoride and free caustic are removed by water washing in the Shriver thickener. The washed product is then dried and packed as thorium hydroxide product.

FIFTH OPERATION - Removal of Acid from Crude Rare Earth Crystals (Centrifuge, Tank 4)

The hydrated rare earth sulfate crystals from the underflow of the classifier (operation 2) are filtered on a pan filter and countercurrently washed with the rare earth process wash liquors before these liquors are sent to the crystallizing tank. This operation serves to remove the bulk of the phosphoric acid and sulphuric acid from the rare earth crystals so that they may be dissolved in water in operation 6 with a minimum acid contamination since acid interferes with the thorium separation.

SIXTH OPERATION - Removal of Thorium From Rare Earths (Tank 19, Press 1, Tank 6)

The thickened rare earth hydroxide from operation 3 is mixed with the washed rare earth crystals from operation 5 and filtrate from operation 8. The rare earth values go into solution as neutral rare earth sulfates, and gangue and thorium remain insoluble 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 crystallizing tank (operation 8).

SEVENTH OPERATION - Recovery of Thorium and Rare Earths from Gangue (Press 1, Tank 6, Press 6, Tank 21)

The thorium phosphate cake in operation 6 is combined with the gangue from the precoat drum filter in operation 2 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 crystal filter to the sulfonator crystallization tanks.

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EIGHTH OPERATION - Formation of Rare Earth Double Sulfate. (Tank 6, Tank 3, Press 2, Tank 10, Press 7)

In the double sulfate precipitation tank, neutral rare earth chloride liquors from operation 6 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 pH8, which causes the soluble yttrium earths to precipitate. The yttrium earths are filter pressed and stored, the filtrate from the operation goes to the plant waste.

The double salt may be treated with the following for the preparation of rare earth products:

a) Hydrofluoric acid to give rare earth fluoride.

b) Caustic soda to form rare earth hydroxide.

c) Soda ash to form polishing powders.

Rare earth chloride, cerium products and didymium earths are produced from rare earth hydroxide. Heavy rare earths are recovered from yttrium residues.