RARIES EARRIS

Extraction
Preparation
and
Applications

Edited by R.G. Bautista and M.M. Wong

TG 146.4-55 R 221 -437.3/7 9063561

RARE EARTHS

Extraction
Preparation
and
Applications

Proceedings of a symposium on Rare Earths, Extraction, Preparation and Applications sponsored by the TMS Reactive Metals Committee, held at the TMS Annual Meeting in Las Vegas, Nevada, February 27-March 2, 1989.

Edited by

Renato G. Bautista
University of Nevada-Reno
Reno, Nevada

and

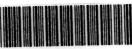
Morton M. Wong

Unocal

Brea, California



A Publication of



E9063561

A Publication of The Minerals, Metals & Materials Society 420 Commonwealth Drive

420 Commonwealth Drive Warrendale, Pennsylvania 15086 (412) 776-9024

The Minerals, Metals & Materials Society is not responsible for statements or opinions and absolved of liability due to misuse of information contained in this publication.

Printed in the United States of America Library of Congress Catalog Number 88-42986 ISBN Number 0-87339-047-4

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by The Minerals, Metals & Materials Society for users registered with the Copyright Clearance Center (CCC) Transactional Reporting Service, provided that the base fee of \$3.00 per copy is paid directly to Copyright Clearance Center, 27 Congress Street, Salem, Massachusetts 01970. For those organizations that have been granted a photocopy license by Copyright Clearance Center, a separate system of payment has been arranged.



© 1988

RARE EARTHS

Extraction
Preparation
and
Applications

PREFACE

In years past, research papers on various aspects of rare earths and related elements have always been included in the technical sessions of the TMS Annual Meetings. Current intense interest in the use of rare earths and related elements for new materials gives renewed impetus to all phases of rare-earth research, from supply of materials to finished products. Therefore, a symposium devoted exclusively to rare earths and related elements has been organized by the Reactive Metals Committee and will be held during the TMS Annual Meeting in Las Vegas, Nevada, February 27-March 1, 1989.

The symposium includes papers covering research and developments in mineral processing; extraction; reaction chemistry; high-purity separation; preparation of metals and alloys; physical properties of alloy; applications in superconductors, magnets, catalysts, phosphors, etc.; and economics and marketing. The international nature of the interest is demonstrated by the contribution of papers from six countries.

The editors are grateful to all authors whose papers provided the substance for this symposium, to the session chairmen and the Reactive Metals Committee members for their valuable support and to the TMS staff, who made this symposium volume a reality. Our thanks are also extended to Jane Pilotte, University of Nevada-Reno, and to Sharon Savord, Unocal, for their extensive secretarial assistance.

R.G. Bautista Mackay School of Mines University of Nevada-Reno Reno, Nevada 89557

M.M. Wong Unocal Science and Technical Division Brea, California 92621

October 1, 1988

TABLE OF CONTENTS

Preface
MARKET AND BENEFICIATION
Noncommunist World Markets for Rare Earth Minerals
The Processing of Rare Earth Minerals
The Role of Lignin Sulfonate in Flotation of Bastnasite From Barite
Bubble Attachment Time Measurements for Select Rare-Earth Phosphate Minerals in Oleate Solutions
Alkyl Hydroxamates as Collectors for the Flotation of Bastnaesite Rare-Earth Ores
A Process on the Recovery of RE Minerals With a Chelating Collector
REACTION CHEMISTRY
Cyclic Stability of Rare Earth Pentanickel Hydrides
Solvent Extraction Equilibria of Tervalent Lanthanides: A Systematic Investigation of Selectivity of Chelate Extraction 99 H. Freiser
Thermodynamic Prediction of Distribution Coefficients for the Solvent Extraction of the Rare Earth Metals
Electro-Oxidation Extraction of Cerium in the TBP-HNO ₃ Two-Phase System

HIGH PURITY SEPARATION

"Continuous Displacement Chromatography" (CDC)
Preparation of High Purity Scandium Oxide by Extraction Chromatography
Adsorptive Preconcentration of Rareearth Oxine Complexes onto Activated Carbon and Determination by Higher Order Derivative X-Ray Fluorescence Technique Using AM ²⁴¹ Annular Source
V. Bhagavathy, M.L.P. Reddy, P.S.T. Sai, T.P. Rao and A.D. Damodaran
Rare Earth Oxides in Gaseous Desulfurization
Process Variables in the Preparation of High Purity Rare Earth Metals
EXTRACTION
Decomposition of Taiwan Local Black Monazite by Hydrothermal and Soda Fusion Methods
Stepwise Hydrochloric Acid Extraction of Monazite Hydroxides for the Recovery of Cerium Lean Rare Earths, Cerium, Uranium and Thorium
Computer Simulation of Rare Earth Solvent Extraction Circuits
Extraction of Rare Earths From a Low-Grade, Kaolinitic Ore by Percolation Leaching
RARE EARTH METAL ALLOYS
Preparation, Fabrication and Properties of a Rare Earth Intermetallic Compound—GdPd
High Coercivity Praseodymium-Cobalt Permanent Magnets243 M.H. Ghandehari

Solidified Neodymium-Iron-Boron Alloys
Studies on the Additions of Mischmetal to Al-Alloy Matrix Composites
Magnesium Alloys Containing Rare Earths for Space Applications: Microstructural Aspects
Economics of Production of Rare Earth Metal Alloys
APPLICATIONS
The Contribution of Lanthanide Oxides to High-Performance Materials, A Common Thread Among Many Diverse Technologies
Processing Chemically Prepared YBa ₂ Cu ₃ O ₇ Precursor Powders
Studies on Reactions in the Y ₂ O ₃ -CuO-BaO System at 1300°C
Rare Earths in Cracking Catalysts
Development of RE Phosphors for Lighting Applications
HIGH TEMPERATURE PROCESSING
Fused Salt Electrolysis of Rare Earth Metals
A Molten Salt Process for Producing Neodymium-Iron Alloys by Reduction of Nd_2O_3 with Sodium
Molten-Salt Electrolysis of Neodium from a Chloride Electrolyte

Fluoride Melts	77
Production of SmCo ₅ Alloy by Calciothermic Reduction of Samarium Oxide	89
Subject Index4	03
Author Index4	05

MARKET AND BENEFICIATION

NONCOMMUNIST WORLD MARKETS FOR

RARE FARTH MINERALS

F.E. Katrak, I.S. Servi, M. Ozog, and J.C. Agarwal

Charles River Associates Incorporated 200 Clarendon Street Boston, Massachusetts 02116

Introduction

Rare earths markets by definition usually include not only the rare earth elements, but also yttrium. They can be subdivided into a very large light rare earth fraction (about 95 percent by weight of all rare earths consumed), consisting mainly of cerium and lanthanum and a smaller fraction (with much higher unit value) consisting of selected high-purity oxides or elements such as yttrium, europium, samarium, or neodymium.

CRA estimates that the noncommunist world market for all rare earths and yttrium was on the order of US\$750 million in 1986.

The main focus of this paper is on the principal uses for rare earths, some CRA-developed proprietary data on their consumption by region, and the selective nature of business opportunities in the rare earth markets. We also provide forecasts on the future trends in these markets.

Consumption of Rare Earths: Publicly Available Data

Published historical data on consumption are limited and often either incorrect or not very useful.

As an example, Table I gives the U.S. Bureau of Mines data for 1979 through 1986, segmented according to four broad use categories. As shown, the broad categories of end uses for these data make it difficult to understand clearly the underlying uses and the nature of the forces driving these markets.

Rare Earths, Extraction,
Preparation and Applications
Edited by R.G. Bautista and M.M. Wong
The Minerals, Metals & Materials Society, 1988

Table I. HISTORICAL DATA ON RARE EARTHS CONSUMPTION (Tonnes Oxide)

1984E 1985 1986	14,087 5,900 4,400 4,334 4,000 3,650 2,601 2,300 3,400 378 500 350	21,400 12,700 11,800	based on U.S. Bureau of Mines Minerals Yearbook, various years.
1983	12,740 3,920 2,352 342	19,354	u of Mine
1982	9,400 5,100 2,200 400	17,100	J.S. Burea
1981	9,100 7,200 4,400 400	20,100	ased on U
1980	9,013 7,446 3,004 653	18,900	, 1988, b
1979	6,900 5,700 2,300 500	16,000	River Associates, 1988,
U.S. Market Segment	Petroleum Catalysts Metallurgical Glass/Ceramics Electronic/Magnetic	Total United States	SOURCE: Charles River

Some excellent comprehensive reviews on rare earths have been published. See, for instance, "Rare Earths Industry Profile and Market Review," <u>Industrial Minerals March 1979</u> and "Rare Earths -- Attracting Increasing Attention," <u>Industrial Minerals April 1984</u>. Reviews of selected market segments are also available in the literature, for instance, Sauvion, G.N. and Ducros, P., "Catalysts: A Growing Market for Rare Earths," <u>Journal of the Less Common Metals</u> 111, p. 23-25, 1985.

The information reported in these and other publications as well as in proprietary reports is, in general, fragmentary. Therefore, Charles River Associates undertook the major task of establishing a detailed proprietary database of the rare earth consumption patterns in world markets.

Consumption of Rare Earths, 1986: CRA Proprietary Database

Noncommunist world consumption of

- Yttrium,
- Europium,
- Neodymium,
- Samarium.
- Gadolinium, and
- Light Rare Earths

segmented into

- The United States,
- Japan,
- Western Europe, and
- The rest of the noncommunist world (RONCW)

for 1986, is summarized in Table II. As shown in Table II:

- Estimated consumption of light rare earths (about 21,200 tonnes) accounts for 93 percent of all consumption of rare earth oxides (about 22,600 tonnes).
- The next largest consumption is that of yttrium, samarium, and neodymium.
- The United States accounts for about 45 percent of the total consumption of combined rare earths, Western Europe for 27 percent, Japan for 20 percent, and the rest of the noncommunist world for 8 percent.
- Estimated consumption of light rare earths in the United States, Western Europe, and the rest of the noncommunist world is well over 90 percent of the total consumption of all combined rare earths; however, in Japan, light rare earths account for around 81 percent of total combined rare earths consumption.

PARCARE

- Japan accounts for major portions of the consumption of heavy rare earths, at about 55 percent of yttrium, 65 percent of europium, 73 percent of samarium, and 65 percent of gadolinium.
- The United States and Japan are roughly equal consumers of neodymium.

Table II. CRA ESTIMATED DEMAND FOR RARE EARTHS
BY TYPE AND GEOGRAPHICAL REGION:
1986 (Tonnes of Oxide Equivalent)

Element	United States	Japan	Western Europe	RONCW	NCW
Yttrium	109	238	68	17	432
Europium	6	29	9	1	44
Neodymium	201	193	10	0	404
Samarium	88	346	37	5	476
Gadolinium	15	46	10	0	71
Light Rare Earths	9,661	3,781	6,006	1,799	21,247
Total	10,080	4,663	6,139	1,822	22,674

Note: Numbers are rounded and may not add up to totals.

SOURCE: Charles River Associates estimates, 1988.

Details of estimated CRA demand by use are discussed later. Because Table II was constructed by trial and error based on many sources of fragmented information, the **error margin** in our estimates is large. We believe that our estimates for consumption of light rare earths are likely to be within the 20 percent range, and that our estimates for heavy rare earths fall in the 30 percent range. Note also that in general, for consumption estimates of light rare earths as shown, the total across the noncommunist world is likely to be more reliable than the breakdown by region.

In order to understand the size of these markets, we have shown, in Table III, the dollar values for each of these rare earth oxide markets. As shown:

- The noncommunist world market for all rare earths (oxides and metals) is approximately \$760 million.
- Even though the U.S. market for all combined rare earths is the largest in terms of quantity (as discussed before), the Japanese market is the largest by our estimates in terms of dollar size, at around \$346 million, followed by the U.S. market, at about

9063561

\$235 million. The reason is that higher-value heavy rare earths consumption is greater in Japan and the United States than elsewhere.

 Samarium and europium are the two most important heavy rare earths in terms of their dollar market size. Samarium and neodymium market values are based on a portion of the demand being for metal, whereas all the other rare earth market sizes are based on oxide values only.

Table III. CRA ESTIMATED MARKET SIZES IN 1986 U.S. DOLLARS BASED ON FORM AND PURITY OF RARE EARTH USED: 1986 (Million 1986 U.S. Dollars)

Element	United States	Japan	Western Europe	RONCW	NCW
Yttrium	12	26	7	2	47
Europium	11	55	16	2	83
Neodymium	19	20	1	0	40
Samarium	35	114	15	2	165
Gadolinium	2	6	1	0	10
Light Rare Earths	157	125	108	23	414
Total	235	345	149	29	759

Note: Numbers are rounded and may not add up to totals.

SOURCE: Charles River Associates estimates, 1988.

The underlying **value** of each of the oxides and metals (in 1986 U.S. dollars per kilogram), in CRA estimates, is as follows:

	Metal	<u>Oxide</u>
Yttrium	110	
Europium	1900	
Neodymium	80	260
Samarium	130	395
Gadolinium	140	
Mixed lights	10	
Cerium	40	
Lanthanum	20	

The detailed segmentation of each rare earth's consumption by end use **and** region is summarized in Tables IV through IX. The actual CRA estimates for consumption by use and region are proprietary data and are not discussed; however, we have shown the approximate consumption in each use and region.



Table IV. CRA ESTIMATED SEGMENTATION OF YTTRIUM CONSUMPTION BY END USE AND REGION: 1986

	United States	Japan	Western Europe	RONCW
Color TV Phosphors	Α	В	А	Α
Other CRTs	D	С	D	D
Tricolor Lamps	D	С	С	N
X-ray Screens	D	N	N	N
Oxygen Sensors				
Auto	D	D	D	D
Nonauto	D	D	N	N
Other Ceramics				•••
Sialon	D	D	D	N
Zirconia	N	С	N	N
Lasers	D	D	N	N
High-temperature Coatings				
MCrAly	D	N	N	N
ODS	N	N	N	N
Thermal Barriers	N	N	N	N
Superconductors	D	D	D	D

Note:

A: 60 percent or more of total consumption in a region

B: 30 percent to 59 percent of total consumption in a region C: 10 percent to 29 percent of total consumption in a region

D: less than 10 percent of total consumption in a region

N: no significant demand

SOURCE: Charles River Associates estimates, 1988.

Table V. CRA ESTIMATED SEGMENTATION OF EUROPIUM CONSUMPTION BY END USE AND REGION: 1986

	United States	Japan	Western Europe	RONCW
Color TV Phosphors	Α	С	В	Α
Other CRTs	D	С	D	D
Tricolor Lamps	В	Α	Α	N

Note:

A: 60 percent or more of total consumption in a region

B: 30 percent to 59 percent of total consumption in a region C: 10 percent to 29 percent of total consumption in a region

D: less than 10 percent of total consumption in a region

N: no significant demand

SOURCE: Charles River Associates estimates, 1988.

8

*