Rare-Earth Minerals and Metals

By Christine M. Moore[1]

Domestic production of rare-earth oxide (REO) contained in bastnäsite and monazite concentrates increased 17% in 1977. Molycorp, Inc., and the Davison Chemical Div. of W. R. Grace & Co., the principal processors of rare earths in 1977, expanded their facilities. Consumption of rare earths increased during the year. Petroleum catalysts remained the major end use, but production and consumption of rare earths for metallurgical uses increased dramatically. The ceramic and glass industries were also major consumers.

Exports of rare earths increased fourfold during the year and imports of monazite nearly doubled. Mischmetal imports also increased.

Legislation and Government Programs.—The General Services Administration (GSA) shipped 2,541 tons REO equivalent, contained in monazite, and 9 and 24 tons REO, respectively, contained in sodium sulfate and rare-earth chloride. Stocks of rare-earth materials held by the Government totaled 4,600 tons REO equivalent at yearend. Government stocks of yttrium oxide (Y_2O_3) remained at 237 pounds during the year.

DOMESTIC PRODUCTION

Concentrate.—Domestic production of REO in bastnäsite and monazite in 1977 increased 17% over the 1976 level. Bastnäsite continued to be the major domestic source of rare earths; the remainder, less than 10%, was produced from monazite.

Molycorp, Inc., the sole domestic producer of bastnäsite concentrate, was acquired by Union Oil Co. of California during the year. According to the company's annual report, production of rare-earth concentrates at Molycorp's Mountain Pass, Calif., operation increased 18% to 16,930 short tons of REO contained in bastnäsite concentrate; production in 1976 was 14,372 tons.

Titanium Enterprises, jointly owned by American Cyanamid Co. and Union Camp Corp., continued to recover monazite as a byproduct of mining a beach sand deposit near Green Cove Springs, Fla., for titanium minerals and zircon. Monazite production during 1977 was more than double the 1976 level.

Humphreys Mining Co. also recovered monazite from heavy-mineral beach sand operations. Humphreys' dredging operation was located near Hilliard, Fla., and the wet, heavy concentrates were trucked to the company's drying plant at Folkston, Ga., for processing. Monazite production by Humphreys decreased significantly during the year due to the mining of titanium sands of lower monazite content.

The U.S. Geological Survey announced the discovery of heavy-mineral sand deposits of potential economic grades in Charleston County, S.C.[2]

Compounds and Metals.—During 1977, Molycorp and the Davison Chemical Div. of W. R. Grace at Chattanooga, Tenn., were the major producers and processors of rare-earth compounds. Molycorp, the principal domestic processor, operated plants at Louviers, Colo., and York, Pa. Production of mixed rare-earth compounds increased during the year.

Producers of high-purity oxides and com-

pounds during the year were Molycorp; W. R. Grace; Nucor Corp., Research Chemicals Div., Phoenix, Ariz.; Reactive Metals and Alloys Corp. (REMACOR), West Pittsburgh, Pa.; and Transelco Div. of Ferro Corp., Penn Yan, N.Y.

Mischmetal production more than doubled in 1977 and shipments of mischmetal increased threefold over the 1976 level. During the year REMACOR and Ronson Metals Corp., Newark, N.J., produced mischmetal. The Rare Earth Metals Co. of America (REMCOA) plant at Arnold, Pa., continued bench-scale studies of mischmetal production during the year, and at yearend the company reportedly decided to postpone plans for full-scale production.

REMACOR announced plans to expand its mischmetal production capacity from 1.2 to 4.0 million pounds per year at a cost of $2 million. Bastnäsite supplied by Molycorp was to be the primary raw material.

Production of rare-earth ferrosilicon alloys by Foote Mineral Co., Exton, Pa., Molycorp, and REMACOR more than doubled during the year.

Molycorp and Research Chemicals were the major processors of yttrium oxide. Research Chemicals also produced other high-purity metals during the year.

Hitachi Magnetics Corp. expanded production capacity for rare-earth-cobalt magnets during 1977 at its Edmore, Mich. plant.

CONSUMPTION AND USES

Domestic rare-earth processors consumed an estimated 15,300 tons of REO contained in raw materials in 1977, an 8% increase from the previous year. Bastnäsite consumption increased 3% and monazite consumption increased 37%. Shipments of rare-earth and yttrium products from primary processing plants to domestic end-use consumers were about 11,000 tons contained REO. High-purity rare-earth and yttrium oxides and metals were about 8% of total shipments, but comprised about 30% of the total value of shipments.

The approximate distribution of rare-earths and yttrium by end use, based on information supplied by primary processors and certain consumers, was as follows: Petroleum cracking catalysts, 41%; metallurgical, including nodular iron and steel, other alloys, and mischmetal, 37%; ceramics and glass, 18%; and miscellaneous, including electrical, arc carbons, and research, 4%.

The use of rare-earth zeolites in cracking catalysts to increase the yield of gasoline from petroleum feedstocks continued to be the single largest use of rare earths. However, a significant increase in the use of rare earths as additives to ductile iron and steel occurred. Production and consumption of mischmetal and rare-earth silicides increased during the year and continued growth of this end use was expected.

The production of lighter and striker flints continued to be a major consumer of mischmetal. Other rare-earth alloys and metals were used in the production of high-temperature alloys and superalloys.

The glass industry continued to be a major consumer of rare-earth compounds, particularly cerium oxide. The established uses of cerium oxide are as an abrasive for polishing glass; as an additive in eyeglasses, television tubes, and camera lenses; and as a decolorizing agent in refining clear glass. Rare-earth oxides of praseodymium, erbium, holmium, and neodymium were used as colorants in glass. Lanthanum oxide was used to improve the refractive quality of camera lenses.

During 1977, an estimated 140 tons of Y_2O_3 contained in raw materials was consumed, a 17% increase over the 1976 level of 120 tons. During the year, production of phosphors for color televisions and fluorescent lights, a major use of Y_2O_3, increased.

Synthetic garnets composed of yttrium-aluminum (YAG), yttrium-iron (YIG), gadolinium-aluminum (GAG), and gadolinium-iron (GIG) were used as microwave filters and control devices, as simulated diamonds, and, when doped with neodymium or erbium, in lasers. Minor quantities of gadolinium-gallium garnets (GGG) in thin-film, magnetic-bubble memory systems were used in communication and computer systems.

Significant quantities of rare-earth oxides and fluorides were used in carbon-arc lamps, which emit a high-intensity white-light used in searchlights and the motion picture industry.

Rare-earth cobalt alloys were estimated to account for 2.5% of the permanent magnet market in 1977. Samarium remained the principal rare earth used in magnets. Samarium-cobalt permanent magnets were used in traveling wave tubes, alternators

and generators, line printers, and various missile applications. Research during the year was directed toward the use of mischmetal, which was more readily available at a lower cost, as a substitute for samarium in the magnets.

STOCKS

Stocks of rare earths in all forms, held by 14 rare-earth producing, processing, or consuming companies decreased 18% during 1977.

At yearend 1977, bastnäsite concentrate stocks held by the principal producer and four other processors had decreased slightly from the level at the beginning of the year. Monazite stocks decreased about 35% during the year; stocks of compounds and mixtures of rare earths decreased 23%, and stocks of mischmetal and high-purity metals decreased 50%.

PRICES

The average declared value of imported monazite from Malaysia and Australia decreased from $205 per short ton in 1976 to $164 per short ton in 1977. The average price per short ton of Australian monazite (minimum 60% REO including ThO_2) as quoted in Metal Bulletin (London) was $171 to $186 (A$154 to A$168) until June 1977 when it decreased to $166 to $176 (A$150 to A$159). Quoted prices for Malaysian xenotime, a yttrium-rich rare-earth mineral, remained at the 1976 level of $2 to $3 per pound c.i.f.

Prices for unleached, leached, and calcined bastnäsite containing 55% to 60%, 68% to 72%, and 85% to 90% REO, were increased from 50, 58, and 68 cents per pound REO, respectively, to 65, 70, and 80 cents per pound REO, respectively, at yearend. Yearend prices quoted in the American Metal Market for cerium and lanthanum concentrates were $0.85 and $1.05 per pound, respectively. Mischmetal prices, as quoted in the American Metal Market, were increased from $3.45 per pound at the beginning of the year to $3.95 per pound at yearend.

Rhodia, Inc. of Monmouth Junction, N.J., a subsidiary of Rhône-Poulenc S.A., quoted rare-earth oxide prices per kilogram (2.2046 pounds) f.o.b., New Brunswick, N.J. as follows:

Product	Percent purity	Quantity (kilograms)	Price
Erbium	96	50	$134.00
Europium	99.99	25	1,370.00
Gadolinium	99.99	500	84.75
Lanthanum	99.995	500	12.45
Neodymium	95	1,000	5.15
Praseodymium	96	1,000	30.75
Samarium	96	3,000	[1]18.40
Terbium	99.9	5	895.00
Thulium	99.9	1	3,300.00
Yttrium	99.99	500	73.00

[1]Price increases of 25% each were scheduled effective Sept. 1, 1978 and Jan. 1, 1979.

Nominal prices for various rare-earth materials also were quoted by Research Chemicals in dollars per pound as follows:

Element	Oxide[1]	Salts[2]	Metal[3]
Cerium	$7.50	$12.00	$50.00
Dysprosium	40.00	27.00	130.00
Erbium	45.00	27.00	160.00
Europium	700.00	325.00	3,000.00
Gadolinium	55.00	36.00	220.00
Holmium	120.00	80.00	300.00
Lanthanum	7.25	12.00	50.00
Lutetium	2,000.00	1,000.00	6,000.00
Neodymium	18.00	12.00	110.00
Praseodymium	32.00	16.00	170.00
Samarium	32.00	16.00	155.00
Terbium	350.00	175.00	845.00
Thulium	1,000.00	550.00	2,600.00
Ytterbium	85.00	70.00	240.00
Yttrium	30.00	18.00	150.00

[1]Minimum 99.9% purity, more than 1 pound.
[2]Minimum 99.9% purity, more than 1 pound; includes chlorides, nitrates, sulfates, oxalates, and acetates.
[3]Minimum 1 pound, ingot form.

FOREIGN TRADE

Exports of ferrocerium and other pyrophoric alloys during 1977 totaled 520,955 pounds valued at $1,042,669, compared with 119,792 pounds valued at $334,973 in 1976. During 1977, a threefold increase in exports of rare-earth and yttrium compounds went primarily to the Netherlands (31%), Japan (30%), the United Kingdom (9%), and Norway (7%). Total shipments of rare-earth and yttrium compounds were 1,931,245 pounds valued at $6,038,111.

Imports of monazite during 1977 totaled 5,480 tons, more than double the 2,103 tons received in 1976. Shipments from Australia totaled 3,149 tons.

Imports of cerium oxide tripled during the year to 2,441 pounds from 814 pounds in 1976. Receipts of other cerium compounds decreased 8% from 13,055 pounds in 1976 to 12,021 pounds in 1977. Imports of cerium ore from Australia during the year totaled 15,537 pounds valued at $28,629. Imports of ferrocerium and other pyrophoric alloys increased 14% to 45,876 pounds in 1977, compared with 40,259 pounds in 1976. The average unit value increased from $4.15 per pound in 1976 to $5.72 in 1977. There were no imports of cerium chloride during the year.

Receipts of mischmetal increased dramatically in 1977 to 498,653 pounds, with 44% of the shipments from Austria and 30% from Brazil. The average unit value of mischmetal receipts increased from $1.62 per pound in 1976 to $2.90 per pound in 1977. Receipts of other rare-earth metal alloys from the Federal Republic of Germany increased 10% during the year to 1,147 pounds valued at $23,508. Imports of rare-earth metals, including scandium and yttrium from the U.S.S.R. and the United Kingdom, increased 23% to 91 pounds in 1977, compared with 74 pounds in 1976.

During 1977, the tariff on cerium oxide, cerium chloride, and other cerium compounds was 15% ad valorem. The tariff on mischmetal was 50 cents per pound. There was a tariff of 5% ad valorem on rare-earth and yttrium metal. A tariff of 50 cents per pound plus 6% ad valorem was imposed on ferrocerium and other alloys. Imports of monazite and cerium concentrate remained duty free.

Table 1.—U.S. imports for consumption of monazite

Country	1973		1974		1975		1976		1977	
	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)	Quantity (short tons)	Value (thousands)
Australia	--	--	--	--	--	--	--	--	3,149	$491
Malaysia	1,991	$244	984	$154	2,462	$508	2,103	$431	2,331	409
Thailand	110	10	336	47	103	24	--	--	--	--
Total	2,101	254	1,320	201	2,565	532	2,103	431	5,480	900
REO content[e]	1,156	XX	726	XX	1,411	XX	1,157	XX	3,014	XX

[e]Estimate. XX Not applicable.

Table 2.—U.S. imports for consumption of rare-earth metals[1]

Country	1975		1976		1977	
	Pounds	Value	Pounds	Value	Pounds	Value
Germany, Federal Republic of	491	$22,592	--	--	--	--
U.S.S.R.	2,659	58,336	--	--	55	$1,875
United Kingdom	57	6,890	74	$9,131	36	9,933
Total	3,207	87,818	74	9,131	91	11,808

[1]Including scandium and yttrium.

WORLD REVIEW

World production of monazite increased 39% over the 1976 level to 17,287 tons in 1977. The largest increase occurred in Australia where production nearly doubled; other countries with increased production included Malaysia and Brazil. Bastnäsite production also increased during the year. France, Japan, the U.S.S.R., the United Kingdom, and the United States remained the only countries to produce a full range of rare-earth compounds and metals during the year.

Australia.—According to the Mineral Sands Producers' Association Ltd., monazite production in short tons was as follows:

State	1975	1976	1977
New South Wales	1,207	1,089	327
Queensland	685	227	683
Western Australia	3,252	3,698	8,636
Total	5,144	5,014	9,646

E. I. du Pont de Nemours & Co., Inc., increased its equity share in Allied Eneabba Pty., Ltd., from 25% to 40%. Allied Minerals N.L. decreased its share in the company from 75% to 60%. Allied Eneabba mined beach sands for monazite at Eneabba, in Western Australia.

Westralian Sands Ltd. merged with Western Mineral Sands Pty., Ltd. and Ilmenite Pty., both owned by Tioxide Australia Pty., Ltd. Tioxide owned 40% of Westralian with the option to increase its share to 51% when Westralian completed a $25 million ilmenite beneficiation plant near Bunbury.

The Wickham separation plant of Rutile and Zircon Mines (New Castle) Ltd. was reportedly inactive during most of the year. A 2-year modernization program at the

Table 3.—Monazite concentrates: World production, by country

(Short tons)

Country[1]	1975	1976	1977[p]
Australia	4,968	5,016	9,646
Brazil	[e]1,600	1,775	[e]2,000
India[e]	3,300	3,300	3,300
Korea, Republic of[e]	10	10	10
Malaysia[2]	3,621	2,071	[e]2,200
Nigeria[e]	20	20	20
Sri Lanka	[e]5	1	[e]5
Thailand	405		
United States	W	W	W
Zaire	328	265	106
Total	14,257	12,458	17,287

[e]Estimate. [p]Preliminary. W Withheld to avoid disclosing individual company confidential data.

[1]In addition to the countries listed, Indonesia and North Korea may produce monazite, but output, if any, is not reported quantitatively, and available general information is inadequate for formulation of reliable estimates of output levels.

[2]Exports.

Cable Sands Pty. Ltd. concentrator at Bunbury was underway.

France.—Rhône-Poulence S.A. announced plans to increase the polishing compounds production capacity at its La Rochelle rare-earth facility to 2,200 tons per year. Total rare earths production capacity at the plant in 1977 was 11,000 tons per year.

Senegal.—NL Industries, Inc. and the Government of Senegal agreed to undertake a feasibility study for the mining of titanium beach sands containing monazite along the Senegal coast. Completion of the study was scheduled for 1979.

United Kingdom.—Johnson Matthey Chemicals Ltd. acquired the remaining 50% equity in Rare Earth Products Ltd. from Rio-Tinto Zinc, Ltd. The plant, located at Widnes, produces rare-earth metals, oxides, and salts.

TECHNOLOGY

Photochemical separation of lanthanides by ultraviolet light from argon fluoride and krypton fluoride lasers was reported.[3] Europium, samarium, and ytterbium as well as elements of the actinide series may be recovered by the process at lower cost than the current separation methods. The new photochemical method also was expected to aid in the reprocessing of nuclear wastes.

Yttria-stabilized zirconium oxide was found to be suitable for use in electrolytic cells for the dissociation of water vapor into hydrogen and oxygen. Ytterbium oxide was found to result in more highly conductive materials for electrolytic cells, but the high cost of the oxide prohibited its use.[4]

The substitution of rare-earth cobalt magnets for Alnico permanent magnets reportedly resulted in lower magnet weight for the same flux density.[5] Response time in line actuators decreased as a result.

Research was conducted on rare-earth oxides as alloying agents for titanium.[6] Lutetium, neodymium, and dysprosium oxides were found to be acceptable for dispersion strengthening of titanium alloys. The addition of yttrium oxide was found to ease metallization of high-alumina bodies with tungsten.

A group of compounds including any one of several rare earths, rhodium, and boron in the general formula $RERh_4B_4$ were found to be superconductors which operate at higher temperatures and magnetic fields than superconducting materials currently in use.[7] Technological improvements and applications of the compounds were discussed.

Cerium was found to provide rust prevention control in steel.[8] The best rust prevention was achieved by fixing all sulfur in the steel as cerium manganese oxysulfide.

High optical sensitivity was observed in cerium-doped strontium barium niobate crystals.[9] Introduction of cerium increased the recording sensitivity and saturation efficiency of the crystals. Use of the crystals in high-speed, rewritable optical memory applications was expected.

The neodymium-doped glass laser at the Lawrence Livermore Laboratory in Livermore, Calif., began operation and proved to be the world's most powerful laser. Room temperature operation of a solid state laser in the blue spectral region was described.[10] The laser used a 0.2% praseodymium-doped LiYF crystal.

Palladium-yttrium alloys were shown to be more permeable to hydrogen than palladium-silver alloys. The alloy was also found to be less susceptible to poisoning by oxidation. More effective utilization of palladium-yttrium alloys in hydrogen diffusion alloys was planned.[11]

Because of their predictable geochemical properties, rare-earth elements were used as tracers of water-rock interactions in hydrothermal systems.[12] The lanthanides reflect changes in their distribution pattern within the deposits depending on the sequence of reactions in the systems.

The Bureau of Mines continued research on rare-earth alloy catalysts, rare-earth oxides additives in refractories, and mischmetal as a replacement for samarium in samarium-cobalt permanent magnets.

A patent was issued for obtaining fluorine-free cerium from bastnäsite ore that had been leached with nitric acid.[13] A patent was issued for an improved reagent for use in the solvent extraction separation of rare earths and yttrium which would permit higher feed solution concentration.[14]

The 13th Rare Earth Research Conference was held at Oglesbay Park, W.Va., in October. The program reviewed all phases of rare-earth research and development and included sessions on solid-state science, spectroscopy, and bioinorganic chemistry. Publication of the proceedings at the October meeting was planned by the Rare Earth Information Center of Ames, Iowa.

[1]Mineral specialist, Division of Nonferrous Metals.

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