~~H~~ Grants Pass

RARE EARTHS RARING TO GO

Rare earths seem to be over the hump - that difficult stage between basic research and large scale commercial production. Biggest immediate reason for the present boom in rare earth research and plant construction is demand created by the Atomic Energy Commission. Although companies now in the field are setting up their operations to fill AEC contracts, they feel that, once they are in the business, they will be in a good position to develop much larger commercial outlets.

Before AEC entered the picture, rare earth products found use in carbons for arc lighting, lighter "flints," glass coloring or decolorizing, glass polishing, and numerous minor outlets. Some applications require rare earth compounds, others like lighter "flints," use misch metal (mixture of rare earth metals) or cerium metal.

AEC is the biggest factor affecting today's rare earth market. First, its need for thorium has given the monazite processing industry a big push. Now it wants individual rare earths as well.

Thorium can be transformed into fissionable uranium-233 in an atomic pile. Plans are being made to use it in a "breeder" blanket in nuclear power reactors such as the one Commonwealth Edison is building near Chicago. The U^{233} will be removed periodically, and thus our supply of fissionable material will be increased.

Just how much thorium will be needed for reactors is a question which nobody can answer right now. Actually, calculations have not even yet been completed to show exactly how much will be needed in the Commonwealth Edison unit.

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Chemical and Engineering News, Vol. 34, No. 6, February 6, 1956, p. 550-552.

Demand for Individual Elements

It is not difficult to see why AEC is interested in individual rare earth elements. Some have thermal neutron capture cross-sections among the largest, and some among the smallest of the elements. There are nuclear applications for both types of material. This is why rare earths never before separated on a commercial scale are being sold today.

There are also potential new commercial demands for individual rare earths. Thulium, for example, can be made radioactive and serve in a portable x-ray device. Cost of irradiation is now quite high, but it is hoped that this can be lowered later to make the device economical.

The market for individual rare earths varies from week to week. Sudden and obscure demands throw everyone into a flurry of bidding. Rumors of tonnage demand for items now made by the pound breeze through the industry at short intervals. Demand for a single rare earth means that large storage facilities are needed for the partially processed cuts containing the unwanted elements. Producers hope this "unwanted" condition will be a temporary one for most rare earths but feel that some particular ones may glut the market for years. In spite of these difficulties and some price drops, companies separating rare earths are optimistic.

Mixtures Hold the Market

Although separation of rare earth mixtures into compounds of individual elements probably offers the greatest chance of future profits, the quantity of separated material is presently very small compared to that sold as mixtures. No dramatic increase is foreseen for mixtures in most applications, but metallurgy is an exception.

Not only are rare earths - as misch metal, or more recently as compounds - used in ferrous metallurgy, but they also are used with magnesium alloys.

Cerium, used in lighter "flints," is suffering somewhat from foreign competitors. Traditionally, a good deal of this has been exported, but now Europeans are producing more of their own. European atomic energy programs may possibly have an even greater effect in the future.

Research for New Markets

Research might open up entirely new markets for rare earths. Davison, for example, thinks they are worth investigating as catalysts. If separation processes are improved so that prices are lowered, then new markets will appear. A mixture of oxides naturally has a relatively low melting point but some individual oxides will make "beautiful" refractories, according to one manufacturer.

Physical data - such as melting points - are often unavailable. Probably there is much restricted data in existence, but if a company could offer engineers exact information about properties, it would be much easier for them to find new applications.

A few individual rare earths have been investigated for metallurgical uses, to see if they are more effective than mixtures. So far they do not, but this work is still in its early stages.

Ion-exchange processes are constantly being improved and are probably the most effective means yet developed for complete separation of rare earths.

However, this technique is most economical when it is desired to make a complete fractionation of pure rare earths at one time. It leaves something to be desired when just one element is wanted.

Solvent extraction has also been used, but the separation obtained is not so sharp. It may become useful for preliminary separations, or for "diving" for a particular rare earth. Of course, "pure" is a relative term. Sometimes a product assaying 95% is so designated and is effective in its application. Usually "pure" means 99% or better.

There has been no real breakthrough in producing rare earths in the metallic state in usable form. The heavier rare earth oxides are especially hard to reduce. Usual reducing agents lead to grossly impure products.

Spedding uses metallic calcium to reduce some of the metals. Lanthanum obtained in this way can be used to reduce heavier rare earth oxides, and the results mixture can be separated by sublimation.

Rare earths have never been too scarce, says Spedding; they just have not been developed. He believes they can be compared with aluminum which stood around on the shelf a long time before it came into production commercially. Present AEC demands may give rare earths the impetus they need to get them into tonnage production.

RARE EARTHS

What Companies in the Field Are Doing Today

Lindsay Chemical Co., West Chicago, Illinois, has been in the business of making thorium from monazite sand since World War I, when it was forced to acquire a new source of thorium for its gas mantle business (C&EN, Sept. 26, 1955, p. 4102). At first the rare earths were of no importance and were discarded, but later on uses were found for them and Lindsay became the leading producer. It still definitely holds the top position so far as volume of monazite derivatives is concerned. With the discovery that thorium could be converted into fissionable uranium-233, Lindsay's interest again shifted to thorium - this time for AEC.

Last year Lindsay set up an ion-exchange pilot plant, similar to the one F. H. Spedding, Jack Powell, and their co-workers developed at the Institute for Atomic Research at Ames, Iowa. This enabled it to add almost all of the individual rare earths to its line, which previously had included only cerium, lanthanum, praseodymium , neodymium, and mixtures. The ion-exchange plant is now being doubled in size.

Lindsay, which on occasion has also processed bastnasite, gets most of its monazite from South Africa. It encourages the search for new sources, and last fall announced it had taken an option on a newly found deposit in Saskatchewan.

Maywood Chemical Co., Maywood, N. J., is also a long time producer of thorium and rare earths. It processes monazite, and sells individual rare earths separated by crystallization. It does not have an ion-exchange plant. Smaller than Lindsay in rare earths, Maywood is doing some expanding in this division.

Rare Earths, Inc., Pompton Plains, N. J., is the third processor of monazite ores presently operating. Rareox, optical quality cerium oxide polishing powder, thorium salts, and rare earth compounds have been the chief products of this eight-year-old company. Recently it was purchased by W. R. Grace, which is expanding in this field through its Davison Chemical Division (see below).

Molybdenum Corp., entered the rare earths business five years ago with its 18 million-ton reserve (rare earth oxide basis) of bastnasite at Mountain Pass, Calif. The company processes rare earths there and at Washington, Pa., to obtain compounds for the metallurgical industry. Bastnasite contains only a negligible quantity of thorium and it is not recovered.

Molybdenum's business is quite different from that of the monazite proessors. Its refining operations are based on wet flotation processes. Product is sold in the form of patented "T-compounds" for improving the rolling qualities of stainless steels, and for other metallurgical uses. Production comes to a substantial total.

Davison Chemical Co., division of W. R. Grace, is installing (with Rare Earths, Inc.) a $2 million monazite-processing plant at Curtis Bay, near Baltimore, Md. Completion date is set for some time early this year. Combined capacity of this plant and the Pompton Plains plant will be about 10,000 tons of monazite sands annually. This is estimated to be about 50% of the capacity of the entire monazite derivatives industry.

Davison, wanting to diversify into some phase of the atomic field, started by looking into the possibility of extracting uranium from its phosphate rock back in 1948. Continuing the search, Davison acquired Rare Earths, Inc., last August.

The Curtis Bay plant will have the advantage of developments made at Rare Earths, Inc. Yields are expected to be 70-6% thorium and 64% rare earths (which will not be separated into individual components at present). Rare Earths/Davison currently are making available purified rare earth elements and are actively developing improved methods of production.

Research Laboratories of Colorado, Inc., at Newtown, Ohio, has an ion-exchange plant for separating rare earths - not from monazite but from Norwegian gadolinite, and experimentally from concentrates of various kinds rich in the so-called yttrium group. Besides yttrium (which is not actually a rare earth, but is found associated with them) the group consists of the heavier rare earth elements such as thulium, ytterbium, and lutetium. Monazite yields the cerium group of lighter rare earths mostly, although Lindsay produces yttrium from it.

United States Yttrium Co., of Laramie, Wyo., expects to start production almost any day. It has an ion-exchange plant and will process thalenite, an yttrium silicate. Thulium will also be available.

Michigan Chemical at St. Louis, Mich., is engaged in research and pilot plant work. It is working on a number of concentrate bases and is interested in producing individual rare earth compounds.

Mallinckrodt's present output of rare earth products is limited to misch metal especially prepared for metallurgical uses, but is is believed to be interested in striking out in other directions too. Recently, Mallinckrodt became a subcontractor for a mining company, Porter Bros. Corp. of Boise, Idaho, for extracting niobium, tantalum, and uranium from euxenite. Since this mineral also contains rare earths, Mallinckrodt should be in a good position to produce rare earths from the euxenite residues.

Crane Co. has a subsidiary, Marine Minerals, Inc., dredging for monazite, zircon, rutile, and ilmenite near Aiken, S. C. It plans to have another subsidiary, Heavy Minerals, process the first two. The latter two are titanium minerals and will go to its Cramet subsidiary. It was the search for titanium ores that led to the monazite discovery. The company is keeping quiet about its plans but is widely thought in the industry to be considering going into rare earths in a fairly big way.

Vitro Corp., also is not too talkative at the moment except to say that it intends to go into thorium and rare earth production on a substantial basis.

Other companies are in various stages in developing rare earth programs. Horizons, Inc., of Cleveland is evaluating the field. Monsanto has some interest. So does Air Reduction. Union Carbide has been making rare earth metallurgical products and is rumored to be considering expanding. Mitten Chemical of Alma, Mich., is in the business.

Research Chemicals, Inc. of Burbank, Calif., has produced small quantities of rare earths for some time.

STATE DEPARTMENT OF GEOLOGY
AND MINERAL INDUSTRIES
702 WOODLARK BUILDING
PORTLAND 5, OREGON

May 20 1947

Sample submitted by F. W. Libbey - W.D.Lowry

Sample received on

Analysis requested Cadmium-selenium-gallium-indium

Analysis by:
T. C. Matthews

Lab. No.	Sample Marked	Results of Analysis	Remarks
	P-5815	Selenium - not found Cadmium - not found Indium - .001 - .01% Gallium - .001 - .01%	
	P-5816	Selenium - not found Cadmium - not found Indium - .001 - .01% Gallium - ,001 - .01%	

Laterite from Butte Falls
+ Grants Pass

The Department did not participate in the taking of this sample and assumes responsibility only for the analytical results.

STATE DEPARTMENT OF GEOLOGY AND MINERAL INDUSTRIES

702 WOODLARK BUILDING
PORTLAND 5. OREGON

April 15, 1947

Sample submitted by F.W.Libbey - W. D. Lowry

Sample received on April 9 1947

Analysis requested Nickel

Analysis by:

Thomas C. Matthews

Lab. No.	Sample Marked	Results of Analysis		Remarks
	P-5815	Nickel	.01 - .1 %	
	P-5816	Nickel	.01 - .1%	
	P-5818	Nickel	.01 - .1%	

laterite from Butte Falls & G. Pass

Sample no. P-5818 is a split of P-5815, containing the washed pebbles only. The Amount of nickel is very nearly the same in all samples, although one line showed P-5818 to have slightly less than the others

The Department did not participate in the taking of this sample and assumes responsibility only for the analytical results.

CHAPTER 17

THE RARE EARTH ELEMENTS (Y and ELEMENTS 57–71)

The rare earth elements form a geochemically coherent group whose more common members can often be detected and determined spectrochemically in a wide variety of minerals, rocks, and soils. As a time-saving procedure in analysis, the most common members are sought first, and if they are absent, it is safe to assume that the others are absent also. Figure 17–1, which gives a typical relative abundance plot of the rare earth elements in a specimen of granite, shows Y, Ce, La, and Nd as the commonest rare earths. It may readily be seen in Fig. 17–1 that the rare earths of even atomic number are more abundant than those of odd atomic number (Harkins' rule). Although the abundance relationship between various rare earth elements varies somewhat in different minerals, rocks, and soils, the group is usually sufficiently coherent to preserve the general abundance-relationship pattern depicted in Fig. 17–1, which may serve as a guide to the analyst. (See Taylor, 1960.)

Goldschmidt (1954) distinguishes different types of rare earth occurrence. For example, the rare earths are found as essential constituents of minerals (e.g., *monazite*); commonly present in pegmatites. (For an account of the distribution pattern of the group in rare earth minerals, see Rankama and Sahama 1950, p. 520, Murata et al. 1953, 1957, Butler 1958.) In a second mode of occurrence, rare earth elements substitute for

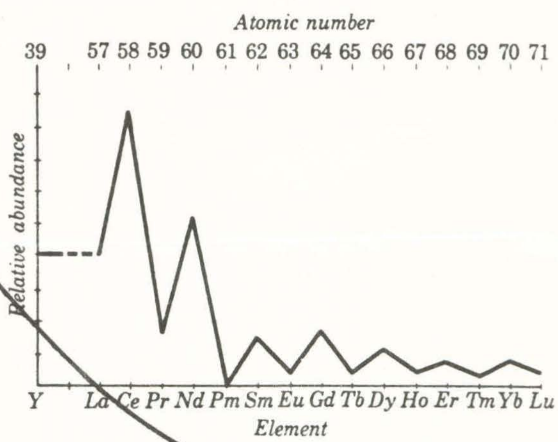

Fig. 17–1. Approximate abundance relationship between Y and the members of the rare earth group in the earth's crust. The commonest rare earth elements are Y, Ce, La, and Nd.

MINERAL INDUSTRY SURVEYS

U. S. DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
WASHINGTON, D. C. 20240

Fred J. Russell, Acting Secretary Elburt F. Osborn, Director

For information call Robert F. Griffith
Telephone: 703-557-0292 Annual, Preliminary

RARE-EARTH ELEMENTS AND THORIUM IN 1970

Total domestic output of rare-earth oxides (REO) in concentrates decreased from the record high of 1969, according to the Bureau of Mines, U.S. Department of the Interior. Molybdenum Corporation of America (Molycorp) mined and processed bastnaesite at Mountain Pass, Calif. Humphreys Mining Co. recovered monazite, containing about 55 percent REO and 5 percent ThO_2, as a byproduct of titanium minerals and zircon with a suction dredge from an ancient beach deposit controlled by E.I. du Pont de Nemours & Co., Inc., near Folkston, Ga. Minor production of low-grade monazite concentrate by Climax Molybdenum Co. from molybdenum mining at Climax, Colo., was discontinued.

Kerr-McGee Chemical Corp., a subsidiary of Kerr-McGee Corp., conducted pilot plant tests on a large heavy-mineral placer deposit in Western Tennessee. The minerals of economic interest are rutile, ilmenite, monazite and zircon.

Rare-earth elements were removed from the list of strategic and critical materials in March 1970. Plans were formulated to offer for sale, the resultant surplus Government stocks at an annual rate not to exceed 1,250 short tons of REO equivalent; 625 tons each in July and December. As of December 1, Government stocks consisted of 13,233 tons of REO equivalent in the following forms: monazite, 5,088; bastnaesite, 3,243; sodium sulphate, 4,249; chlorides, 653. During the year, General Services Administration sold 288 short dry tons of contained REO in rare-earth sodium sulphate. The national stockpile objective for thorium, which was reduced in 1969, remained at 40 short tons of ThO_2 equivalent.

Apparent domestic consumption of rare-earth materials was about 10,000 tons of REO equivalent, and of thorium, 120 tons of ThO_2 equivalent. The largest single application for the rare-earth elements continued to be for catalyst formulations used principally in petroleum refining. These catalysts contain a rare-earth zeolite (molecular sieve) as the active component. Other uses in order of magnitude by volume were: glass polishing and as an additive, nodular iron and steel, carbon arc electrodes, and pyrophoric alloys. High-value low-volume applications included color television phosphors and samarium-cobalt permanent magnets.

Prepared December 10, 1970, in Division of Nonferrous Metals.

MINERAL INDUSTRY SURVEYS

U. S. DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
WASHINGTON, D. C. 20240

Fred J. Russell, Acting Secretary | Elburt F. Osborn, Director

For information call Richard F. Stevens, Jr.
Telephone: 703-557-0500 | Annual, Preliminary

RHENIUM in 1970

Demand for rhenium, primarily as a replacement for platinum catalysts in the petrochemical industry, increased significantly in 1970, according to the Bureau of Mines,U.S. Department of the Interior. Production of rhenium salts and metal powder continued to increase; but consumption and prices both rose substantially during the year. The rapid growth in demand for rhenium in catalytic applications more than offset the decrease caused by the termination of most of the rhenium-refractory metal alloy programs sponsored by the U.S. Atomic Energy Commission (AEC).

Rhenium continued to be recovered, as a secondary byproduct from the molybdenite contained in southwestern porphyry copper ores, by the Kennecott Copper Corp. at its molybdenum roasting facility near Garfield, Utah, by S.W. Shattuck Chemical Co., Inc., Denver, Colorado, and by M & R Refractory Metals, Inc., at its Camden plant near Winslow, N.J. During 1970 most of the Kennecott material was shipped to the major domestic rhenium metal producer, Cleveland Refractory Metals (CRM), Solon, Ohio, a division of Chase Brass & Copper Co., Inc. (a subsidiary of Kennecott Copper Corp.) which has continued to increase its capacity for rhenium metal production. Kennecott also sold rhenium bearing molybdenum concentrate to Shattuck and M & R. During the year, a new source of rhenium, the molybdenite recovered from the porphyry copper ores of Magma Copper Co.'s San Manuel mine in Pinal County, Arizona, became available.

Imports of unwrought rhenium metal (and scrap) decreased 74 percent during 1970 to about 210 pounds. Imports were received from the U.S.S.R. (42 percent), West Germany (37 percent), and France (21 percent). The material from France and West Germany is believed to have been recovered from molybdenite obtained from porphyry copper ores mined in Chile while rhenium imported from the Soviet Union was recovered from Russian porphyry copper ores. The average price of imported unwrought rhenium during the year, excluding U.S. duty of 7 percent ad valorem, was $645 per pound (France), $455 per pound (West Germany), and $322 per pound (U.S.S.R.). There were no imports of wrought rhenium. Rhenium exports (wrought and unwrought) totaled less than 10 pounds.

Approximately 75 percent of the more than 2,000 pounds of rhenium metal consumed during the year was used in the development of rhenium and rhenium-platinum catalysts for petroleum refining. Some rhenium metal was consumed in the research and development of ductile, high-temperature tungsten and molybdenum-base alloys.

Prepared December 29, 1970, in Division of Ferrous Metals.

Wall St. Journal
7/14/65

Europium Oxide Output Started at New Plant By Molybdenum Corp.

Facility to Produce 6,000 Pounds Annually for Color-TV Firms; 18 Months' Production Is Sold

By a WALL STREET JOURNAL *Staff Reporter*

NEW YORK — Molybdenum Corp. of America has started production of europium oxide at a new, previously announced $1.5 million plant located at the company's large rare earths mine at Mountain Pass, Calif., William R. Kuntz, president, announced.

Molybdenum Corp. will produce 6,000 pounds of europium annually at this plant for sale to the color-television industry. Europium combined with yttrium results in a new red phosphor for coating television tubes that helps deliver a brighter, true-color image. Red phosphors used previously weren't satisfactory because the red was too dull and the green and blue had to be deadened to stay in balance with the weaker red.

Mr. Kuntz said contracts have been secured for the company's entire production of europium for the next 18 months. The company wouldn't disclose its exact sales price for europium oxide, but said it is well in excess of $500 a pound.

The official said Molybdenum Corp. expects to recover the entire $1.5 million investment in the new plant in less than a year. Lewis B. Harder, chairman of Molybdenum Corp., added that over the long term he expected profit from the rare earths segment of the company to exceed that of the concern's molybdenum production.

Molybdenum Corp. is expected to start production of molybdenum next January from a new mine at Questa, N. M. at an annual rate of 10 million pounds. Pre-production cost of this facility is $33 million and the total cost is estimated at about $40 million.

Mr. Kuntz said the Mountain Pass mine and plants are producing rare earth oxides at a full-capacity rate of 9 million pounds annually. Sales of the rare earths in 1964 are estimated at 12 million pounds, or more than four times 1964 sales. The excess of sales over production will be met from previously accumulated inventories at the property. He added that Molybdenum Corp. has initiated plans for a larger mill facility to meet growing markets.

Besides its newest use in television tubes, rare earths, consisting of about 16 elements, are being used in oil-cracking catalysts to attain higher yields of petroleum; in polishing glass for camera and optical lenses and plate glass; in the iron and steel industry; in carbon arcs; in ceramics, and for lighter flints. Other special applications include microwave transmission gear, vacuum tubes and lasers.