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THE RARE EARTHS: INDUSTRY AND APPLICATIONS

by BRUNO CAMPANA *

Summary

Although the following work is 2 years old, it can be regarded as a fairly comprehensive description of Rare Earths applications and market.

Definition, properties, industrial significance, producers and indicative prices of Rare Earths minerals and compounds of various purity are given, on the basis of American, European and Japanese sources, and on the light of investigations by the writer's Geological and Geophysical Office in Australia.

The growing importance of Rare Earths products is shown. They are finding increasing applications in the *petrochemical industry* (cracking and reforming catalysts); as *catalysts for gas disposal to prevent air pollution*; as *catalysts for synthesis of organic compounds*; as *fuel elements in the atomic energy industry* (samarium, europium, gadolinium, dysprosium) and *as control rods and shielding elements*; as *phosphor for colour television* (yttrium and europium); in *metallurgy* (steel, ductile iron, magnesium, coppers, bronzes, aluminium, refractory metals, cobalt-base alloys); in the *glass industry*; in *ceramic manufacture*; in the *lighting, enamels and colour industry* and in the *microwave field* (garnets as microwave device and Rare Earths metal-cobalt compounds as permanent magnet, lasers, etc.).

1. DEFINITION OF RARE EARTHS

The term Rare Earths has been used both in technological and commercial context to designate a group of 15 elements, whose atomic numbers range from 57 to 71. More scientifically they are also called *lanthanides*, and have been described and subdivided as follows:

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TABLE II

Atomic Number	Name	Symbol	Group Division
57	Lanthanum	La	"Light R.E." group or Cerium Group ("Ceriterden")
58	Cerium	Ce	
59	Praseodymium	Pr	
60	Neodymium	Nd	
61	Prometium	Pm	
62	Samarium	Sm	
63	Europium	Eu	
64	Gadolinium	Gd	"Heavy R.E." group or Yttrium Group ("Yttererden")
65	Terbium	Te	
66	Dysprosium	Dy	
67	Holmium	Ho	
68	Erbium	Er	
69	Thulium	Tm	
70	Ytterbium	Yb	
71	Lutetium	Lu	

Yttrium is also generally considered with the R.E. sequence (its atomic and ionic radii lying close to the corresponding value for terbium and dysprosium). Its atomic number is 39, and occurs generally in association with the "heavy" R.E. sub-group, particularly in xenotime.

2. PROPERTIES AND FIELDS OF APPLICATIONS

It was formerly believed that all the elements of the R.E. group had very similar properties; but modern technology has shown that in fact the R.E. physical properties differ widely. This is particularly true for:

Optical properties which have led for instance to various and important applications to phosphor for colour television (yttrium and europium);

Magnetic properties, applied to magnetic material (R.E. garnets as a microwave device and R.E. metal-cobalt compounds as permanent magnet);

Nuclear properties, with various applications to atomic energy industry (samarium, europium, gadolinium, dysprosium as fuel elements, and also as control rods and shielding elements);

Chemical properties, with applications to:

1. Cracking and reforming catalysts for petrochemical industry.
2. Catalysts for gas disposal to prevent air pollution.
3. Catalysts for synthesis of organic compounds.

Also to be mentioned in this context the growing R.E. applications in *metallurgy* (steel, ductile iron, magnesium, coppers, bronzes, aluminium and cobalt-base alloys and refrac-

tory metals), in the *glass industry*, in the *ceramic industry*, in the *lighting*, enamels, *colours industry* and others.

Table III shows the main R.E. applications to date. The various uses are quantified below, together with their possible growth in the next 20 years.

3. THE RARE EARTHS MARKET PRODUCTS

The accurate assessment on a world basis of present uses and future developments of the R.E. elements is not readily achieved. Technological and economics data are published throughout the world in many reviews, reports, statistical bulletins etc., but the very structure of the R.E. industry, the numerous and changing fields of applications, and the great variations of prices (in relation with the forms of marketing, degree of concentration and purity of the R.E. compounds or metals) leave room for uncertainties in accurately assessing the present state and in predicting the future course of this industry.

In this report an attempt is made to assess the R.E. sources and the more important market product such as:

- (a) *Primary R.E. chemicals*, produced from minerals cracking (generally as *R.E. chloride* and *sulphate*).
- (b) *R.E. mixed chemicals: fluoride, nitrate, carbonate, acetate, oxides, hydrate, oxalate*.
- (c) *Partly separated or concentrated R.E. chemicals*.
- (d) *High purity oxides*.
- (e) *R.E. misch-metals and metals*.

The commercial value of a given R.E. product varies greatly, according to the form of its marketing, i.e. the quantity sold and the degree of processing, concentration, and purity of the products. Thus the price of yttrium (1971) is:

- as oxide in the mineral *xenotime*
(minimum 25% Y_2O_3) \$ 1.60 per pound
- as separated oxide (*95% purity*)
(in 2 to 99 lb package) \$ 40.00 per pound
- as pure oxide (*99.9% purity*) \$ 60.00 per pound

For europium the variations are even more drastic:

- as oxide in *xenotime* (0.2–0.4% europium oxide) nil
- as oxide in 15% concentration
(commercial grade) \$ 200 per pound
- as oxide 99.9% purity (phosphor grade) \$ 600 per pound

These great variations are common to all the R.E. elements of the “heavy group”; but are also found, in the market price of the “light” group. Thus the cumulated price of cerium, lanthanum praseodymium, neodymium are:

- as oxides in the mineral *monazite* \$ 0.08 per pound
- as separated oxides
(99% purity, in 2–99 lb package) approx. \$ 70.00 per pound

These examples show that *the profitability of the R.E. industry is essentially based on:*
the low cost of the mineral sources of R.E.
the high price of the processed products

In this report an attempt is also made to quantify the present consumption of the various R.E. products, taking into account the quantities used and the selling prices of the last 3 years.

As far as possible the main R.E. producers and processors of R.E. shall be indicated.

The possible growth of the R.E. industry in the next 20 years shall be outlined, together with a breakdown of present and future R.E. consumption in the various fields.

4. THE RARE EARTHS SOURCES. MAIN RAW MATERIALS, PRODUCERS AND PRICES

4.1. Sources of "light" Rare Earths

Sources of the light Rare Earths (Cerium Group) are virtually confined to the minerals *bastnaesite* and *monazite*. Their composition is given below (table IV).

4.1.1. *Bastnaesite* is a R.E. fluo-carbonate, with up to 70% R.E.O. in concentrated ore, or 7–8% R.E.O. in the ore as mined. The world's largest deposit of *bastnaesite* is mined at Mountain Pass in California, by Molybdenum Corporation of America; this Company became in 1965 (with the europium oxide facilities going into operation) the world's largest supplier of R.E. source-materials and chemicals such as:

- *bastnaesite* concentrates (by flotation or leaching of *bastnaesite* ore: 55–72% R.E.O.–
From roasted or calcined *bastnaesite* ore: 85–90% R.E.O.).
- lanthanum hydrate (60% La_2O_3)
- cerium and neodymium – praseodymium oxides (80%).
- samarium – gadolinium oxide (65%)
- europium oxide (15% minimum?)

Production

It is difficult to further quantify the growth of the Molybdenum Corporation in the field of Rare-Earths at Mountain Pass mine. It can be safely stated that R.E. represent in fact the growing field of this company, as shown by the following report: (1)

TABLE IV

R.E.O.		BASTNAESITE CALIFORNIA	MONAZITE AUSTRALIA	XENOTIME MALAYSIA	XENOTIME JOHN GALT	URANIUM RESIDUES	
		%	%	%	%	%	
(/)	"Light Group"	Lanthanum	32.0	20.2	0.5	0.2	0.8
(/)		Cerium	49.0	45.3	5.0	0.2	3.7
(/)		Praseodymium	4.4	5.4	0.7	0.1	1.0
(/)		Neodymium	13.5	18.3	2.2	0.3	4.1
		Samarium	0.5	4.6	1.9	1.0	4.5
(/)		Europium	0.1	0.05	0.2	0.4	0.2
(/)	"Heavy Group"	Gadolinium	0.3	2.0	4.0	3.2	8.5
		Terbium			1.0	1.1	1.2
		Dysprosium			8.7	9.2	11.2
		Holmium			2.1	2.4	2.6
		Erbium			5.4	7.1	5.5
		Thulium	0.1	2.0	0.9	1.1	0.9
		Ytterbium			6.2	6.1	4.0
		Lutetium			0.4	0.9	0.4
(/)		Yttrium			60.8	66.4	51.4
		Thorium	nil	4.8		nil	nil

(/) - Main Commercial R.E.

- Composition of the R.E. sources: *bastnaesite*, *monazite*, *xenotime* and uranium residues (Percent of total R.E.O.)

(1) "Mining Journal", Vol. 280, No. 7169, P. 27, London, 12/1/1973.

“The most recent report from Molybdenum Corporation of America points out the strong growth for the so called Rare Earth minerals. The company has estimated that the value of sales in this sector exceeded \$ 15 million last year. This would be an advance of 25 per cent on the 1971 results . . . and reflects to a notable extent the use of rare earths additives in the manufacture of high strength, low alloy steel.

Molycorp has also drawn attention to the expansion of europium and yttrium sale for the production of colour television tube phosphor. It would seem that previous overstocking of these phosphors by industry has now been worked off. The outlook for this usage seems bright.”

These data on what appears to be the largest R.E. producer in the world, are significant in two respects: they show on the one hand *the growing role of the R.E. industry*, and on the other hand that *success in this field is strictly related to a vertical integration of production*: from the mineral raw materials with negligible to low commercial value, to refined products of high purity, running into hundreds of dollars per pound.

In 1969 Molybdenum Corporation produced 13,650 tons of R.E.O. in bastnaesite concentrates from 259,000 tons of ore. The production was obtained from the Mountain Pass mine, in California, where they yearly production capacity has been *40 million pounds* of R.E.O. until 1972. “Plant expansion, scheduled for completion later this year, . . . will increase production capacity to around *60 million pounds/year*. Production at Mountain Pass in 1973 is planned at *48 million pounds* of R.E.O., double the production of 24 million pounds last year.” (1)

This would imply a mining output of *300,000 tons of ore*. Assuming constant prices and a constant production ratio between the various market products, the Rare Earths production (ore concentrate + chemicals) of Molybdenum Corporation at Mountain Pass would reach \$ 25–30 millions.

Prices of bastnaesite concentrates

In 1969 the price of unleached bastnaesite ore with 55 to 65% of R.E.O. was \$ 0.30 per pound of contained R.E.O. Leached bastnaesite ore, with 68–72% R.E.O., was quoted at \$ 0.35 per pound of contained R.E.O., while calcined bastnaesite ore with 88 to 92% R.E.O. was sold at \$ 0.40 per pound of contained R.E.O. (2)

4.1.2. *Monazite* is a thorium-bearing R.E. phosphate, won as a by product from alluvial tin mining and other placer deposits (heavy minerals sands etc.). Pure monazite concentrate contains almost 70% combined R.E.O. However the quality of concentration varies, so that the commercial concentrate contains in fact between *55% and 66%* R.E.O. Table IV gives its composition, together with the composition of bastnaesite and xenotime.

Production

India, Malaysia, Australia and Brazil are the world's main producers of monazite. In 1969 the world production reaches *12,053 tons*, geographically distributed as follows (U.S.S.R. and China not included):

Although monazite contains a little yttrium (2–3%), it is essentially a raw material for the “light” R.E. elements (see table IV). There is some disagreement on the respective merits of monazite and bastnaesite as a source of the R.E. elements. Some producers use both minerals, but reports from a leading European R.E. producer indicates that monazite is clearly favoured, in spite of its thorium content. In fact most of the European producers appear to use monazite as a R.E. source.

(1) “Mining Journal”, Vol. 280, N. 7172, P. 97, London, 2/2/1973

(2) Parker, J.G. “Rare Earths Minerals and Metals” – Mineral Yearbook, Vol. I–II, P. 954. U.S. Dept. of Interior, 1969

TABLE V

	Tons of Monazite concentrate 1969	Estimated R.E.O. Lb.
India	3,850	
Australia	3,452	
Malaysia	2,400	
Brazil	2,203	
Others	148	
Total	<u>12,053</u>	<u>15,000,000</u>

Of the four dominant monazite producers (India, Australia, Brazil and Malaysia), Australia and Malaysia export ore concentrate only.

India processes most of its monazite production, mainly for Rare-Earth chloride, carbonate and hydroxide and thorium hydroxide. Already in 1962 the processing plant at Alwaye had a capacity of 3000 tons of monazite per year.

Brazil is also processing part of her monazite production. The plant run by the Comissão Nacional de Energia Nuclear has a capacity of 2,000 tons of monazite a year, and its products include R.E. chloride and thorium hydroxide. Another company produces misch-metals, and a third organization processes monazite to rare-earth chloride, mostly for exportation to Europe.

Price of monazite concentrate. Prices of Australian monazite concentrate with a minimum of 55% R.E.O. varied from about \$ 160 to \$ 200 in the last 3 years, equal to \$ 0.08–0.09 per pound of R.E.O. contained.

4.2. Sources of "heavy" Rare Earths

Sources of R.E. of the "heavy group" are practically confined to xenotime and residues of spent uranium solutions.

4.2.1. Xenotime

Primary deposits of xenotime (i.e. deposits *in situ*), have not been found, except at John Galt, in Western Australia.

Production

So far this mineral has been won in Malaysia and also in Australia, as a by-product of tin and beach sand operations, and is generally considered as the best source of yttrium, even though most of the American yttrium oxide production derives from residues from the Blind River Uranium Mines, in Canada.

The Japanese market on the other hand is largely supplied by xenotime, recovered as a by-product of placer tin mining in Malaysia.

The Malaysian production has varied in the last 4 years from perhaps 50 to to 150 tons of xenotime, containing about 30,000 to 90,000 pounds of yttrium oxide.

Price

Malaysian xenotime concentrate with a minimum of 25% yttrium oxide (Y_2O_3) has varied in the last 3 years in London from \$ 2 to \$ 4 per pound of oxide contained. Japanese R.E. producers quote at present \$ 1.60 per pound, minimum content 30% Y_2O_3 .

4.2.2. Uranium Residues

These form the second important sources of R.E. of the "heavy" group. The residues

were recovered commercially in 1965, when yttrium came into substantial demand for colour television.

Production

A production capacity of about 300,000 pounds of yttrium oxides was established, leading to overstocking until 1970–71. At present it appears that overstocking has been worked off. (1)

Prices

In 1966–69 Canadian residues were selling \$ 12 per pound of yttrium oxide contained (2).

4.3. World's Reserves

The following data (Table VI) on the main world reserves of R.E. raw materials have been compiled from various publications. The corresponding content of R.E.O. are also indicated, neglecting those materials which are at present uneconomic as a source of a given R.E. or yttrium, (such as bastnaesite, monazite, euxenite or loparite for yttrium production).

4.4. The Australian R.E. Reserves in the World's Market

It is of great interest, for the development of the John Galt R.E. deposit, to consider the Australian R.E. reserves as a whole, and to compare them with the resources of producers.

Table V and Table VI indicate that the Australian R.E. reserves are both large and diversified. Indeed no other country can offer such a complete suite of high-grade R.E. reserves. Australia is already the major producer of "light" R.E. raw material, in form of *monazite concentrate* which European experts favour as a source of "light" R.E. With the discovery of the John Galt Xenotime, Australia has also acquired a unique position as a potential producer of yttrium and of europium, together with the complete suite of the "heavy" R.E. elements.

The John Galt primary deposit is regarded as unique, at least in the non-communist world, due to the fact that xenotime occurs as concentration in quartz veins, and not as scattered accessory minerals of granites or pegmatites. Its value as a potential major source of yttrium, is enhanced by the presence of europium in a percentage that appears at present the highest known, being 3–4 times the europium content of bastnaesite and twice the europium content of Canadian uranium residues.

In spite of these unique assets in R.E. resources, there is no facility to process R.E. material in Australia, beyond the stage of ore concentrate. It would then appear that, in a growing R.E. industry, processing can be envisaged in Australia as part of the refining stage which logically follows the discovery of important mineral resources in a country that is technologically advanced. This possible development of the Australian R.E. industry is discussed below.

(1) "Mining Journal", Vol. 280, No. 7169, P. 27, London 12/1/1973

(2) "Trends in Usage of Rare Earths" – Report by the National Material Advisory Board. Publ. NMAB-266. Washington, D.C., 1970

TABLE VI

Main world resources of rare earth minerals (economically processable at present)

COUNTRY	MINERAL	RARE EARTH OXIDES		YTTRIUM OXIDE (SHORT TONS)	EUROPIUM CONTENT %
		"LIGHT" GROUP: LANTHANUM TO GADOLINIUM (SHORT TONS)	"HEAVY" GROUP: TERBIUM TO LUTETIUM (SHORT TONS)		
U.S. California	Bastnaesite	270,000 (1)			0.1
Florida					
Georgia	Monazite	700,000			
India	Monazite	3,000,000			
Brazil	Monazite	180,000			
Egypt	Monazite	120,000			
Canada	Uranium residues	2,400	2,500	5,130	0.2
Australia	Monazite	+ 500,000			
Australia	Mary Kathleen Allanite	Important			
Australia	John Galt Xenotime (2)		3,700	8,600	0.4
Malaysia	Xenotime		???		

(1) Proven by pattern-drilling. There are in addition substantially larger quantities indicated by scout-drilling (Parker J.G., 1969).

(2) Reserves are geologically indicated and inferred.

5. THE R.E. MARKET PRODUCTS AND PRICES

The R.E. raw materials (bastnaesite, monazite, xenotime and residues of uranium solution) are processed and brought into market under various trading names, and especially by *purity designation*. Basically they can be divided into 5 groupes:

- (A) Primary R.E. chemicals
- (B) Mixed R.E. chemicals
- (C) Partly separated or concentrated chemicals
- (D) Oxides and high-purity oxides
- (E) Misch-metal.

5.1. Primary R.E. chemicals

are the products of cracking *bastnaesite* or *monazite* concentrates, which are converted into R.E. chloride and R.E. double sulphate.

R.E. Chloride is the basic feed material for the production of most of the R.E. compounds: R.E. fluoride, misch-metals, etc. Therefore this product, as such, commands a very important market. India and Brazil are producing a substantial tonnage for export.

R.E. double sulphate is readily converted into R.E. Chloride, and can be stored as an intermediary product to other R.E. chemicals.

Prices R.E. Chloride has been selling for \$ 0.22 – \$ 0.26 per pound, (equivalent to \$ 0.48 – \$ 0.56 per pound of R.E.O.), against \$ 0.08–0.09 in monazite concentrate.

5.2. *Mixed R.E. Chemicals*

(of the so called “commercial grade”) are available in a variety of forms, such as *fluoride, nitrate, carbonate, acetate, oxalate* and *hydrate*.

Prices range from 0.60 to \$ 1.00 per pound on an oxide equivalent basis.

The following were the prices (retail) quoted by the American Potash and Chemical Co. (1971):

TABLE VII

	PRICE PER POUND			
	1-4 Lbs	5-9 Lbs	10-49 Lbs	50-99 Lbs
Rare Earth Chloride	\$0.62	\$0.52	\$0.42	\$0.39
Rare Earth Nitrate	1.44	1.20	0.96	0.88
Rare Earth Acetate	1.44	1.20	0.96	0.88
Rare Earth Fluoride	2.13	1.77	1.42	1.30
Rare Earth Oxalate	2.34	1.95	1.56	1.43

5.3. *Partly separated or concentrated R.E. chemicals*

These are produced in a variety of composition and grade, with one R.E. salt (or group of R.E. salts) prevailing on the others, or concentrated to the point of becoming commercial as such. The more important products, and related prices, of this category are the following.

Cerium with 90% Ce content is available as an impure cerium hydrate, sold at \$ 0.45 per pound of contained cerium oxide, (as pure cerium hydrate is sold at \$ 1.00 to \$ 1.50 per pound).

The following were the prices (retail) quoted in 1971:

TABLE VIII

	PRICE PER POUND			
	1-4 Lbs	5-9 Lbs	10-49 Lbs	50-99 Lbs
Ceric Hydrate, com.	\$2.59	\$2.16	\$1.73	\$1.58
Ceric Hydrate, com.	3.13	2.61	2.09	1.91
Ceric Hydrate, purified	8.10	6.75	5.40	4.95
Ceric Oxide, com.	3.30	2.75	2.20	1.95
Ceric Oxide, purified	9.00	7.50	6.00	5.50
Cerous oxalate, purified	4.95	4.12	3.30	3.03
Cerous Chloride, com.	4.50	3.75	3.00	2.75
Cerous Chloride, purified	6.75	5.63	4.50	3.58
Cerous Fluoride, com.	5.40	4.50	3.60	3.30
Cerous Fluoride, purified	7.92	6.60	5.28	4.84
Cerous Nitrate, purified	4.50	3.75	3.00	2.75
Ceric Ammonium Nitrate, com.	2.70	2.25	1.80	1.65
Ceric Ammonium Sulfate, com.	2.70	2.25	1.80	1.65
Ceric Sulfate	2.70	2.25	1.80	1.65
Rare Earth Sodium Sulfate...	0.54	0.45	0.36	0.33
Rare Earth Hydrate	1.32	1.10	0.88	0.80
Rare Earth Carbonate	1.73	1.44	1.15	1.06
Rare Earth Oxide	2.70	2.25	1.80	1.65

"*Didymium*" is produced as a by-product automatically when 90% cerium oxide is made. It is then used as a source of lanthanum, praseodymium and neodymium, but is also used as such in catalysts.

Prices range from \$ 0.60 to \$ 1.00 per pound. The following were the prices (retail) quoted in 1971:

TABLE IX

	PRICE PER POUND			
	1-4 Lbs	5-9 Lbs	10-49 Lbs	50-99 Lbs
Didymium Chloride	\$ 0.63	\$ 0.53	\$ 0.42	\$ 0.39
Didymium Carbonate	1.53	1.28	1.02	0.95
Didymium Oxide	2.34	1.95	1.56	1.43
Didymium Hydrate	2.25	1.88	1.50	1.38
Didymium Nitrate	1.17	0.98	0.78	0.72
Didymium Acetate	1.80	1.50	1.20	1.10
Didymium Fluoride	2.14	1.79	1.43	1.31

Lanthanum, Neodymium and Yttrium chemicals were sold in 1971–1972 at the following prices:

TABLE X

	PRICE PER POUND			
	1-4 Lbs	5-9 Lbs	10-49 Lbs	50-99 Lbs
Lanthanum Ammonium Nitrate	\$ 3.15	\$ 2.63	\$ 2.10	\$ 1.93
Lanthanum Oxalate	4.81	4.43	3.54	3.25
Lanthanum Chloride	4.95	4.12	3.30	3.03
Lanthanum Nitrate	4.95	4.12	3.30	3.03
Lanthanum Acetate	10.80	9.00	7.20	6.60
Lanthanum Hydrate	10.80	9.00	7.20	6.60
Lanthanum Carbonate	10.80	9.00	7.20	6.60
Lanthanum Fluoride	12.60	10.50	8.40	7.70
Lanthanum Sulfate	5.40	4.50	3.60	3.30
Neodymium Oxalate, 95%....	2.52	2.10	1.68	1.54
Neodymium Oxalate, 95%	18.00	15.00	12.00	11.00
Neodymium Oxide, 65%-70%	4.14	3.45	2.76	2.53
Neodymium Oxide, 95%	21.60	18.00	14.40	13.20
Neodymium Carbonate, 65-70%	2.25	1.88	1.50	1.38
Neodymium Fluoride, 65-70%	2.52	2.10	1.68	1.54
Yttrium Oxalate, 60-85%...(♯)	18.00	15.00	12.00	11.00
Yttrium Oxide, 60-85%....(♯)	36.00	30.00	24.00	22.00
Yttrium Nitrate, 60-85%...(♯)	21.60	18.00	14.40	13.20
Yttrium Chloride, 60-85%...(♯)	21.60	18.00	14.40	13.20

(♯) Prices on basis 100% purity; actual price based on analysis.

5.4. Oxides and High-Purity Oxides

It is estimated that in terms of value, oxides form about 40–45% of the total sale of R.E. chemicals and compounds.

Yttrium and Europium Oxides are largely responsible for the predominant position of high-purity oxides in the R.E. field. Thus, in 1969, the value of the Rare Earths shipments in the U.S. was nearly \$ 19 million, to which *yttrium* and *europium oxides* contributed for about 7 million. The use of these two oxides in the colour television field has been the main factor in this development, but R.E. oxide, though still comparatively expensive, are receiving increased usates in other fields (See Table XIII).

The price (retail, 1971) of oxides of various purity are giben in table XI.

Europium Oxide. For 99.9% purity (phosphor grade), europium is sold at \$ 475 to \$ 900 per pound (according to order). For 15% purity it is sold to high-purity processors at \$ 200 per pound. (Japanese quotation, November 1972).

5.5. Misch-metal

Misch-metal is a metallic alloy which consists of a crude mixture of cerium, lanthanum,

and other light R.E. metals, in the approximate ratios in which they are found in monazite concentrate. It is obtained from mixed R.E. chlorides by electrolytic process. It is used mainly as an addition agent for nodular iron, and especially for the manufacture of lighter flint, due to the pyrophoric property of mischmetal.

Its price in 1969 was of the order of \$ 3.00 per pound.

TABLE XI

		Min Pkg. Gms.	Per Gm. 1 to 99 Gms.	Per Gm. 100 Gm. Pkg.	Per Lb. 1 Lb. Pkg.	Per Lb. 2-99 Lb. Pkg.
Lanthanum Oxide			\$ 10.53	\$ 8.77	\$ 7.02	\$ 6.43
Ceric Oxide.....	99.9%		9.00	7.50	6.00	5.50
Neodymium Oxide.....	99%	10	0.15	0.13	35.00	32.50
ditto	99.9%	10	0.20	0.15	40.00	37.50
Praseodymium Oxide.....	85%	10	0.15	0.13	27.00	24.00
ditto	90%	10	0.18	0.14	28.65	25.45
ditto	99%	10	0.20	0.15	40.00	37.50
ditto	99.9%	10	0.25	0.20	50.00	40.00
Samarium Oxide.....	80%	10	0.15	0.13	30.00	27.00
ditto	90%	10	0.18	0.15	37.50	30.00
ditto	95%	10	0.20	0.18	45.00	36.00
ditto	99%	10	0.25	0.20	50.00	40.00
ditto	99.9%	10	0.30	0.25	60.00	50.00
Europium Oxide.....	15%					200.00*
ditto	99%	1	4.50	1.65		
ditto	99.9%	1	5.50	2.00	750.00	600.00
Gadolinium Oxide.....	80%	5	0.20	0.18	45.00	36.00
ditto	90%	5	0.25	0.20	50.00	40.00
ditto	99%	5	0.55	0.40	105.00	85.00
ditto	99.9%	5	0.65	0.43	125.00	100.00
Samarium-Gadolinium Oxide	(45%-45%)	10	0.18	0.15	37.50	30.00
Terbium Oxide.....	99%	1	2.00	1.50	850.00	675.00
ditto	99.9%	1	2.50	2.00	900.00	720.00
Dysprosium Oxide.....	99%	5	0.55	0.40	105.00	85.00
ditto	99.9%	5	0.65	0.43	125.00	100.00
Erbium Oxide.....	99%	5	0.55	0.40	105.00	85.00
ditto	99.9%	5	0.65	0.43	125.00	100.00
Yttrium Oxide.....	95%	10	0.25	0.20	50.00	40.00
ditto	99%	10	0.30	0.20	60.00	50.00
ditto	99.9%	10	0.35	0.25	70.00	60.00
ditto	99.99%	10	0.40	0.30	80.00	75.00
ditto	99.999%	10	0.60	0.45	120.00	115.00
ditto	99.9999%	10	1.50	1.20	300.00	295.00
Holmium Oxide.....	99%	5	0.55	0.40	105.00	85.00
ditto	99.9%	5	0.65	0.43	125.00	100.00
Ytterbium Oxide.....	99%	5	0.70	0.53	160.00	128.00
ditto	99.9%	5	0.90	0.70	200.00	160.00
Thulium Oxide.....	99.9%	1	5.00	4.00	1800.00	
Lutetium Oxide.....	99.9%	1	6.70	5.00	2250.00	

* Quotation of November 1972 by major Japanese processors. The quoted price is the price of imported lower purity (15%) Europium, which they refine to phosphor grade (99.9%).

6. RARE EARTHS CONSUMPTION ESTIMATED GROWTH AND PROCESSORS

Statistical data available do not allow, at this stage, a very accurate account of the world's consumption of R.E. It is however possible to quantify the *United States R.E. production*, using reliable data for the year 1969.

Also data on possible growth until 1975, and twenty five year projections have been published by American specialists (1).

Tables XII, XIII and XIV are compiled from this source.

The Japanese R.E. consumption is also approximately known, although only in terms of imported products, (generally unprocessed material or low-grade chemicals). It is however difficult to obtain data on the "added value" by Japanese processors.

On the European market, only a small amount of information could be assembled for the purpose of this report. Lacking published statistical data, an accurate survey can only be achieved by direct enquiries with R.E. processors and consumers.

6.1. *The U.S.A. Consumption and Estimated Growths*

6.1.1. *Mixed R.E. chemicals and low-purity separated compounds*

Table XII gives the estimated consumption of mixed R.E. in the U.S.A. for the year 1969, together with the estimated growth until 1975. From this table it is seen that:

The total consumption of mixed R.E. chemicals and low-purity compounds in *terms of R.E. oxide content*, is estimated at *15,616,000 pounds*. Its market value is estimated at \$ 15,000,000.

The Mixed R.E. Chemicals used at present are mainly those of the light (Cerium) group derived from bastnaesite or monazite. There appears to be a growing demand for R.E. of the heavy (Yttrium) group in the field of magnesium-based alloy.

The main consumption of *mixed R.E. chemicals* in terms of weight, is in the field of petroleum catalysts, which uses about 2/3 of the total consumption. At present R.E. usage for this purpose is almost entirely confined to the United States. Therefore there is probably a growing demand in other countries in the near future.

6.1.2. *Separated R.E. Compounds – High Purity Oxides*

The U.S.A. consumption of *separated R.E. compounds* in 1969, and its estimated growth in 1975, are shown in Table XIII.

The following remarks are pertinent.

As separated R.E. compounds, yttrium, europium and gadolinium oxide are by far the dominant compounds of the market. It is estimated that their value reaches *80% of the separated R.E. market*, and about *40% of the aggregated R.E. market value* (i.e. of mixed R.E. chemicals and separated R.E. compounds).

This is due to the high price of separated yttrium europium and gadolinium oxide (Table XI) and their large usages as phosphors for colour television.

As stated above, in 1969 yttrium and europium oxide contributed with about \$ 7 million, out of a total of \$ 19 million R.E. domestic shipments in the United States. However, by weight, these two oxides represented only 1% of the total.

The market growth for phosphor yttrium and europium is shown in Table XIII and XIV. It is seen that in the U.S.A. it should pass from 117,000 pounds in 1969 to about 200,000 pounds in 1975, (table XIII) and would reach 1,260,000 pounds in 1995.

(1) "Trends in Usage of Rare Eraths" – Report by the National Materials Advisory Board – Publ. NMAB-266, Washington, D.C., 1970.

TABLE XII

U.S.A. ESTIMATED PRODUCTION AND USES OF MIXED R.E. CHEMICALS (IN POUND OF R.E.O. EQUIVALENT)

USES	TYPE OF R.E.	1969 POUNDS	1970 POUNDS	1971 POUNDS	1972 POUNDS	1973 POUNDS	1974 POUNDS	1975 POUNDS
(1) <u>Metallurgical</u>								
• Lighter Flint	Misch metal	300,000	310,000	320,000	330,000	340,000	350,000	360,000
• Ductile Iron	Mixed R.E.	1,500,000	1,700,000	1,900,000	2,100,000	2,300,000	2,500,000	2,800,000
• Magnesium Base-alloys	(a) Light R.E. (b) Heavy R.E.	40,000 1,000	50,000 3,000	60,000 10,000	75,000 25,000	90,000 60,000	110,000 110,000	130,000 180,000
• Permanent magnet	Misch metal	0	38,000	113,000	189,000	302,000	377,000	566,000
• Steels	Mixed R.E.	250,000	300,000	400,000	600,000	1,000,000	1,500,000	2,000,000
• Coppers, bronzes aluminium and cobalt-base alloys	Mixed R.E.	25,000	35,000	45,000	60,000	75,000	100,000	425,000
High Temperature alloys since 1975								
(2) <u>Non-metallurgical</u>								
• Petroleum Catalysts	Mixed R.E.	10,400,000	10,400,000	11,000,000	11,500,000	11,700,000	12,000,000	12,200,000
• Glass Polishing	Mixed R.E.	2,000,000	2,000,000	2,300,000	2,300,000	2,500,000	2,500,000	2,700,000
• Carbon arc	Mixed R.E.	800,000	815,000	8,300,000	850,000	870,000	900,000	950,000
• Miscellaneous	Mixed R.E.	300,000	300,000	430,000	450,000	500,000	550,000	600,000
<u>TOTAL ESTIMATED CONSUMPTION OF MIXED RARE EARTH</u>		15,616,000	15,951,000	17,378,000	18,479,000	19,737,000	20,997,000	22,911,000

TABLE XIII

ESTIMATED U.S.A. CONSUMPTION OF SEPARATED R.E. (in pound of R.E.O. equivalent) IN 1969 AND ESTIMATED GROWTH FROM 1969 TO 1975

USES	TYPE OF ELEMENT SEPARATED R.E.O.	1969	1970	1971	1972	1973	1974	1975
(a) <u>Optical</u>								
. Laser		no data available						
. Phosphors (Television)	1. Yttrium 2. Europium 3. Gadolinium	108,000 9,000 19,000	110,000 10,000 18,000	124,000 11,000 21,000	139,000 12,000 23,000	154,000 13,000 26,000	171,000 15,000 28,000	190,000 17,000 30,000
(b) <u>Magnetic</u>								
. Metallic	Yttrium, Lanthanum, Cerium, Pras, and Samarium		230	350	470	580	700	1,200
. Non-metallic	Yttrium	no data available						
(c) <u>Electrical</u>	Lanthanum, Yttrium Cerium	no data available						
(d) <u>Ceramic</u>								
. Glass additives	(1) Cerium (2) Lanthanum (3) Neodymium	700,000 50,000 10,000	750,000 51,000 10,000	800,000 53,000 11,000	850,000 56,000 11,000	900,000 60,000 12,000	1,000,000 65,000 12,000	1,100,000 75,000 13,000
. Glasses and pigments	Praseodymium	30,000	31,000	33,000	35,000	37,000	40,000	43,000
. Refractories	Yttrium, Cerium							
(e) <u>Metals and alloys</u>								
. Nuclear Energy	Europium } Gadolinium } Samarium } Dysprosium } Erbium }	100	160	400	560	769	980	1,200
. Super alloys	Lanthanum } Cerium } Yttrium }	2,000	5,000	10,000	17,000	25,000	35,000	50,000
(f) <u>Scientific Research</u>	All R.E.O.	25,000	26,000	28,000	31,400	34,600	38,000	45,000
TOTAL		943,100	1,011,390	1,091,750	1,175,430	1,262,949	1,405,680	1,565,400

It is believed that the growth should be even greater in the rest of the world, due to a larger market and a less advanced production of colour television devices.

6.2. *Estimate of U.S.A. Rare Earths growth up to 1995*

American specialists have tentatively estimated the growth of the R.E. industry during the periode 1969–1995. The projected consumption for the year 1969, 1975 and 1995 is shown in Table XIV. In this table the R.E. products are divided in *mixed R.E. chemicals* and *separated R.E. compounds*, with a breakdown of the U.S.A. consumption and growth in the various fields of application.

It is seen that:

The consumption of mixed R.E. chemicals is estimated to grow from 15,616,000 pounds in 1969 to 48,410,000 pounds in 1995, with an increase in value from about \$ 15,000,000 to \$ 48,000,000 at the current market price.

The total consumption of separated R.E. compounds would increase from 943,000 pounds in 1969 to 4,210,000 pounds in 1995.

Yttrium and europium oxides for TV phosphors and lasers would increase from 136,000 pounds in 1969 to 1,260,000 pounds in 1995, at a yearly rate of growth of about 8%. In the same period sale value of these oxides would increase from about \$ 7,000,000 to \$ 65,000,000.

6.3. *The U.S.A. Processors of R.E. (1)*

The U.S.A. rare-earth, yttrium and thorium industry has consisted of from two to a dozen primary-mineral producers, two to four dominant primary-mineral processors, and as many as twenty or more firms and laboratories engaged in refining individual rare-earth elements. *Monazite producers for the most part have been content to sell their concentrates to primary-mineral processors.* Only one producer, Molybdenum Corporation of America, has branched out into the processing and refining of end products. *The three other dominant mineral-processors have depended upon purchased monazite, most of which is imported from Australia of Malaysia.*

6.3.1. *Mineral Production*

The U.S.A. rare-earth industry started in 1893 as a result of the demand for thorium to be used in producing incandescent gas mantles. The first U.S.A. production of monazite came from North Carolina, but from 1911 to 1948 imports from India and Brazil supplied all domestic demand.

From 1949 to 1966, Florida was a small but consistent producer of monazite, which was recovered from beach sands as a byproduct of ilmenite, rutile and zircon. Titanium Alloy Manufacturing Division of National Lead Co., operated the Skinner mine and beneficiation facility near Jacksonville, Fla. From 1953 to 1956, Florida Ore Processing Co. recovered monazite at Brevard, and in 1957 and 1958, Rutile Mining Co. produced some byproduct monazite in Duval County, near Jacksonville. Significant monazite production ended in Florida in 1965, but small quantities were recovered by reworking tailings piles at the Skinner property in 1967–68.

From 1955 to 1958, Marine Minerals Company, Aiken, S.C., a subsidiary of Heavy Minerals Company, recovered monazite and xenotime. Heavy Minerals Company owned by Vitro Corporation of America, Crane Co., and Pechiney of France, upgraded this monazite at its Clearwater, S.C., plant.

(1) Parker, J.G.; Baroch, C.T.: "The Rare Earths Elements, Yttrium and Thorium". P. 72–75. U.S. Bureau of Mines, Inf. Circ. 8476, 1971.

TABLE XIV
1969, 1975, AND 1995 PROJECTED CONSUMPTIONS OF RARE EARTHS IN THE U.S.A.
 (in pounds of oxide or oxid. equivalent)

	USES	1969	1975	1995	Growth Rate per years	
MIXED RARE EARTHS	Lighter Flint	300,000	360,000	440,000	1%	
	Ductile iron	1,500,000	2,800,000	5,300,000	4%	
	Magnesium-base alloys	"lights"	40,000	130,000	190,000	2%
		"heavies"	1,000	180,000	480,000	5%
	Magnets		566,000	2,800,000	8%	
	Alloys	25,000	425,000	2,000,000	10%	
	Steels	250,000	2,000,000	2,000,000	12%	
	Catalyst (Petroleum)	10,400,000	12,200,000	12,200,000	1%	
	Glass polishing	2,000,000	2,700,000	2,600,000	-	
	Carbon arc	800,000	950,000	1,300,000	2%	
	Miscellaneous	300,000	600,000	1,100,000	8%	
		SUB TOTALS	15,616,000	22,911,000	48,410,000	
SEPARATED R.E. COMPOUNDS	Phosphors and Laser	136,000	245,000	1,260,000	8%	
	Electronic		2,000	40,000		
	Magnets		1,000	25,000		
	Glass additives	760,000	1,150,000	2,500,000	4%	
	Ceramic tiles	30,000	33,000	49,000	2%	
	Nuclear	100	10,000	20,000		
	Super alloys	2,000	50,000	250,000	8%	
	Research	25,000	45,000	65,000	2%	
		SUB TOTAL	943,100	1,536,000	4,210,000	
		GRAND TOTAL	16,584,100	24,447,000	52,620,000	

Starting in 1966, Humphreys Mining Company processed alluvial deposits belonging to E.I. du Pont de Nemours & Co., Inc., at Folkston, Charlton County, Ga.

In Idaho, Baumhoff-Marshall, Inc., started dredging monazite in 1951 from river gravels. In the period 1951 through 1955, eight other Idaho-based mining firms, principally Warren Dredging Corp and Idaho-Canadian Dredging Co., produced monazite, but by 1955 only Baumhoff and Idaho-Canadian reported production. Then, in 1958 and 1959, Baumhoff reported recovering byproduct monazite from retreatment of stockpiled titanium concentrate. The only large euxenite operation, was that of Porter Bros. Corp. in Bear Valley,

Idaho. From 1955 through 1959, the euxenite was processed under a government contract for columbium-tantalum oxides; the final processing was done by Mallinckrodt Chemical Works, St. Louis, Mo. A "green mud" residue from the processing operation was stored by the G.S.A. until 1965, when it was sold for its yttrium content. In 1966, Porter Bros. facilities in Bear Valley were acquired by Michigan Chemical Corp., a subsidiary of Chicago and North Western Railway Company.

During 1955–58 a small production of euxenite samarskite, gadolinite, xenotime, yttrifluorite, and thorite came from various pegmatite deposits in the Rocky Mountain area, particularly in Colorado. Thorite was produced in small quantities in Idaho and Montana during 1958 and 1959.

Molybdenum Corp. of America mines bastnaesite ore by an open-pit method and concentrates it by flotation at Mountain Pass, Calif., 60 miles southwest of Las Vegas, Nev. Claims at the California site cover more than 1,100 acres and reserves are in the millions of tons of rare-earth oxides. The company has mined and produced concentrate at this location since May 1952 but for much of the time since October 1954, because of sufficient inventory, the mill operated at only one-fourth to one-third capacity. A flotation mill, capable of producing 15,000 tons of rare-earth oxide concentrates per year, was expanded to 25,000 tons capacity by December 1966. Some of these concentrates are processed for their europium oxide content at the Mountain Pass solvent extraction plant. Bastnaesite concentrates are either shipped to the company's York, Pa. Rare-earth and lanthanum chloride plant, are sold directly to consumers, or are stockpiled at Mountain Pass.

6.3.2. Processing and Refining

The principal U.S.A. processors and refiners of rare-earth elements, yttrium, and thorium are listed in Table XV and classified as follows: *processors of primary minerals, producers of bulk-tonnage commercial rare-earth materials* or of *high-purity rare-earth materials*, and *processors of thorium*. All processors of rare-earth materials also process yttrium.

Until the late 1960's, *American Potash & Chemical Corp.*, Rare Earth Division, at West Chicago, Ill., was the largest U.S.A. producer of rare earth products, and it is still the largest chemical processor of monazite. Previously the West Chicago property was owned by the Lindsay Chemical Co., the pioneer in the domestic rare-earth industry and manufacturer of gas mantles using thorium nitrate since its founding in 1902 as the Lindsay Light Company. In 1935 the name was changed to Lindsay Light and Chemical Company, and in 1952 to the Lindsay Chemical Company. A monazite processing plant, completed late in 1954 and built primarily to supply the AEG with thorium nitrate, *cost \$ 3 million and had an annual capacity of 9,000 tons monazite*. Facilities for producing high-purity rare-earth compounds were added in 1955 with the completion of an ion-exchange plant.

The West Chicago plant, using both monazite and bastnaesite as feed material, produces substantial quantities of cerium oxide, hydrate, and other cerium compounds as well as large quantities of rare-earth chloride, oxide and fluoride. In 1966 it was one of the chief U.S.A. producers of high-purity yttrium oxide, and since then *yttrium oxide capacity has been raised to 150,000 pounds per year*, principally due to the completion in mid-1967 of a new solvent extraction unit. Production also includes high-purity rare earth metals, thorium nitrate and other thorium compounds. In 1968, American Potash became a subsidiary of Kerr-McGee Corp.

Molybdenum Corp. of America initially built only a flotation plant at its Mountain Pass property. Later, it added an acid treatment plant to beneficiate further its high-grade concentrates. In 1965, the company added a europium recovery plant consisting of the chemical processing and solvent extraction of europium. Initially this plant had an annual capacity of 6,000 pounds of europium oxide which was doubled, to 12,000 pounds, in

May 1966. It was raised again, to 20,000 pounds by the end of 1966, (and again to 60,000 pounds in 1973). Also a lanthanum hydrate plant was installed at Mountain Pass in the first quarter of 1967.

TABLE XV
U.S.A. Processors of rare-earth elements, yttrium, and thorium

COMPANY	LOCATION	RARE - EARTH AND Y TTRIUM MINERAL PROCESSING	COMMERCIAL RARE-EARTH MATERIALS AND YTTRIUM	HIGH PURITY RARE-EARTH MATERIALS AND YTTRIUM	THORIUM PROCESSING
American Metallurgical Products Co., Inc.	New Castle, Pa.	-	(1)	-	-
American Potash & Chemical Corp.,					
Rare Earth Division	West Chicago, Ill	X	X	X	X
Atomegic Chemicals Co.	Carle Place, N.Y.	-	-	X	-
The Babcock & Wilcox Co.	Lynchburg, Va.	-	-	-	X
The Dow Chemical Co.	Midland, Mich.	-	-	-	X
W.R. Grace & Co.,					
Davison Chemical Division	Chattanooga, Tenn.	X	X	X	X
Do.....	Pompton Plains, N.J.	X	X	-	-
Gulf General Atomic, Inc.	San Diego, Calif.	-	-	-	X
Kerr Mckee Corp	Oklahoma City, Okla.	-	-	-	X
Lunex Co.	Pleasant Valley, Iowa.	-	-	X	-
Michigan Chemical Corp.	St. Louis, Mich.	X	X	X	-
Molybdenum Corp. of America	Mountain Pass, Calif.	X	X	X	-
Do.....	Louviers, Coló.	-	-	X	-
National Lead Co.	Albany, N.Y.	-	-	-	X
Nuclear Fuel Services	Erwin, Tenn.	-	-	-	X
Nuclear Materials & Equipment Corp.					
Research Chemicals	Apollo, Pa.	-	-	-	X
Nuclear Corp. of America					
Ronson Metals Corp	Phoenix, Ariz.	-	-	X	-
Union Carbide Corp	Newark, N.J.	-	(1)	X	-
United Nuclear Corp	Alloy, W. Va.	-	(2)	-	-
Ventron Corp., Metal Chemicals Division	New Haven, Conn.	-	-	-	X
	Beverly, Mass.	-	-	-	X

(1) Mischmetal production.

(2) Metal additives-silicon-lanthanides.

Besides its mine, mill, lanthanum hydrate concentrate plant and europium solvent extraction plant at Mountain Pass, Calif., the Molybdenum Corp of America has facilities at Washington, Pa., producing special rare-earth compounds, mostly oxides, for the steel industry, and at York, Pa., making rare-earth chloride and nitrate. In October 1966, Yttrium Corporation of America, owned jointly by Molybdenum Corp. of America and the Pyrites Co., opened a solvent extraction plant with *an annual capacity of 180,000 pounds of yttrium at Louviers, Colo.* Raw material was obtained under contracts from Denison Mines Ltd. and Rio Algom Mines, Ltd., Canada, and Metal Traders, Inc., New York City. This plant is now wholly owned by Molybdenum Corp of America.

At its plant in Golden, Colo. Metal Traders, Inc., had a research contract with the Colorado School of Mines Research Foundation, Inc., whereby the green-mud residues bought from G.S.A. were processed for their yttrium and rare-earth content. By the end of 1966, a concentrate had been produced containing over 100 tons of yttrium oxide. The supply of green mud was exhausted in 1967, and new supplies will have to await the production of more euxenite.

W.R. Grace & Co., Davison Chemical Division, is another important monazite processor with plants at Pompton Plains, N.J. and Chattanooga, Tenn. In November 1956, Davison obtained a plant at Erwin, Tenn., when it absorbed Rare Earths Inc. which founded the operation in 1953. In 1969, Nuclear Fuels Services, Inc., a subsidiary held jointly by W.R. Grace & Co. and American Machine & Foundry Co., operated the Erwin plant at which thorium concentrates can be purified by solvent extraction, converted to thorium dioxide (1,000 pounds per day), and refined to metal (500 pounds per day).

In 1956–57 monazite was processed by Davison Chemical at Curtis Bay (Baltimore), Md., under AEC contract, but the plant was not satisfactory. The Chattanooga, Tenn., plant was acquired by W.R. Grace from Vitro Chemical Co. in 1965. The caustic soda process was used by Vitro at Chattanooga where Grace has installed new equipment indicating the intention to produce high-purity salts and metals. The sulfuric acid process has been used at Pompton Plains, N.J., where Grace has specialized in preparing rare-earth oxide polishing powders. In 1965 Grace reported that it has produced small quantities of mischmetal and high-purity metal. In 1966 the company produced substantial quantities of rare-earth oxides and fluorides as well as a small quantity of yttrium oxide.

Vitro Chemical Co. of Chattanooga, Tenn., was an important processor of monazite from 1959 until it sold its plant to W.R. Grace in May 1965. From 1957 to 1959 the plant had been operated by Heavy Minerals Co. Organized in 1953, Heavy Minerals Co. was owned 40 percent by Vitro, 40 percent by Crane Co., and 20 percent by Pechiney. Heavy Minerals Co., had acquired most of the raw material monazite and xenotime, from the Aiken, S.C., property of its subsidiary Marine Minerals Co. The Chattanooga plant produced rare-earth and thorium salts, some thorium and thorium-magnesium alloys, and a small quantity of high-purity rare-earth metals in 1965, Vitro's final year.

Since 1956 *Michigan Chemical Corp of St. Louis Mich.* has used ion-exchange methods to produce purified rare-earth compounds; *it has specialized in compounds of yttrium and the heavy subgroup of the rare-earth elements.* The ion-exchange facilities consist of the major facility of 165 columns, 30 inches in diameter and 20 feet in height, which can produce ton quantities, and 10-inch-diameter, 10-foot-high columns which produce pound quantities of the less abundant materials. There are also a solvent extraction unit for separating and purifying certain rare-earth elements and an integrated plant for reducing and refining rare-earth metals in commercial quantities. The Porter Bros. mining and concentrating operation in Idaho was acquired by Michigan Chemical Corp. late in 1966 to assure a long term source of raw material. This supplemented 3-year contracts with two Canadian uranium producers for yttrium oxide feedstocks.

Nuclear Corp. of America, Research Chemicals Division, Phoenix Ariz., was located in Burbank, Calif., until 1961 when it acquired the assets of U.S. Semiconductor Products, Inc., Phoenix, Ariz. The division produces high-purity rare-earth compounds and metals and *specializes in yttrium oxide production*. In 1966 the company moved into new Phoenix quarters in which rare-earth materials can be processed from ore to finished oxide and metal.

Mitten Chemicals, Inc., of Alma, Mich., a small producer of yttrium and rare-earth oxides and salts, was acquired by Sylvania Electric Products, Inc., early in 1967.

The following are companies which formerly produced rare-earth and thorium salts: Maywood Chemical Works, Maywood, N.J., which stopped manufacturing them in 1960; St. Elio Corp., Cincinnati, Ohio, which went out of business in 1960 after producing since 1957; Kleber Laboratories, Inc., Burbank, Calif., which was in business from 1961 to 1962 and American Scandium Corp., Cincinnati Ohio, which commenced producing scandium compounds in 1960 and, although it has similar capabilities in rare-earth salts, left the field in 1965.

There were only two U.S.A. mischmetal producers in 1969. *American Metallurgical Products Inc.*, Pittsburgh, Pa., with the smaller production, made special types of mischmetal usually for metallurgical use in other than lighter flints.

Ronson Metals Corp., Newark, N.J., the larger of the two, is a subsidiary of Tonson Corp. formed in September 1959 after Ronson Corp. acquired the facilities, processes, and patents of Cerium Metals Corp., Niagara Falls, N.Y. Its predecessor, New Process Metals Inc., had been a subsidiary of Ronson Corp. since 1950. However, as an independent producer, it had manufactured ferrocerium lighter flints since 1915. In 1960, Ronson Metals Corp expanded its facility 30 percent. Besides making mischmetal and lighter flints, it produces didymium metal, an alloy composed mostly of neodymium and praseodymium, and several high-purity metals. Also, it has a working agreement with Th. Goldschmidt A.G., Essen, Germany. Much of Ronson's output goes into production of lighter flints, some by its New Process Metals Division. The Cerium Metals & Alloys Division manufactures other rare-earth and thorium metal and alloy products.

Mallinckrodt Chemical Works, St. Louis, Mo., produced mischmetal from the early 1950's until 1963. In 1957-60 the company processed Idaho euxenite for its columbium and tantalum content for the AEC and recovered thorium and rare-earth elements in the residues which went into GSA stockpiles.

U.S.A. mischmetal producers of the decade between 1950 and 1960 include Cerium Metals Corp., Niagara Falls, N.Y., and General Cerium Corp., Edgewater, N.J., both of which went out of business in 1960.

Since 1954 Lunex Co., Pleasant Valley, Iowa, has specialized in vacuum reduction of high-purity metals from compounds made elsewhere.

Thorium metal producers not previously mentioned include Metal Chemicals Division (now Ventron Corp.), Beverly, Mass., and Westinghouse Electric Corp., Lamp Division, Bloomfield, N.J. National Lead Co. of Ohio at Fernald was the only large producer of thorium metal, operating a plant for AEC from 1954 through 1960.

6.4. *Data on the Japanese R. E. Market*

A 3-day visit to Japan allowed the writer to collect some basic information on the Japanese Rare Earth market. Because of the lack of numerous statistical data, the survey of Japanese imports and consumptions remains incomplete. However, valid conclusions can already be drawn from available sources.

It is a characteristic of the Japanese R.E. industry to import R.E. raw material, such as

ore concentrates (bastnaesite, monazite, xenotime) or low-purity R.E. chemicals, and to refine it to various stages, up to oxides and metals of very high purity.

6.4.1. Imported R.E. Raw Materials (ore concentrates and primary chemicals) .

Bastnaesite (source material for cerium, lanthanum).

- Imported volume in 1971: 250 metric tons.
- Import price: 65 yen/pound of Total R.E. oxide (T.R.E.O.).
- (Imported from U.S.A.: T.R.E.O. content 72–73%)

Monazite (source material for cerium, lanthanum).

- Imported volume in 1971: 100 metric tons.
- Import price: 22 yen/pounds T.R.E. content 60–63%
- (Imported from Australia and Malaya: Thorium content 5–6%)

Xenotime (source material for yttrium):

- Imported volume in 1971: 30 metric tons.
- Import price: 500 yen/Kg. of pure Y_2O_3 T.R.E.O. content 55–60% Y_2O_3 content 25% min.
- (Imported from Malaya)

R.E. Chloride (source material for cerium, lanthanum and yttrium).

- Imported volume: 2,000 metric tons
- Import price: 45 yen/pound c.i.f.
- (Imported from: Brazil India)

6.4.2. Consumption of R.E. Chemicals and oxides

Cerium Hydrate. This chemical is imported as one source material for the production of cerium oxide. (Another source is bastnaesite, which is currently being imported into Japan from the U.S.A. However bastnaesite is being replaced by import of cerium hydrate).

- Consumption of cerium hydrate in 1972 has been of the order of 1,300,000 pounds.
- Import Price has been quoted as follows: 180 yen/pound c.i.f. (= \$ 0.60)
With Total Rare Earth content 85% min., CeO_2 content 90% min.

Lanthanum Oxide

- Consumption in 1972 has been of the order of 360,000 pounds.
- Import Price: 900 yen/pounds c.i.f. (= \$ 3.00), La_2O_3 content 99.99% min., imported from France and U.S.A.)

Yttrium Oxide

- Consumption in 1972: 45–50,000 pounds
- Import Price: 1400 yen/pound (= \$ 4.60) of pure Y_2O_3 c.i.f., with total R.E. content of 95% min., and Y_2O_3 content of 60–70% min. (Imported from France, U.K. & U.S.A.)

Europium

- Consumption in 1972: 4,000 pounds high purity oxide (phosphors grade, i.d. 99.9%)
- Import Price in 1972: \$ 200/pound of Eu_2O_3 in R.E. material containing at least 15% Eu_2O_3 .

6.5. The Japanese Processors of R.E. (1)

The relatively large number of firms in this country have mostly restricted themselves to producing oxides, fluorides, and mischmetal and lighter flints. The few which have specialized in producing high-purity material are concerned mostly with the cerium group.

In 1960, Ishihara Industrial Co., Osaka, recovered byproduct monazite and zircon

(1) Parker, J.G; Baroch, C.T.: "The Rare Earths Elements, Yttrium and Thorium". P. 78. U.S. Bureau of Mines, Inf. Circ. 8476, 1971

from processing ilmenite from deposits in Trengganu, Malaysia. In 1963, monazite concentrates used by Japanese industry came from Korea, Malaysia and Thailand. Other starting materials include crude rare-earth chloride, mostly from India.

Santoku Metal Industrial Co., Kobe, processes mineral concentrates, including those of xenotime. It produces and sells rare-earth oxides for the glass industry. It also makes fluorides and mischmetal, and extrudes ferrocerium lighter flints. Santoku not only produces thorium dioxide but also has developed a new ion-exchange and fluorination method for making yttrium oxide and metal.

The following companies are producers of compounds only: *Nihon Rare Earth Co.*, Waken-gun, Okayama Prefecture, which had a rare-earth oxide capacity of 2,000 kilograms (Kg) per month in 1963; *Sankin Rare Earth Co.*, part of Mitsui Metal Mining and Mitsui Trading Companies, which has a rare earth oxide plant at Miike, Fukuoka; *Toda Industry Co.*, Hiroshima City, which has a 1,000 Kg per month rare-earth oxides plant; and *Shin-Nihon (New Japan) Metal Chemical Co.*, Kyoto City, which could produce 10,000 Kg. of rare-earth oxides and 10,000 Kg. of rare-earth fluoride per month in 1963.

Other companies produced compounds as well as mischmetal, and lighter flints. These included the following: *Tohoku Metal Chemical Co.*, Taira City, Fukushima, which can extrude 5,000 Kg. of lighter flints per month and produce 2,000 Kg. of rare-earth oxides per month; *Ogino Chemical Institute*, Higami-Gun, Hyogo, which could produce 9,000 Kg. per month of mischmetal, 3,000 Kg. per month of cast flint and had cerium oxide and thorium oxide production facilities; and *Kindai Chemical Industry, Osaka*, since 1965, the rare-earth division of Tokushima Oil Refining Co. which in 1963 could produce small quantities of cerium and lanthanum oxides, 5,000 Kg. of mischmetal per month, and 2,000 Kg. of lighter flints per month. *Sanko Rare Earth Co.*, Shizuka, produced small quantities of rare-earth fluoride and mischmetal and started a new 3-ton-per-month lighter flint process in mid 1965.

Most of the Japanese rare-earth oxide producers sell to the glass industry. Tohoku, Santoku, and Sankin are reportedly using ion exchange and fractional crystallization to produce good quality lanthanum oxide which is used in Japanese camera lenses. In 1965, *Shinetsu Chemical Industry Co.*, was readying a plant at Takefu, Fukui Prefecture, to produce 10 to 12 tons of high-purity yttrium oxide per year using a Japanese-developed ion-exchange method. *Nihon Yttrium Co.*, Mitaka, Tokyo, is a new joint venture of Mitsui Metal Mining and Refining Co. and Tohoku Metal Industry Co. It has an annual capacity of 6 to 10 tons high-purity yttrium oxide.

Thorium oxide production facilities to meet Japan's demand exist at Ogino, Kindai, Santoku, Shin-Nihon, and Tohoku, and have a total capacity of 50 tons per year.

6.6. Data on the European R.E. Market

Accurate global figures on the European R.E. consumption and prices are not available, due no doubt to the policy of the R.E. processors to regard these figures as confidential. However the following information has been obtained from some of the main R.E. producing or consuming firms such as the Cie Pechiney Y St. Gobain, Goldschmidt A.G., Vakuumschmelze G.m.b.H., the Krupp concern and the Treibacher Chemische Werke.

6.6.1. Research and Development of technological uses of R.E.

(a) Use of R.E. as an alloy component in the steel production

Ce-Mischmetal, with up to 20% La, binds sulphur, an unwanted component in raw steel. Normal quantities added to steel: 1–2 Kg. misch-metal/t steel. Sulphur content is lowered from 0.1–0.2% to 0.005–0.001%. Two Kg. of mischmetal/t steel involve an added cost of 25.– DM.

Other advantages of the R.E. addition are:

Deoxidation

Improvement of the working properties

Elimination of graphite

Lowering of anisotropy, which improves the strength

Increased resistance to intercrystalline corrosion.

Presently Mg is used, for it is cheaper than mischmetal. Future uses: possibly addition of mischmetal in pressure tanks. Krupp estimates that alloys with R.E. mischmetal will make up 1–10% of total steel production of 40 million tons.

Main mischmetal supplier in Germany: Th. Goldschmidt AG, Essen (see below).

(b) *Other uses, but in minimal quantities*

In Neodym lasers (1/10 g)

Eu in TV tubes (mg/tube)

Reactor technique: R.E. employed in regulating rods, good neutron absorbers, especially Eu, Sm, Gd, Hf. Presently borcarbide is still preferred.

(c) *Uses in the production of stronger permanent magnets*

Sm-Co compounds possess excellent magnetic properties already at room temperatures.

Composition:

Atomic proportion: 1 Sm : 5 Co

weight % 34 Sm : 66 Co, or RE–Co–Fe–Mn

atomic proportion: 1 : 3 : 2

General formula: RECo₅

Uses in:

Travelling wave tubes

Special motor generators

Battery-operated watches

High-quality magnets

6.6.2 *R.E. consumption of Vacuumschmelze GmbH*

Vacuumschmelze AG, a major German magnet producer for the electrical industry, is wholly owned by Siemens AG. Main production Alnico magnets, which consist of an alloy of 43% Fe, 33% Co, 6% Al, and 18% Ni. Germany buys 130 t of Alnico magnets/month.

As already mentioned, the addition of R.E. results in much higher power. It is estimated that within 3–4 years the R.E. containing magnets will be produced in Germany at a rate of 30 t/month.

Best magnets are obtained with the addition of Sm and Pr. However, the present high cost of Sm (500.– DM/kg) represents a negative factor in this particular development.

Vacuumschmelze GmbH estimates a production of 3 t/month of R.E. – containing magnets for 1975. Of these, 20% will be Sm, that is a consumption of 600 Kg Sm/month.

6.6.3 *Th. Goldschmidt AG*

Present western world consumption of R.E.: 15,000 t REO; of these only 50–100 t heavy R.E. (“Yttererden”), the rest light R.E. (“Ceriterden”).

Goldschmidt AG produces 2,500 t REO/year:

500 t are used for lighter flints (4.8×10^9 flints!)

almost 2,000 t for the steel industry (supplies mostly U.K. and Italy)

modest quantities for ceramic colours, polishing compounds, catalysts.

Goldschmidt AG buys R.E. concentrates as:

monazite sands from Australia, Indonesia, Thailand (relatively high Th content):

bastnaesite from U.S.A. (Molybdenum Corporation) and from Africa (generally Th free).

Although Molybdenum Corporation has not yet its own metal production, there is the possibility that this American company could become a competition to Goldschmidt AG. For this reason Goldschmidt AG would certainly welcome any powerful producer as a market supplier of R.E. concentrates.

Goldschmidt AG gives the following specifications for the needed concentrates:
light R.E. concentrates with at least 65% (better 70%) of R.E.O. low content of radioactive elements, and a radioactivity of less than 1,000 pico curie/g.

6.7. *The European, Brazilian and Indian Processors of R.E. (1)*

6.7.1. *Austria*

Treibacher Chemische Werke A.G., Treibach, which was founded by Karl Auer von Welsbach, produces rare-earth compounds as well as misch-metal and lighter flints.

6.7.2. *Belgium*

Société Anonyme de Pont-Brule, Brussels, owned by Cie. de Saint Gobain S.A., Produits Chimiques de Tessenderloo S.A., and Entreprises Chimiques et Electriques S.A., produces mischmetal and rare-earth alloys from imported fused chlorides.

6.7.3. *France*

Société Pêchiney-Saint-Gobain, (now Soc. Pêchiney-Kuhlmann) Paris, is the dominant processor in France. Its La Rochelle plant treats rare-earth and thorium concentrates and markets all types of products throughout Europe. *S.A. d'Exploitation des Ets Tricot*, Pargny-sur-saulx; *Société Ets Lejeune*, Mirbel; and *Société Kuhlmann Paris*, produce ferrocium and mischmetal. France produces no rare-earth minerals but imports monazite concentrates from Madagascar and, to a lesser degree, from Australia, Brazil and India. Thorium being a fertile nuclear material, is closely controlled by the Commissariat à l'Energie Atomique (CEA), the French Atomic Energy Commission. The CEA extraction plant at Le Bouchet processes monazite and retains the thorium. The CEA has conducted the exploitation and production of monazite and uranothorianite in Madagascar.

6.7.4. *West Germany*

The largest producer of rare-earth materials in West Germany is *Th. Golschmidt A.G., Chemische Fabriken, in Essen*.

Facilities are maintained for processing rare-earth mineral concentrates and for producing rare-earth compounds and metals in pure and technical grades, rare-earth polishing powders didymium metal, misch-metal, mischmetal silicide, and ferrocium lighter flints. Goldschmidt processes bastnaesite by direct chlorination at high temperatures with the resulting formation of anhydrous rare-earth chlorides. In producing high purity rare-earth materials, the company makes large scale use of solvent-extraction methods.

Prometheus Metallwerke, Kempten, in the Allgau district of Bavaria, produces mischmetal and ferrocium lighter flints using rare-earth chloride bought as raw material primarily from India and Brazil. Bavaria-Zundmetall G.m.b.H., also in Kempton, makes lighter flints. *Metallgesellschaft A.G., Frankfurt am Main*, produces rare-earth master alloys for nodular iron in cooperation with *Suddeutsche Kalk- und Stickstoffwerke A.G., Trostberg*.

6.7.5. *Finland*

Typpi Oy, a state-owned company at Oulu which produces nitrogen as its basic product, was founded in 1944. In 1963, it announced that its new plant would be used to extract

(1) Parker, J.G; Baroch, C.T.: "The Rare Earths Elements Yttrium and Thorium". Pages 76-77. U.S. Bureau of Mines, Inf. Circ. 8476, 1971.

byproduct rare-earth oxides from phosphatic material such as the Kola Peninsula apatite. Planned production was 100 tons of oxides per year, most of which the company expected to export. The company has announced plans to quadruple its oxide production, using lanthanide concentrates. Other minerals in the concentrates are barite, fluorite, and rare-earth bearing apatite.

6.7.6. Italy

Rare-earth materials are made in Italy but the industry is small. *Elettrochimica Italiana delle Terre Rare, Florence*, produces mischmetal. In addition, it is using ion exchange to produce praseodymium oxide for use as a yellow ceramic stain. An affiliated Swiss company is making ferrocerium lighter flints.

6.7.7. United Kingdom

The two principal processors of rare-earth and thorium ore concentrates in the United Kingdom are *Thorium Ltd.*, London, with its plant at Widnes, Lancashire, and *Johnson Matthey Chemicals Ltd.*, also of London.

Thorium Ltd., a subsidiary of Rio Tinto-Zinc Corp., produces several grades of thorium oxide and thorium nitrate, pure and technical grades of various cerium compounds, pure lanthanum, neodymium, yttrium, and europium oxides, and commercial grades of praseodymium and neodymium oxides. Separation and purification by solvent extraction are used in producing high-purity oxides. In 1964 the company began to rely exclusively upon California bastnaesite for its rare-earth production and upon thorium and yttrium concentrate from Rio Algom Mines' Elliot Lake operations.

Johnson Matthey Chemicals Ltd. uses ion-exchange methods for producing high-purity rare-earth oxides and salts. It prepares high-purity rare-earth metals by reducing the fluorides, in an argon atmosphere, with lithium, calcium, or lanthanum in tantalum crucibles and then remelting in a vacuum. In 1966 the firm produced a 3.7-kilogram ingot of gadolinium. The company has facilities for fabricating the metals and can supply rare-earth metal and alloy sheets and wires.

Late in 1967, Thorium Ltd. and Johnson Matthey formed a new company, Rare Earth Products Ltd., which took over the parent companies' activities in rare-earth compounds and metals production. The combination of techniques used by the parent firms is expected to develop lower costs and speedier separation methods. Johnson Matthey retained its interests in manufacturing certain products incorporating rare earths, such as phosphors, ferrites, and laser materials and very high-purity rare-earth salts. Thorium Ltd. received the Queen's Award for Technological Innovation as a result of its pioneering efforts in solvent extraction as applied to the purification of rare-earth materials.

London & Scandinavian Metallurgical Co. Ltd., London, processes bastnaesite concentrates at Rotherham, Yorkshire, and produces rare-earth chemicals and compounds for various purposes including metallurgical applications. British Rare Earths Ltd., formerly Potter & Clarke (Development Projects) Ltd., Barking, Essex, produces rare-earth chemicals and thorium oxide from monazite concentrates probably obtained from Malaysia or Australia, British Flint and Cerium Manufacturers Ltd., a subsidiary of Spark Holdings Limited, London, makes mischmetal and lighter flints; Magnesium Elektron Ltd., Swinton, Manchester, produces thorium alloys. It is said that Metals Research Ltd., Melbourn, Royston, Hertfordshire, produces high-purity single crystal rare-earth metals.

6.7.8. Portugal

Monacerium, Ltd., of Lisbon is said to produce mischmetal and rare-earth alloys.

6.7.9. Brazil

Comissão Nacional de Energia Nuclear (CNEN) regulates all Brazilian rare-earth and thorium production. Monazite was concentrated at the *Usina de Cumuruxatiba* in the village of Cumuruxatiba (25 miles north of Prado) in Bahia State. The main plant uses electrostatic and electro-magnetic separation. Operating 24 hours a day, it had a heavy sand capacity in 1964 of 1,200 tons per month. At that time the monazite content was said to be 18 percent. Other monazite mining and beneficiation is performed at *CNEN's property and plant at Barra de Itabapoana*, State of Rio de Janeiro. Under contract with CNEN, the monazite concentrates were processed by Orquima Industrias Quimicas Reunidas S.A. in San Paulo until 1965 when the plant was officially expropriated with full payment by the CNEN. The plant which used the caustic soda method, had a capacity of 2,000 tons monazite per year; its products included rare-earth chlorides and thorium hydroxide. *Companhia Industrial Fluminense*, Sao Joao del Rei, State of Minas Gerais, produces mischmetal from Brazilian rare-earth chloride. Administração do Processamento da Monazita processes monazite to rare-earth chloride, mostly for exportation to Europe.

6.7.10. India

Travancore Minerals Ltd. was a heavy sand mining and concentrating company owned by the governments of India and the States of Kerala and Madras. Since the early 1950's it supplied monazite concentrate, principally from its plant at Manavalakurichi, Madras State, to the Alwaye processing plant of Indian Rare Earths Ltd., Bombay, another company owned jointly by the Indian and Kerala State governments. Travancore Minerals Ltd. was liquidated in 1965 and the company's assets assumed by Indian Rare Earths Ltd.

Indian Rare Earths Ltd. was established in 1950 by a contract between the Travancore (now Kerala) government and two French companies, Société Bankes Marocaines de Crédit and Société de Produits Chimiques des Terres Rares. Since December 1952, the company has processed monazite for rare-earth chloride, carbonate, and hydroxide, and thorium hydroxide; the chloride has been exported. By late 1962, the processing plant at Alwaye had a rated capacity of 3,000 tons of monazite per year. A plant to produce cerium fluoride for arc carbons has been built at Alwaye. Another plant at Trombay (near Bombay), commissioned in 1955 by the *Indian Atomic Energy Commission*, produces thorium nitrate and oxide from the thorium hydroxide made at Alwaye. Lanthanum oxide and mischmetal have been produced on a pilot plant scale at Trombay, preparatory to setting up commercial scale production at Alwaye.