STATE OF OREGON
DEPARTMENT OF GEOLOGY AND MINERAL INDUSTRIES
Head Office: 1069 State Office Bldg., Portland 1, Oregon
Telephone: CApitol 6-2161, Ext. 488

Field Offices

2033 First Street
Baker

239 S.E. "H" Street
Grants Pass

****

THORIUM, THE RARE EARTHS, AND THEIR USES

By
T. C. Matthews*

Introduction

One of the richest areas for exploration in the field of metals today is in that versatile group of elements known as the rare earths. The 15 elements commonly grouped together as rare earths are those with atomic numbers 57 through 71 (see Chart 1). Added together they are about as abundant as copper in the earth's crust. Found with these 15 elements are their closely related cousins, thorium and yttrium; and because of their similarity any discussion of processing or development of uses must include them. The rare-earth elements are conveniently divided into two major groups. The cerium group of "light" rare-earth elements contains those from lanthanum to europium, inclusive. The yttrium group of "heavy" rare-earth elements contains those from gadolinium to lutetium plus yttrium, atomic number 39. Chart 1 lists the rare earths, showing selected characteristics.

The rare earths are remarkably alike in their chemical behavior because of their atomic structure. This characteristic has made chemical separation so difficult that only in recent years have metallurgists and engineers had relatively pure metals to use in testing and alloying. It has been found that the rare earths offer enormous potentials and already many of these metals are being used in a variety of industrial fields.

History

In the early 1900's, incandescent gas lamps were lighting the homes, industries, and streets of America. The heart of these glowing lamps was the gas mantle. The basic material required for the manufacture of mantles was thorium nitrate, which was obtained from Germany prior to World War I. The Allied blockade during that conflict stopped shipments of thorium nitrate, forcing domestic companies, of which Lindsay Chemical Company of Chicago was a leader, to develop methods for making the nitrate in the United States. The only commercial ore of thorium at that time, and the primary one at present, was monazite sand, which contains from five to twenty times as much of the rare earths as it does thorium. Most of the rare earths were discarded during the early days, since at that time they had little or no commercial value. After World War I, significant uses for the rare earths were developed and monazite became valuable for the rare earths as well as for the thorium it contained.

Thorium and rare-earth minerals

While nearly all thorium compounds are produced from the mineral monazite, and most rare-earth compounds are produced from monazite and bastnaesite, there are a number of other minerals which have produced these compounds in the past or will do so in the future. Some of

---

* Spectroscopist, State of Oregon Department of Geology and Mineral Industries.

Chart 1

The Rare Earths and Thorium*

Element		Atomic No.	Relative abundance	Density	Neutron absorption X-section (approx.)	Oxide formula	Price per lb. comm. oxides	Price per gram oxide 99.9%
Yttrium	Y	39	105	4.472	1.4	Y_2O_3	80% - $24.00	$ 1.10
Lanthanum	La	57	35	6.162	8.9	La_2O_3	99% - $10.90	.90
Cerium	Ce	58	155	6.768	.70	CeO_2	90% - $ 2.20	.75
Praseodymium	Pr	59	25	6.769	11.2	Pr_6O_{11}	50% - $20.00	1.75
Neodymium	Nd	60	90	7.007	44	Nd_2O_3	75% - $ 2.52	1.10
Promethium	Pm	61	0		No stable isotopes			
Samarium	Sm	62	35	7.540	10,000	Sm_2O_3		1.80
Europium	Eu	63	1	5.166	4,300	Eu_2O_3		50.00
Gadolinium	Gd	64	35	7.868	36,000	Gd_2O_3	99% - $ 2.00	3.00
Terbium	Tb	65	5	8.253	44	Tb_4O_7		35.00
Dysprosium	Dy	66	35	8.556	1,000	Dy_2O_3		5.00
Holmium	Ho	67	5	8.799	64	Ho_2O_3		10.00
Erbium	Er	68	30	9.058	166	Er_2O_3		5.55
Thulium	Tm	69	5	9.318	120	Tm_2O_3		75.00
Ytterbium	Yb	70	35	6.959	36	Yb_2O_3		12.50
Lutetium	Lu	71	5	9.849	108	Lu_2O_3		65.00
Thorium	Th	90	60	11.5	7.0	ThO_2	97% - $ 8.25	11.22

*Prices are taken from price lists by Lindsay Chemical Company and the Gows Chemical Company.

these minerals, although quite high in rare-earth elements, have been found only in small deposits. Others, known to exist in larger deposits, present still unsolved metallurgical problems before they can be of use. The usual occurrence of thorium and rare-earth minerals is as accessory minerals in granitic rocks. Some of them occur in veins and placers. A partial list of thorium and rare-earth minerals is given below:

Monazite. Essentially a phosphate of cerium and lanthanum, containing most of the other rare earths and small variable quantities of yttrium, thorium, and uranium. Economic deposits are found generally in placers derived from granitic rocks, but a large commercial lode deposit has recently gone into production in South Africa. Monazite contains 3 to 10 percent thorium oxide and 50 to 60 percent rare-earth oxides.

Bastnaesite. A fluocarbonate of the rare earths, primarily cerium and lanthanum, usually containing less than 1 percent uranium and thorium. It occurs in veins associated with fluorite, barite, and carbonates.

Thorite. A silicate of thorium containing 25 to 63 percent thorium oxide and as much as 10 percent uranium oxide.

Thorianite. An oxide of thorium with small amounts of the rare earths, which may contain 70 percent thorium oxide.

Gadolinite. A complex silicate of beryllium, iron, and the yttrium and cerium rare earths.

Allanite. A complex variable silicate of aluminum, iron, the cerium rare earths, and, in smaller quantities, those of the yttrium group.

Crytolite. An altered zircon containing uranium, thorium, ytrrium, and other rare earths.

Fergusonite. A niobate and tantalate of yttrium, with erbium, cerium, uranium, etc., which is found in pegmatites.

Pyrochlore. Chiefly a niobate of the cerium metals, calcium, and other bases, containing thorium, titanium, and fluorine. It is known in large, low-grade deposits.

Xenotime. Essentially an yttrium phosphate. Cerium and erbium are sometimes present, also thorium. It is a primary source of the yttrium group metals.

Euxenite. A niobate and titanate of yttrium, cerium, erbium, uranium, and iron.

Samarskite. Similar to euxenite.

Polycrase. Similar to euxenite.

Yttrotantalite. A tantalate and niobate of iron, calcium, yttrium, and other rare earths.

Uses of thorium

The largest single use of thorium materials today still is in the manufacture of gas mantles. These are made from thorium nitrate, the standard commercial salt and the base for the manufacture of other thorium compounds and metal. The chemical industry uses thorium compounds as catalysts in producing ammonia from nitric acid, producing sulphur trioxide from sulphur dioxide, and producing water gas from carbon monoxide. Some thorium salts find application in creams and lotions, because of their astringent and tonic properties. Thorium is incorporated with tungsten to produce mechanical shock-resistant filaments for vacuum tubes because of its electron emissive power.

The practice of adding as much as 3 percent thorium to magnesium alloys is increasing. A notable example is the Dow-developed HK31 because of its greater fatigue resistance, good forming properties, and strength at elevated temperatures. The alloy, weighing only one-fourth as much as steel, can be heat treated and welded and is available from fabricators in cast and wrought forms. It is being used in the earth satellite, Project Vanguard.

Thorium is especially important because of its value as fuel for the nuclear breeder reactor. Natural isotope 232 is not fissionable, but when it is bombarded by slow neutrons it is transformed into thorium 233, which degrades through protactinium 233 to uranium 233, a fissionable element. This is the breeder reaction, in which more neutrons are produced than are consumed. The major unsolved problem is production of low-cost thorium metal which is refined by the Ames vacuum process to 99.97 percent purity. It is reported that as much as five parts per million of gadolinium will absorb enough neutrons to stop the reaction. Three breeders are now in the works, of which the largest is the 250,000-KW Indian Point heat plant under construction for Consolidated Edison of New York. A breeder this size will need about 21,000 pounds of thorium per year, which will require processing more than 230 tons of 6 percent monazite.

Uses of individual rare earths

Cerium, the most abundant member of the rare-earth group, is an iron-gray metal. It is soft and ductile and burns brilliantly when heated. The metal is a powerful reducing agent and is used effectively in alloys. Cerium oxide is widely used as a polishing agent for optical and other forms of glass. It is used as an opacifier in porcelain coatings for signs and in the manufacture of dielectric ceramic bodies. Cerium hydrate is used as an ingredient in the glass face plates of color television tubes to prevent darkening of the tube face and also in the special optical glass for atomic energy piles. In glass, cerium oxide imparts ultraviolet absorbency without materially affecting the color of the glass. Oxide of high purity is used in windows to view atomic reactor proceedings.

Lanthanum increases the hot workability of steel and the hardness of magnesium. The oxide is an ingredient of infrared transparent glass and of highly refractive optical glass, particularly for aerial photographic lenses. The hydrate is used as a drier for paint and alcohols.

Neodymium and praseodymium, like many of the other rare earths, have characteristically sharp absorption bands. Because neodymium and praseodymium absorb the yellow sodium lines at 589 to 590 mu,* they are used in lenses for welders' and glass blowers' goggles. The usual glass coloring agents lower the light permeability and index of refraction, but the use of neodymium or praseodymium does not affect these qualities. Neodymium, used in tableware, yields a changing color tone between red and lilac, and praseodymium a color tone between green and yellow. Praseodymium oxalate is used in the fabrication of high-temperature crucibles. Neophane glass, containing neodymium, is ideal for spectacle lenses. These two elements are also used in the manufacture of artificial gems and infrared-absorbing glass.

Gadolinium has by far the highest thermal neutron cross-section (great tendency to capture neutrons or a high opacity to neutrons) of any known element. It will therefore be useful in nuclear reactor control rods and in neutron shields. It also has possible uses as a phosphor activator and as a low-temperature transistor.

Yttrium has a very low thermal neutron cross-section and is believed to also have use in reactor construction. It is used in fluoride-free glass and in electrically conductive ceramics.

Dysprosium has a high thermal neutron cross-section and has uses as a phosphor activator.

Europium is a neutron absorber and is used as an activator in lithium iodide scintillation counter crystals.

Thulium, made radioactive, emits x-rays of proper length and strength for diagnostic use. A pea-sized bit of thulium will last a year as a source of rays in a small portable x-ray unit.

Lutetium and samarium have isotopes which are naturally radioactive. Lutetium is being used as a tracer in medical research. Samarium is a neutron absorber, used in reactor construction, and when added to glass produces luminescence.

Erbium has an absorption band which makes it useful in the production of infrared-absorbing glass and is a phosphor activator.

Uses of rare-earth mixtures

Although separation of rare earths into compounds of individual elements probably offers the greatest chance for future profits, the quantity of separated material is presently small compared with that used as mixtures. Since the characteristics of individual rare earths are similar, mixtures of rare earths such as those obtained directly from the various ores are often entirely adequate. Such a compound is rare-earth chloride, which serves as a dryer for paint and ink and is used in textile waterproofing and dyeing. It acts as a caries inhibitor in toothpaste and is used in chrome plating baths and for hot-dip coatings on aluminum.

Rare-earth fluorides and oxides are used as cores for high-luminosity carbon electrodes. Ordinary carbon arc lamps dissipate much of their high intensity in the infrared spectrum.

---

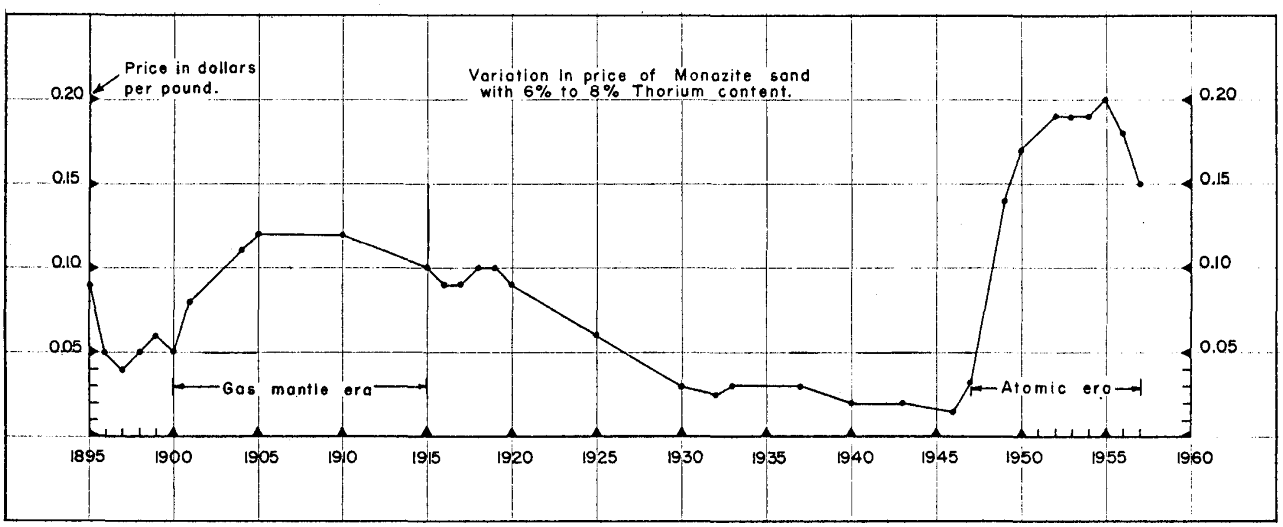
* Equivalent to spectral wave lengths of 5890 to 5900 angstrom units.

Addition of rare-earth compounds results in a brilliant white light which makes high-speed photography and projection of moving pictures possible. Army, Navy, and airport searchlights also use these rare-earth cored carbons.

The largest single use of rare-earth chloride is in the preparation of misch metal (mixed rare-earth metals). For many years it has been alloyed with about 30 percent of iron to make lighter flints, and now it is being used in alloys of aluminum, magnesium, and steel to increase strength and hardness. Such alloys are used in jet planes, gas turbines, and other equipment demanding increased tensile strength at high temperatures. Small quantities added to steel in the ladle result in a strong, fine-grained metal with great resistance to low temperature oxidation and corrosion. Rare earths added to cast iron act as powerful deoxidizers and help remove sulphur from the metal. They are responsible for cast iron that is resistant to corrosive atmospheres and to scaling at high temperatures.

Another commonly used mixture consists of the didymium elements. The common usage of the term means a mixture of neodymium and praseodymium, but Lindsay Chemical Company prefers to restrict the name didymium to the cerium-free group of rare earths extracted from monazite sand. Such mixtures are reasonably constant in composition and no doubt are considerably cheaper to manufacture. Didymium carbonate is used as a glass decolorizer and in temperature compensating condensers for radio and television. Since the mixture provides a neutral gray glass with a sharp cutoff of ultraviolet light, it is used in manufacturing lenses for better-grade sun glasses.

Chart 2



Market values

According to E&MJ Metal and Mineral Markets, June 13, 1957, monazite type ore with a minimum rare-earth plus thorium content of 55 percent brings 14 cents per pound, massive; sand 55 percent grade is 15 cents; sand 66 percent grade is 18 cents. It is probable that the thorium oxide content of these ores must not be less than 6 to 8 percent. No prices are quoted for bastnaesite, but the mineral probably commands a price comparable to monazite. Michigan Chemical Corporation stated that there are no fixed prices for the other ores. The grade of ore required and the price paid will depend on a number of factors including mineral purity, transportation, and amenability to concentration. Chart 2 shows the approximate variations in the price of monazite during the past 60 years.

The market for thorium and rare earths appears to be restricted at present to certain chemical companies. Therefore any project involving these materials should be assured of a market before proceeding to the production stage. Prices paid for rare-earth ores in general are not as high as the prices quoted for refined materials would lead one to believe. The cost of refining is extremely high, especially when nearly pure compounds are desired.

Prices of commercial oxides and 99.9-percent pure oxides are shown on Chart 1 (p.76). Prices of representative miscellaneous materials are listed below:

Thorium nitrate (gas mantles), 46% ThO_2	$ 3.60 per pound
Thorium metal, 2% impurities, powder	35.00 per kilogram*
Thorium metal, 2% impurities, .005 sheet	50.00 per kilogram
Thorium metal, reactor grade	43.00 per kilogram
Rare-earth chloride, 44% total oxides	0.42 per pound
Rare-earth oxide, 94% total oxides	1.80 per pound
Misch metal	4.50 per pound
Ferrocerium (for lighter flints)	8.00 per pound
Pure cerium metal	18.00 per pound
Didymium chloride, 44% total oxides	0.72 per pound
Didymium carbonate, 65% total oxides	1.02 per pound

Companies understood to be processing or refining thorium or rare-earth ores or compounds include the following:

Lindsay Chemical Company, West Chicago, Illinois
Marine Minerals, Inc. (Crane Company), Aiken, South Carolina
Maywood Chemical Company, Maywood, New Jersey
Metal Hydrides, Beverly, Massachusetts
Michigan Chemical Corporation, Saint Louis, Michigan, and Golden, Colorado
Norton Company, Worcester, Massachusetts
Rare Earths, Inc. (Davison Chemical Company), Pompton Plains, New Jersey
St. Eloi Corporation, 3509 Debolt Road, Newtown, Ohio
The Gows Chemical Company, Inc., Box 443, Laramie, Wyoming
United States Yttrium Company, Laramie, Wyoming
Westinghouse Electric Corporation, Lamp Division, Bloomfield, New Jersey

Bibliography

Baroch, Charles T., 1957, Rare earths: Eng. and Min. Jour., vol. 158, no. 2, p. 107.
Crawford, J.E., 1956, 1957, Thorium: Eng. and Min. Jour., vol. 157, no. 2, p. 109, and vol. 158, no. 2, p. 101.
E&MJ Metal and Mineral Markets, 1954-1957.
Franklin, J.W., and Eigo, D.P., 1955, Thorium: Eng. and Min. Jour., vol. 156, no. 11, p. 75.
Gammil, Adrian M., 1957, Atomics and the rare-earth industry: Michigan Chemical Corp., product schedule.
Lamb, Frank D., 1956, Rare earths: Eng. and Min. Jour., vol. 157, no. 2, p. 111.
Lindsay Chemical Company, 1957, Cerium, rare earth, and thorium chemicals.
____________, 1957, Thorium and rare-earth ores: Western Associated Min. News, April 1957.

* 1 kilogram = 2.2 pounds.

Pray, Lloyd C., 1957, Rare-earth elements: Mineral Inf. Service, State of Calif. Div. of Mines, June 1, 1957.

St. Eloi Corporation, 1956, price list and data sheet.

The Gows Chemical Company, Inc., 1957, Pure rare-earth oxide, price schedule.

U.S. Bureau of Mines, Minerals Yearbooks, various issues.

Vickery, R. C., 1956, The rare earths up from obscurity: Research and Engineering, April 1956.

****

GEOLOGIC MAP OF PORTLAND QUADRANGLE PUBLISHED BY U.S. GEOL. SURVEY

"Geology of the Portland quadrangle, Oregon-Washington," by Donald E. Trimble, has just been published by the U. S. Geological Survey as Map GQ 104. The map has a scale of 1 inch to the mile and depicts in color and pattern the various geologic formations present. A text describing these formations accompanies the map on a single folded sheet. The map may be obtained from the Denver Federal Center, Denver, Colorado. Price is $1.00.

Mapping of the Portland quadrangle was done by Mr. Trimble during the years 1948 to 1953 as part of a larger field investigation in the Portland region, results of which will be published in bulletin form by the Survey at a later date.

The area occupied by the Portland quadrangle is a broad structural basin in which the bedrock is largely mantled by surficial deposits. The bedrock consists of two series of Tertiary basaltic lavas, Columbia River basalt and Boring lava, separated by more than 1,000 feet of sedimentary rocks of the Troutdale formation. A careful study of the Troutdale formation in this and adjacent areas has revealed an upper and lower member in the unit. The surficial deposits in the quadrangle consist of Pleistocene clayey silt believed to be of windblown origin capping the Portland hills; widespread lacustrine gravel, sand, silt, and clay deposited by ponded Pleistocene flood waters; Pleistocene alluvium; and Recent sand, silt, and bog deposits.

Mineral resources in the area consist of construction materials and ground water. Sand and gravel, available in abundant supply in the Pleistocene lacustrine deposits, are used extensively for road metal and concrete aggregate. Columbia River basalt and Boring lava are used satisfactorily for road metal, riprap, and building stone. Two clay deposits in the area support brick and tile plants. Columbia River basalt and Troutdale gravels are the chief sources of ground water in the Portland quadrangle.

****

NEW CHROME OPERATION

The Cynthia chrome mine, Josephine County, has been reactivated by the Thunderbird Mining Corporation of Medford, organized by Frank Grover, Nate Smith, and E. C. Brittsan. The mine is located in the NE$\frac{1}{4}$ sec. 15, T. 41 S., R. 5 W., at about 5,000 feet elevation in the rugged Whiskey Peak area. Starting last June, about 5 miles of road were constructed from the end of Cougar Creek Road through Cougar Gap, and around the south side of Whiskey Peak to the mine. The first shipments of chromite were made the middle of August and to date (September 12, 1957) about 100 tons of good grade chromite, assaying from 46 to 48 percent Cr_2O_3 with a 2.3 to 2.5 Cr:Fe ratio, has been received at the Grants Pass chrome-purchasing depot. Earlier production of the mine was taken out on the trail by pack animals. During World War I some ore was reportedly packed out by Chancy Florey, Medford; and about 35 tons in 1942 by Max Hughes, Murphy, Oregon.

****

PETROLEUM ENGINEER JOINS DEPARTMENT STAFF

Vernon C. Newton, Jr., has joined the Department staff as Petroleum Engineer and in that capacity will handle problems connected with oil and gas exploration in the State. Mr. Newton is a native of Alhambra, California, and a graduate of the University of Southern California, where he specialized in geology and petroleum engineering.

During World War II, Newton served with the 301st Infantry in France and Germany. Following his graduation in 1949 from the University, he received 5 years training and experience in the various phases of oil-well drilling while working first with Amerada Petroleum Corporation and later with Union Oil Company of California. At Union Oil he ~~acted in capacity of~~ Assistant ~~Division~~ Petroleum Engineer. Mr. Newton became interested in petroleum exploration in the Northwest and came to Oregon in 1954. Since that time he has done mineral exploration and diamond drilling in Nevada, and has worked for the Oregon State Highway Department and the U.S. Soil Conservation Service.

****

TITANIUM METAL INDUSTRY

Titanium Metal Industry Statistics, short tons

	1st Quarter 1957	Total 1956
Titanium tetrachloride production for making metal	1/ 27,000	1/ 62,000
Sponge metal production	5,897	14,595
Sponge metal imports for consumption	915	2,048
Sponge metal consumption	4,013	10,936
Scrap metal consumption	738	2,033
Ingot production.	4,536	11,688
Ingot consumption	4,734	10,860

1/ Estimated by producers.

In keeping with the past upward trends in the production and use of titanium metal, the domestic titanium metal industry displayed increased activity in the first quarter of 1957, producing 41 percent more sponge metal and 10 percent more ingot than in the last quarter of 1956. The new high level of sponge production was achieved despite the shortage of argon gas which threatened to disrupt production at several sponge metal plants.

The price of titanium sponge metal remained unchanged during the first quarter of 1957 and was quoted at $2.75 per pound for Grade A-1 and $2.50 per pound for Grade A-2.

A new development during the first quarter of 1957 was the announcement that Oregon Metallurgical Corp., Albany, Oregon, and Firth Sterling, Inc., Pittsburgh, Pennsylvania, had entered into a joint venture whereby Firth Sterling will process titanium ingots made by Oregon Metallurgical into bars and forged rounds. (From U.S. Bureau of Mines Quarterly Titanium Metal Report No. 1.)

****

GROUND-WATER EXPLORATION NEAR COOS BAY CONTINUES

Construction of a third pumping station was begun Wednesday, September 18, 1957, on Oregon coast sand dunes north of Coos Bay-North Bend where Pacific Power & Light Company has been conducting extensive field investigations directed at development of underground sources of fresh water supply for bay area industry. Site of the newest PP&L work is about 1 mile north of the Southern Pacific railway bridge crossing of the bay shipping channel and half a mile west of the railroad spur at Cordes.

The latest installation, designed after PP&L made studies based on data assembled during the utility's 30-month-long preliminary explorations, will consist of three, perhaps four, vertical wells, according to C.P.Davenport, PP&L engineer in charge of the work. The wells will be 41-inch-diameter holes in which will be set slotted wood pipe of 14-inch diameter. The wood pipe will be surrounded with filter-zones of sand and gravel. Some 4,000 feet of 10-inch diameter steel pipe will carry the water to an outfall at the edge of the bay, it was reported. Drillings will be a few hundred yards apart and about 70 piezometers will be placed in the vicinity to determine the water table configuration during pumping.

****