Industrial Applications of the Rare Earths, an Overview*

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Abstract

The first applications of the rare earths appeared at the end of the last century. During the nearly hundred years that have followed a wide range of uses has emerged but still about 90% of the rare earths are being used as concentrates and mixtures. The bulk of present consumption of approximately 25 000 tons is divided between three major areas: catalysis, glass/ceramics and metallurgy. Applications in electronics, magnets etc. represent only a few per cent by volume but since they require individual high-purity rare earths the value is significant or around a quarter of the total sales. Some examples of current applications are given with special emphasis on the opportunities which lie in the utilization of the chemical properties of the individual rare earths.

1. Introduction

After the discoveries of the first rare earths, yttrium by Gadolin in 1794 and cerium by Berzelius, Hisinger and Klaproth in 1803, it took nearly a hundred years before practical applications in industrial scale emerged. Austrian scientist Carl Auer von Welsbach (1858–1929) made at the turn of the century the important inventions which marked the beginning of the rare earths industry.

Auer von Welsbach was one of the most prominent rare earth chemists in the last century. He was the discoverer of the elements neodymium and praseodymium and he also nearly became the first to separate the element 71. In 1891, a patent was granted to him for a new type of incandescent gas mantle containing thorium and cerium. The role of cerium (1%) was minor in this application but, nevertheless, due to the superb properties of the mantle, the production scale was enormous: by 1930 more than 5 billion Auer mantles had been sold. The second invention of Auer von Welsbach, flints based on pyrophoric alloy of mischmetal, turned equally to a success and led to the expansion of the industry and search for new rare earth raw materials outside Europe [1, 2].

Table I lists the applications of rare earths by 1920 [3]. Considering the low toxicity of the rare earths [4, 5] it is not surprising to find some medical applications in the list, too.

TABLE I. Early Applications of the Rare Earths [3, 7]

In use by 1920
Incandescent mantles
Pyrophoric alloys
Cerium in arc carbons
Colorants in glass and enamel
Various catalysts
Ceric salts as oxidants
Medical applications
Applications in textile industry
Additional uses by 1950
Ceria for glass polishing
Glass decolorizing (CeO_2 + Nd_2O_3)
Cerium (mischmetal) in ferrous metallurgy
Applications in nonferrous metallurgy
Activators in phosphors

The first applications were based on rather impure rare earths or mixtures, which is understandable in the light of the separation processes available at that time. For most rare earths only the very tedious fractional precipitation and crystallization processes could be used. However, oxidation of trivalent cerium to the tetravalent state provided a simple way to fairly pure cerium salts. In 1930 an electrolytic reduction process was developed for europium, ytterbium and samarium [6] and this provided a shortcut in the separation of the reducible metals. It was not until 1950s that separation processes based on ion exchange and complex formation reactions made rare earths of high purity (>99.9%) commercially available in quantity [8–10]. However, the prices remained prohibitive for many applications. For instance, in 1956 100 grams of europium oxide (99%) costed 9000 $ and even the prices of dysprosium and erbium oxides were 5000 $/100 g [11].

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2. Applications Today

In the eighties the annual consumption of rare earths, calculated as oxides, has been around 25 000 tons [12–15]. The growth rate is now very slow compared to that of ten years ago when the consumption rose from 15 000 tons in 1970 to 23 000 tons in 1974. This slow down is largely due to the diminishing use of rare earths in the steel industry where calcium and magnesium have partly replaced them.

Nevertheless, metallurgical applications are still one of the three major areas of applications. The two others – catalysis/chemical and glass/ceramics – have gained in importance in past years although there are differences between the major markets (Figs. 1 and 2). It is interesting to note that these major applications were known already forty years ago (Table I).

The percentage of rare earths used in electronic, magnetic, optoelectronic and in highly specialized applications is small (2–4%) but growing at a rate of 15% [13]. As these applications usually demand separated high purity elements other than lanthanum and cerium, the value of this group is significant or in the order of 25% of the total sales.

Taking a closer look at the various applications, the utilization of the unique optical properties of the rare earths ions could be taken as an example. Table II lists the applications where absorption or emission of electromagnetic radiation is involved. Besides traditional uses in the glass industry as colorants and decolorants, there are interesting new

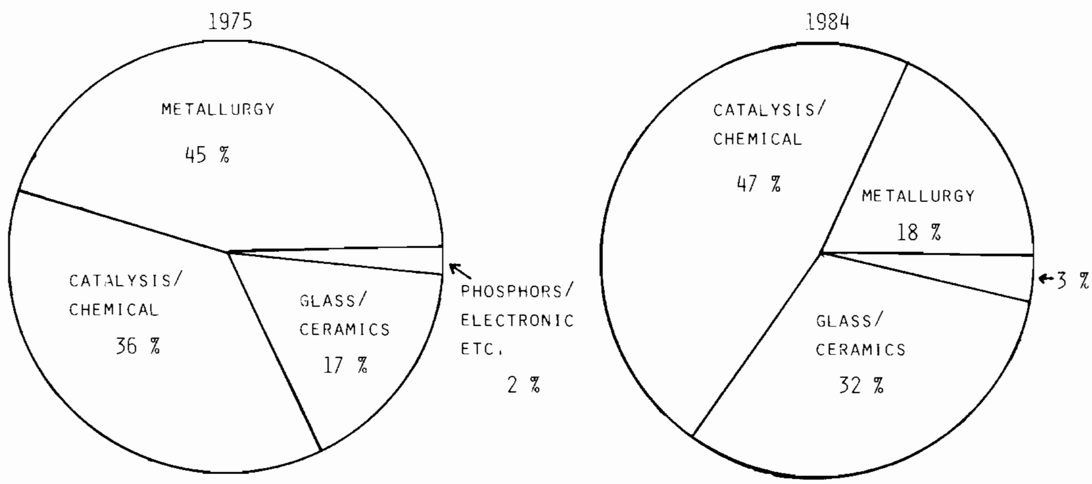

Fig. 1. The changing pattern of rare earth consumption 1975–1984.

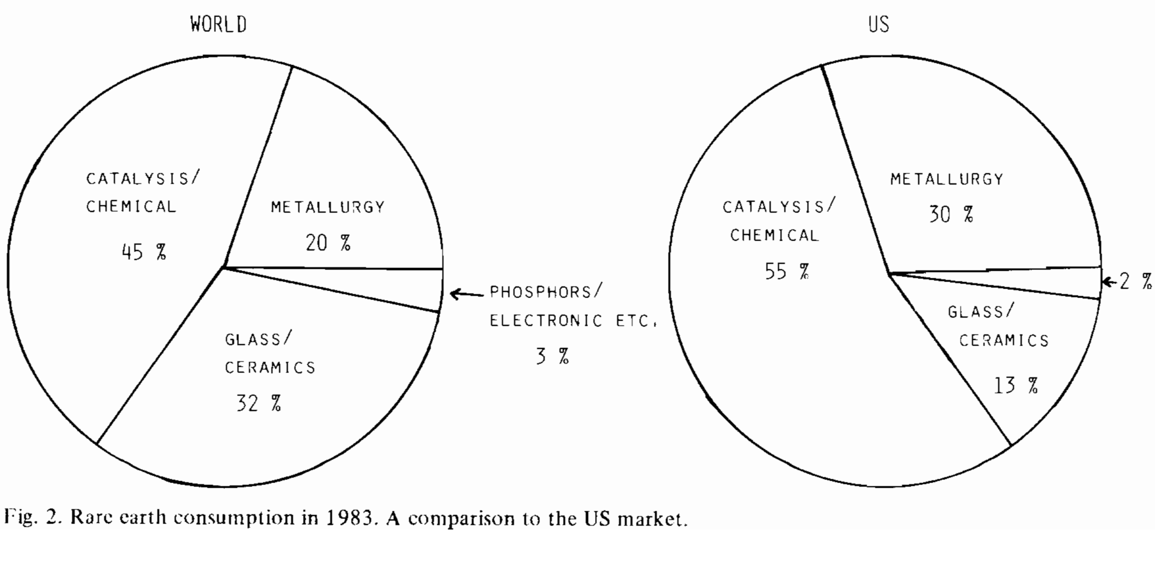

Fig. 2. Rare earth consumption in 1983. A comparison to the US market.

TABLE II. The Applications of Rare Earths Based on Absorption and Emission of Radiation

Application	Example	Reference
Glass color	Nd_2O_3	33, 34
Glass decolorizing	$CeO_2 + Nd_2O_3$	33, 34
IR transparency	La_2CaS_4	35
Optical glass	La_2O_3	34
UV, X-ray, γ-radiation		
protection	Ce	33, 34
Pigment	$ZrSiO_4{:}Pr^{4+}$	41
Lasers	$Y_3Al_5O_{12}{:}Nd^{3+}$	42
Phosphors:		
color TV	$Y_2O_2S{:}Eu^{3+}$	36
fluorescent lamps	$BaMgAl_{10}O_{20}{:}Eu^{2+}$	37
X-ray intensifying screens	$LaOBr{:}Tb^{3+}$	38, 39
electroluminescent devices	$ZnS{:}Tb^{3+}$	40
temperature sensors	$La_2O_2S{:}Eu^{3+}$	43
Microwave absorption	$Y_3Fe_5O_{12}$	44
IR up-conversion	$YF_3{:}Yb^{3+}, Er^{3+}$	45

applications in such areas as electroluminescent displays, fluorescent lamps, IR up-conversion systems and temperature sensors.

The development in many applications has followed the same pattern: classical materials have been replaced by rare earth based materials which are usually more expensive but have superior properties. Later second or even third generation rare earth products have appeared on the market. Examples of this kind of development include TV and X-ray phosphors as well as magnets where the $SmCo_5$ material is now being replaced by Nd–Fe–B alloys [16].

3. Outlook

3.1. Availability

The world rare earth reserves are now estimated to be 45 Mtons out of which 80% are located in China [14]. Even if the full production capacity of the industry would be utilized, the reserves would last hundreds of years.

Another question is at what price the elements and their compounds are available. The current prices roughly fall into three groups which reflect the distribution of the elements in nature and their current demand. Lanthanum and cerium oxides are relatively inexpensive. Their list prices in small quantities (1–20 kg, 99.9%) are around 20 $/kg while the metals cost 5–6 times more. The oxides Pr, Nd, Sm, Gd and Y cost 80–140 $/kg, those of Er, Yb, Ho are 2–4 times more expensive. The price range for Tb and Eu oxides is 1200–1900 $/kg while the very scarce thulium and lutetium cost up to 8000 $/kg as oxide [17]. Most rare earths (around 90%) are still used as concentrates or mixtures, however, and the prices are significantly lower than those quoted above.

An interesting case is scandium which is produced only on the kg scale, the world production being around 25 kg [18]. The availability is at the present poor even at the high prices asked. There seems to be no exploration or mining specifically for scandium but it is recovered as a by-product from several non-rare earth sources such as uranium and tungsten concentrates. The current interest in scandium is partly due to the fact that it is used to partially replace gallium in gadolinium gallium garnets (GGG) [46].

It may be concluded that should a higher demand develop for any of the rare earths due to novel applications, for instance, the industry could probably step up the production and meet the market requirements in a relatively short time. This also applies for scandium because the known reserves would allow a level of production several times higher than the present, apparently insufficient one.

3.2. Chemical Applications

Some interesting applications have already been obtained by utilizing a specific chemical property of a rare earth or combining two properties to obtain the desired effect. This approach obviously offers many additional, still unexplored opportunities. In the following some of the unique properties are listed and relevant application examples given.

Oxidation/reduction potential

The Ce^{4+}/Ce^{3+} couple is a powerful oxidizing agent where the potential can be regulated by the media (in 1 M $HClO_4$ 1.70 V, in 1 M H_2SO_4 1.44 V [19]). It has been used in volumetric analysis since the last century and also in organic oxidations for decades but only recently the reactions have been systematically studied [20, 21]. Besides the classical ceric ammonium nitrate (CAN), several other compounds are now available for selective oxidations [22]. The ceric ions can be electrochemically regenerated *in situ* [23]. The divalent oxidation states especially Sm(II) and Yb(II) are also increasingly utilized in organic synthesis [20].

Solubility

Rare earth fluorides are sparingly soluble and CeF_3 has been used to control the fluoride concentrations in chromium electroplating baths. Addition of rare earths affects also favorably the dissolution of potassium feldspar possibly through the formation of CeF_3 or CeOF and slow release of HF from it [24].

Coordinating ability

The fairly large ionic radii and electrostatic nature of the bonds leads to high coordination numbers (8–12) when steric factors permit. Scandium differs by having an octahedral coordination in most of its compounds [25].

A recent example of the application in coordination chemistry is offered by the use of paramagnetic Gd complexes in the enhancement of medical NMR imaging. Diethylenetriaminepenta-acetic acid (DTPA) forms a strong chelate with Gd in aqueous solution ($\log K = 22.5$) which can be used to transport Gd in the body [26]. Another example is the phytate ligand which has six oxygen donor sites to coordinate Gd [27]. Besides the thermodynamic and kinetic stability of the complex, toxicity and selectivity are important factors. In the case of the Gd-phytate complex intravenous injection experiments with rats have shown its enhancing power on liver NMR image.

Reactivity

Rare earth metals are very reactive forming thermodynamically stable compounds especially with oxygen. Examples include the well-established use of mischmetal in the steel industry [28], and the exceptional stability of Y_2O_3 up to its melting point of 2430 °C.

Catalytic properties

In addition to the traditional application in cracking catalysts, the rare earths have several other applications in heterogeneous catalysis [29, 30]. The catalytic activity is in most cases probably a complex effect of several factors including surface properties, redox potential, non-stoichiometry, ionic size etc.

Recently, there has been considerable interest in homogeneous polymerization catalysts where neodymium complexes with organic ligands and organolanthanoid compounds have been studied especially [31, 32].

4. Concluding Remarks

The rare earths are clearly the largest group in the periodic table comprising one quarter of the stable metallic elements. Many of their properties are largely similar and thus one element in bulk applications can be replaced by another. However, most of the novel high-technology uses are based on differencies in properties rather than in similarities. The availability of the 16 stable elements – many of then at reasonable prices and in sufficient quantities – should provide challenging opportunities for basic and applied research to find new applications.

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References

1 E. Schmal, 'Carl Auer von Welsbach', Deutsches Museum, Abhandlungen und Berichte, 20, Heft 1, Verlag von R. Oldenbourg, München, 1952, pp. 1–22.
2 E. Greinacher, in K. A. Gschneidner, Jr. (ed.), 'Industrial Applications of Rare Earth Elements', American Chemical Society, Washington, D.C. 1981, p. 3.
3 J. F. Spencer, 'The Metals of the Rare Earths', Longmans Green, London, 1919, p. 234.
4 T. J. Haley, *J. Pharm. Sci., 54,* 663 (1965).
5 P. Arvela, in H. Grobecker, G. F. Kahl, W. Klaus, H. Schmitt and P. A. von Zwieten (eds.), 'Progress in Pharmacology', Vol. 2, Gustav Fischer Verlag, Stuttgart, 1979, p. 73.
6 L. F. Yntema, *J. Am. Chem. Soc., 52,* 4264 (1930).
7 R. C. Vickery, 'Chemistry of the Lanthanons', Butterworths, London, 1953, p. 269.
8 F. H. Spedding, *Proc. Rare Earth Res. Conf. 11th,* Traverse City, Mich., U.S.A., 1974, p. 266.
9 E. V. Kleber and B. Love, 'The Technology of Scandium, Yttrium and the Rare Earth Metals', Pergamon, Oxford, 1963.
10 R. J. Callow, 'The Industrial Chemistry of the Lanthanons, Yttrium, Thorium and Uranium', Pergamon, Oxford, 1967.
11 R. M. Mandle and H. H. Mandle, *Prog. Sci. Technol. Rare Earths, 1,* 416 (1964).
12 B. T. Kilbourn, *Ceram. Bull 63,* 678 (1984).
13 P. Falconnet, *J. Less-Common Met., 111,* 9 (1985).
14 J. B. Hendrick, in 'Mineral Facts and Problems', Bureau of Mines, Washington, D.C., 1985, p. 835.
15 B. T. Kilbourn, *Ceram. Bull., 65,* 736 (1986).
16 K. H. J. Buschow, *Mater. Sci. Rep., 1,* 1 (1986).
17 J. B. Hendrick, in 'Minerals Yearbook 1984', Vol. 1, Bureau of Mines, Washington, D.C., 1985, p. 751.
18 B. Petkof, in 'Mineral Facts and Problems', Bureau of Mines, Washington, D.C., 1980, p. 793.
19 G. F. Smith and C. A. Getz, *Ind. Eng. Chem. (Anal. Ed.), 10,* 191 (1938).
20 H. B. Kagan and J. L. Namy, *Tetrahedron, 42,* 6573 (1986).
21 J. R. Long, in K. A. Gschneidner, Jr. and L. Eyring (eds.), 'Handbook of the Physics and Chemistry of the Rare Earths', Vol. 8, North Holland, Amsterdam, 1986, Chap. 57, p. 335.
22 H. Firouzabadi and N. Iranpoor, *Synth. Commun., 13,* 1143 (1983).
23 S. Torii, H. Tanaka, T. Inokuchi, S. Nakane, M. Akada, N. Saito and T. Sirakawa, *J. Org. Chem., 47,* 1647 (1982).
24 O. Erämetsä, A. Johansson and M.-L. Sihvonen, *Acta Polytechn. Scand., Ch. 95,* 1 (1970).
25 M. Leskelä and L. Niinistö, in K. A. Gschneidner, Jr. and L. Eyring (eds.), 'Handbook of the Physics and Chemistry of the Rare Earths', Vol. 8, North Holland, Amsterdam, 1986, Chap. 67, p. 203.
26 H. J. Weinmann, *Am. J. Radiol., 142,* 619 (1984).
27 F. Conti, M. Delfini, F. Scopinaro and U. Croatto, *Inorg. Chim. Acta, 140,* 355 (1987).
28 L. A. Luyckx, in K. A. Gschneidner, Jr. (ed.), 'Industrial Applications of the Rare Earth Elements', American Chemical Society, Washington, D.C., 1981, p. 43.
29 G. N. Sauvion and P. Ducros, *J. Less-Common Met., 111,* 23 (1985).
30 B. T. Kilbourn, *J. Less-Common Met., 126,* 101 (1986).
31 M. Bruzzone, in T. J. Marks and J. J. Fragala (eds.), 'Fundamental and Technological Aspects of Organo-f-Elements Chemistry', D. Reidel, Dordrecht, 1985, p. 387.

32 Quyang Jun, in Xu Guanyxian and Xiao Jimei (eds.), 'New Frontiers in Rare Earth Science and Applications', Vol. I, Academic Press, Orlando, 1985, p. 606.
33 P. Maestro, *J. Less-Common Met., 111*, 43 (1985).
34 L. W. Riker, in K. A. Gschneidner, Jr. (ed.), 'Industrial Applications of the Rare Earth Elements', American Chemical Society, Washington, D.C., 1981, p. 81.
35 W. B. White, D. Chess, C. A. Chess and J. V. Biggers, *Trans. SPIE, 297*, 38 (1981).
36 J. R. McColl and F. C. Palilla, in K. A. Gschneidner, Jr. (ed.), 'Industrial Applications of the Rare Earth Elements', American Chemical Society, Washington, D.C., 1981, p. 177.
37 B. M. J. Smets, *Mater. Chem. Phys., 16*, 283 (1987).
38 J. A. Rabatin, in K. A. Gschneidner, Jr. (ed.), 'Industrial Applications of the Rare Earth Elements', American Chemical Society, Washington, D.C., 1981, p. 203.
39 L. H. Brixner, *Mater. Chem. Phys., 16*, 253 (1987).
40 M. Leskelä and M. Tammenmaa, *Mater. Chem. Phys., 16*, 349 (1987).
41 R. A. Eppler, *Ceram. Bull., 56*, 213 (1977).
42 R. Reisfeld and C. K. Jørgensen, 'Lasers and Excited States of Rare Earths', Springer, Berlin, 1977.
43 K. A. Wickersheim and R. B. Alves, *Ind. Res. Dev.*, 82 (Dec. 1979).
44 J.-P. Castera, *J. Appl. Phys., 55*, 2506 (1984).
45 F. Auzel, in B. Jéżowska-Trzebiatowska, J. Legendziewicz and W. Strek (eds.), 'Rare Earths Spectroscopy', World Scientific, Singapore, 1985, p. 502.
46 J. Griffiths, *Ind. Miner., No. 4*, 19 (1986).