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Technology and Uses of Monazite Sand

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MONAZITE has had a Cinderella-like history. Although nearly 90 per cent pure rare-earth compound (rare-earth phosphate) it was sought at first not for the rare earths but for the sake of a minor constituent—thorium. The thorium, essential for the Welsbach gaslight mantle, was present in only small quantities and the principal constituents, the rare earths, were largely discarded. Gradually, however, the rare earths have developed uses of their own and today have left the thorium far behind in value.

OCCURRENCE

Monazite was first produced commercially about 1886, in North Carolina, where it was collected in small sluices by farmers who found it in stream beds on their land. The deposits were later exploited on a larger scale, but were mostly abandoned in a few years, when monazite from Brazil came upon the market in far larger quantities. Domestic production ceased entirely in 1906.

The Brazilian source is still active, together with Indian, Dutch East Indies, and Australian deposits. Several other localities in the United States have yielded monazite, but none of these has produced commercially as yet.

Monazite occurs originally in pegmatites and gneisses, through which, unfortunately, it is scattered in highly dispersed form. All commercially useful deposits consist of transported monazite sands liberated by erosion and concentrated by the action of water, which has sluiced away lighter materials and concentrated the heavy ($D = 5.0$ to 5.2) grains of monazite, together with ilmenite, zircon, garnet, and other dense minerals. The Carolina deposits were in stream beds; most of the other deposits mentioned are on or near the seashore, where the action of the waves has served to concentrate the monazite.

In most cases today, the sands are worked to obtain the ilmenite and zircon, as well as monazite. The minerals are separated by means of sluices, dry tables, and magnetic separators, and each is finally obtained nearly pure. No crushing or grinding is necessary. The concentrates are shipped in fiber bags.

COMPOSITION OF MONAZITE

As Table 1 illustrates, monazite is the anhydrous orthophosphate of the cerium group of rare-earth elements. A small amount of yttrium and terbium group phosphate is also present.* All the rare-

TABLE 1.—*Typical Analysis of a Monazite Sand (India)*[a]

	PER CENT
Thorium oxide	8.1
Cerium oxide	30.6
Lanthanum oxide	15.7
Neodymium oxide	10.5
Praseodymium oxide	2.9
Samarium oxide	1.0
Europium, gadolinium, and terbium oxides	0.7
Yttrium oxide	0.4
Dysprosium, holmium, erbium, thulium, ytterbium, and lutecium oxides	0.1
Silicon oxide	2.4
Calcium, aluminum, and iron oxides	1.0
Uranium oxide	0.3
Phosphorus pentoxide	26.2

[a] The values given for the rare earths following samarium are approximate, being based upon analyses of concentrated fractions derived from monazite. The composition given represents Travancore monazite carefully freed from other minerals.

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* Elements 57 to 62, inclusive, constitute the cerium group, elements 63 to 65 inclusive the terbium group, and elements 39 and 66–71

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earth elements are of course isomorphous, and react generally as one element.

Monazite nearly always contains thorium, which is chemically rather than mechanically present, together usually with an approximately equivalent amount of silica. The thorium content varies with the source of the ore.

Derivatives of Monazite and Their Uses

Mesothorium

The radioactivity of monazite follows from its content of thorium and its decomposition product, mesothorium, which is an isotope of radium. However, the mineral also contains traces of uranium and hence radium. Mesothorium is similar in every way to radium and is useful for the same purposes. It decays at a much faster rate, however, having a half-life of 6.7 years as compared with 1590 for radium. Monazite actually contains a greater weight of radium than it does of mesothorium, but because of the greater decay rate the activity is nearly all due to mesothorium. It is possible to recover radioactive material equivalent to one gram of radium from about 300 tons of monazite. This value varies with the thorium content of the ore.

Thorium

For many years monazite sands were priced according to their thorium content, which was the sole useful constituent. The oldest and best known use for thorium is the incandescent mantle, still used for street lighting in many cities. The well-known Aladdin kerosene lamps and Coleman gasoline lanterns are widely used in rural districts. The armed forces have used millions of mantles in the present war.

inclusive the yttrium group. These groups are not sharply characterized; the division is based partly on the solubility of the double sulphates and partly on their distribution in certain minerals.

Other uses of thorium are less well known. The oxide of thorium is used in radio tubes, as a constituent of special optical glasses, as a high-temperature refractory (M.P. 5000°F.), and as a catalyst for petroleum cracking.

Rare-earth Salts

The natural mixture of cerium and other rare earths as recovered from monazite has many large-tonnage uses in different forms. The mixed rare-earth oxide and the fluoride are used as a core material in searchlight and projector-arc carbons, where the brilliant spectrum of the rare-earth elements increases the visible light output. Rare-earth chloride is electrolyzed in the fused condition to produce rare-earth metal, which alone or alloyed with iron forms the well-known "flints" used in lighters. Rare-earth chloride and acetate are used as waterproofing agents and fungicides in textile manufacture. Rare-earth oxalate is used medicinally as an agent to prevent nausea and seasickness.

Cerium

The high cerium content of monazite is fortunate, as this element has unique and useful properties and may be readily separated from the other rare earths. Because of its two valence states, cerium in some of its compounds is a valuable oxygen carrier and catalyst. In this way it is used for decolorizing glass, through its power of holding iron in the ferric state. Thus ordinary window and bottle glass, as well as higher grades, may be produced with cheaper grades of glass sand. In paint and printing-ink driers, cerium naphthenate, though not widely used, permits special effects to be obtained in some cases, since tremendous quantities of drier may be added without the usual ill effects.

Various other catalytic reactions with cerium are known. Cerium metal is used in alloys, various salts are valuable laboratory reagents, and the oxide (or hydrated oxide) is used as a coloring agent in ceramic glazes.

A most important use is as a polishing agent for lenses, prisms, and other surfaces. The development of a suitable form of cerium oxide for this use helped break a critical bottleneck in optical equipment in the early days of the war. The tremendous demand for tank periscopes, gun sights, binoculars, range finders, photographic lenses, and other optical goods found the manufacturers of lens-polishing equipment hopelessly swamped. Rouge had been used for centuries as the polishing agent, but in approximately three years has been almost completely supplanted by optical-grade cerium oxide. The outstanding advantage of cerium oxide, the use of which for optical polishing was unknown in this country before the war, is the tremendous speed with which a perfect polish is obtained. Optical-grade cerium oxide polishes two and three times as fast as the best rouge, and in addition has several other advantages (such as cleanliness) greatly appreciated by lens polishers. With this new polish, the optical industry was enabled to double or triple its output with existing machinery. Today even spectacle lenses are polished with cerium.

The peculiar combination of properties required for lens polishing is not fully understood. The particle size is important, but even more so is the ability to "break down" or disintegrate during the actual polishing process. The ultimate particle size obtained is a fraction of a micron.

Lanthanum

Lanthanum was of little use to anyone before the war, but this element has played an important part in the defeat of Germany as the major constituent of a marvellous new photographic lens developed for use in aerial reconnaissance. The glass used for this lens contains no silica, but consists entirely of the oxides of rare elements, with lanthanum oxide as the base. The glass, of very high density, has a high index of refraction and a relatively low dispersion, making possible lenses of improved color correction with fewer elements and with curved surfaces of larger radius.

Neodymium

Neodymium finds its principal use in the glass industry, where it serves to neutralize the greenish tinge caused by iron. Whereas cerium decolorizes glass chemically by oxidation of iron, neodymium is a physical decolorizer, since it imparts a complementary hue. Both are often used in ordinary types of glass.

In larger proportions, neodymium produces an orchid tint of great beauty used in expensive stemware, and also in "Soft-Lite" spectacle lenses, where the ultraviolet opacity of neodymium glass is utilized. For large-scale uses, neodymium is often employed in its natural mixture with the other rare earths, except cerium. The mixture, known commercially as "didymium,"* contains about 33 per cent neodymium; the other rare earths present (mostly lanthanum) have little or no effect on glass in the amounts used. Large quantities of this mixture are also used in the manufacture of electronic apparatus, particularly where a ceramic dielectric body is required having a zero temperature coefficient.

This summary of uses is abbreviated, and includes only the monazite derivatives available in tonnage quantities, but it serves to show the variety of fields into which the unique properties of the rare

* Didymium, strictly speaking, consists only of the "twin elements" neodymium and praseodymium, but the term is used commercially to denote the mixture with lanthanum and samarium. The approximate composition is neodymium 33.5 per cent, lanthanum 50 per cent, praseodymium 9.5 per cent, samarium and other rare earths 7 per cent.

earths bring them. Many uses are still restricted because of the war; others are being proposed and developed continually.

Separation of Monazite into Its Constituents

Monazite may be opened in several ways, but the only one that has been extensively used is that of roasting with strong sulphuric acid. The heating must be carried out cautiously in a closed cast-iron vessel, as the reaction is exothermic. About 8 lb. of barium sulphate or other suitable barium salt is added to each ton of monazite sand before roasting, the purpose of which is to assist in isolating the radium and mesothorium.

The roasting is carried out in such a way that the thorium forms insoluble metaphosphate sulphate, and the rare earths are left in soluble form, to be leached out with water.* The barium, radium, and mesothorium remain with the thorium as insoluble sulphates. The thorium precipitate is boiled with caustic soda and then dissolved in sulphuric acid, whereupon the soluble thorium sulphate may be separated from the mesothorium, barium, and radium sulphates. These materials are further purified and the radioactive salts concentrated by fractional crystallization.

The thorium undergoes a long series of purifications, and is finally obtained, chemically pure, in a variety of forms, such as oxide, nitrate, carbonate, and chloride.

The solution of the rare earths mentioned above is free from thorium and may be converted to any desired form for sale or further treatment. The rare-earth mixture is usually sold as hydroxides, chlorides, fluorides, or oxides.

A large part of the mixed rare-earth material is not sold as such but is separated further. The separation of cerium from the rest of the earths may be carried out in a number of ways, all based upon the oxidation of cerium to its higher valence (tetravalent), *in which form many of its* salts are insoluble or hydrolyze, whereas the salts of the other rare earths, all trivalent, remain soluble. The cerium, once separated, is purified and marketed as hydrate, chloride, nitrate, or oxide. Some of these processes, such as that for optical cerium, require careful control to produce exactly the desired properties in the finished product.

The "didymium" from which the cerium has been removed is sold usually as the oxide or the carbonate for use in glass or ceramic manufacture. A portion of the didymium, however, is separated still further. At this stage the elements present are: lanthanum, neodymium, praseodymium, samarium, and very small amounts of other rare earths of atomic numbers 63 to 71. All of these earths have almost identical properties as far as the ordinary chemical reactions are concerned, and are isomorphous in all of their compounds. Because of a slight variation in solubility of certain salts, however, the elements may be separated by the method known as fractional crystallization, which consists of repeatedly crystallizing and recombining a large number of fractions through dozens of cycles. Although tedious, the process may be carried out on any desired scale, and in the past few years has been used to produce some hundreds of tons of pure lanthanum salts. The other elements may be isolated in any desired degree of purity by suitable prolongation of the fractionation.

Summary

Monazite is a phosphate of the rare-earth metals. It occurs in stream beds or beach sands, where it has been concentrated by wave action. Large deposits are

* U. S. Patent No. 1366128.

found in Brazil, India, Australia, and the Dutch East Indies. Thorium, lanthanum, cerium, and neodymium salts are produced in large tonnages from monazite, and find their way into such everyday products as spectacle lenses, window glass, cigarette lighters, moving-picture projectors, and medicines, in addition to more specialized uses. The separation of these materials from monazite involves a long series of complex chemical and physical processes.

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