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Review

Rare earths: the unseen metals

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ABSTRACT

High profile and primary commodities such as copper, zinc and others share the global limelight with respect to mining, industrial processes, and numerous end products for household and commercial markets. Apart from base metals, noble metals enjoy stock market notoriety and media attention. In contrast, rare earths furtively experience a plethora of residential, institutional, and industrial applications. The relatively abundant metallic elements commonly known as the "rare earths" present a low key image worldwide. The group is normally comprised of 15 lanthanides of which cerium is the most abundant plus scandium, thorium, and yttrium. The main host minerals consist of bastnäsite, monazite, and xenotime. Other sources include allanite and spent heavy mineral sands from uranium processing operations such as in Australia. Countries such as China and the United States are the largest producers of rare earth materials while over 30 other countries both contribute smaller quantities for worldwide consumption and generate commercial products. Global reserves of rare earth elements are dominated by China (43%), the CIS (19%), and the United States (13%). The People's Republic of China accounted for the majority of the world's annual production of raw rare earths in the year 2002. The perceived "rare metals" have a strategic importance while being well suited to electronic and other diverse end uses. The supply and demand of rare earth products during the past decades have been relatively steady and subject to fluctuations in delivered price. As a condensation of the state-of-the-art in this fascinating industry, the paper serves to highlight the properties, sources, and recovery of these forgotten metals which find use in numerous unseen applications. It is intended to apprise the reader of the salient facts of these useful metallic elements that globally go unnoticed since they are overshadowed by the popularity and grandeur of precious metals such as gold and platinum.

Keywords: Extractive metallurgy; Production; Properties; Rare earths

1. INTRODUCTION

The term "rare earths" was applied in the 18th century upon discovering the group of 15 elements in the lanthanide series which were then believed to rarely occur in nature. The rare earths were discovered by a Swedish Army Lieutenant in 1787 when he collected a black mineral called ytterbite (later renamed gadolinite) from a quartz and feldspar mine near the village of Ytterby. The rare earths were difficult to isolate due to their similar chemical structures. Johann Gadolin, a Finnish chemist, managed to separate an impure yttrium as the first element from the mineral ytterbite in 1794. Sweden and Norway produced rare earths commercially in the 1880's from the mineral monazite. Invention of the Welsbach incandescent lamp mantle in 1884 became a milestone for later recovery. Production subsequently commenced within Brazil in 1887 while India began recovery of the ore in 1911. Monazite was mined in North Carolina, USA, in 1893 (Hedrick, 2001). Cerium (Ce), which is the most abundant rare earth element at 60 parts per million (ppm), places 25th in the series of 78 common elements identified in the Earth's crust. The crustal abundance of cerium approaches that of zinc and exceeds that of both copper and tin (Bounds, 1998).

Although yttrium is not a lanthanide, it was included in the overall group of 18 metals since it often naturally occurs in solid solution with these elements as a result of its similar ionic radius. Yttrium (Y), which has a stable and naturally occurring isotope ^{88}Y, is the second most abundant rare earth element in the Earth's crust at a concentration of 33ppm. Albeit that one isotope of yttrium is relatively stable, this element has a total of 35 other isotopes which range in stabililty over the wide range of nanoseconds, milliseconds and through to days with respect to decay (Jefferson Lab, 2003).

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Scandium (Sc), which is the first of the transition elements, was included because its smaller atomic and ionic size result in its occurence within ores containing rare earths (USGS, 2003a). Scandium, which has one naturally occurring isotope ^{46}Sc, is a soft and silvery-white metal similar in appearance and weight to aluminum. Scandium's isotope (Sc-46) is used as a tracer in the analysis of crude oil (NRC, 2003). Scandium is the 31st most abundant element in the Earth's crust at an average crustal concentration of 22ppm which surpasses that of lead, mercury, and precious metals. Scandium, which does not selectively consolidate with common ore-forming anions, rarely occurs in concentrated quantities (Hedrick, 2001). Scandium is widely dispersed in the lithosphere and Hedrick (2003) reported that it forms solid solutions with an excess of 100 known minerals. Since scandium has a higher melting point than aluminum it is used by designers of spacecraft. It is interesting that scandium finds wide application in sporting goods equipment such as in the production of metallic baseball bats along with its use in the telecommunications industry (NRC, 2003). As a contrast, Chemistry (2003) expressed the abundance of rare earths in the universe on the basis of weight. The concentration of yttrium and scandium were reported at 7 and 30ppb respectively in terms of weight. Some literature cites that "true lanthanides" only consist of 14 elements (Bounds, 1998). Thorium (Th) was added to the group due to its similar chemical properties. Thorium historically was considered a rare earth due to its close association with rare earths in nature. Some regulatory agencies now regard thorium as radioactive waste in lieu of being considered as a by-product of rare earth production. Some academicians may exclude promethium (Pm) from the rare earth category since it only occurs as a product of nuclear fission. Depending upon definition, the total count of a broad "rare earths" category is either 16 or 18 elements.

It was realized later in the 20th century that the crustal abundance of rare earths as a group was comparable to other major elements dispersed within the Earth's crust. Rare earths are found in similar concentrations to copper, nickel, lead, silver, and tin. Thulium (Tm) and lutetium (Lu) are the least abundant upon reporting at only 0.5ppm but occur at a higher concentration than antimony, bismuth, and thallium (USGS, 2003b). Thulium is more abundant than silver and cadmium. The group has found widespread application worldwide in physical states such as metals, oxides, and other compounds such as chlorides. The metallic elements with atomic numbers ranging from 57 to 71 inclusive were named by Johann Gadolin (Rare Earth Elements, 2003). Elemental forms of rare earths are characterized as iron gray to silvery lustrous metals that are malleable, soft, ductile, and reactive at elevated temperatures especially when finely divided. Melting points range from 798°C to 1663°C for cerium and lutetium respectively. Rare earths, which have similar chemical properties to aluminum, are included among the most electropositive elements while their chemical bonding is virtually totally ionic. The electronic structure of lanthanides differ from each other by the step-wise addition of electrons to the 4f subshell such as f^0 to f^{14} for lanthanum and lutetium respectively (Bounds, 1998). Lanthanum is employed in water treatment reagents to reduce phosporous levels in potable water (Lynas, 2002). Their unique properties of (i) catalytic activity (ii) enhancement of metallurgical properties (iii) coloring ability plus (iv) electrical and magnetic properties are employed in a wide variety of industrial applications. Albeit that substitutes are available for many end uses of rare earths, these are generally less effective. For example, palladium and ultrastable zeolites may be used in lieu of rare earths for petroleum cracking but result in a different range of products (Mineral Commodity Summaries, 1992). Rare earth catalysts reduce the number of stages required in polymer manufacture while replacing toxic components comprised of heavy metals.

One unobtrusive application of rare earths represents one of the oldest uses for mankind. Mischmetal is an alloy composed of 51-53% Ce, 22-25% La, 15-17% Nd, 3- 4% Pr, 2-3% Sm, 3% Tb, 3% Y, and 5% Fe which finds several metallurgical applications in superalloys, armour plate and stainless steel, high carbon steels, and high strength, low alloy (HSLA) steel. Mischmetal is pyrophoric and produces a spark when scratched thereby being used in cigarette lighters, automatic lighting devices for fuels such as natural gas and propane, miner's safety lamps, flares, and tracer ammunition for the military. Industrial applications include automotive catalytic converters, petroleum refining catalysts (ie., fluid cracking), fuel cells, glass polishing, coloring and optical lenses, CRT glass, colorants for glazes, coatings, refractories and stabilisers, electronic ceramics, and permanent magnets. The glass industry is a very large consumer of rare earths with respect to composition, refractive index and other attributes. Cerium oxides are normally used as a purifying and de-colorising agent in glass treatment. For example, neodymium glass is used for high technology lasers (Rhodia, 2002a). The strong magnetic properties of rare earths endure at high temperatures. The strongest permanent magnets are composed of neodymium-iron-boron and find application in electric motors, generators, computers, and magnetic rail tracks (Smart, 1999). General Motors utlizes as many as 200 small NdFeB electric motors in one vehicle. Neo magnets are used in CD drives while the headphones of all MP3 players contain neodymium magnets for greater performance. Cerium and yttrium oxides are typically employed as sintering aids in the fabrication of enamels and glazes (Smart, 1999). The ceramic industry utilizes rare earth based products to create various colors. For example, yellow pigment is derived from praseodymium, purple from neodymium, while burgundy pigment uses a combination of cerium and praseodymium. Colors such as praseodymium yellows are stable up to 1400°C during the manufacturing process.

Rare earth elements (REE) are used as metallurgical additives and in various alloys such as the hardening and strengthening of aluminum and magnesium. Rare earth derivatives are employed as corrosion inhibitors in conjunction with surface treatment of metals. For example, yttrium which is half the weight of lead, a carcinogen, is used to manufacture non-toxic paints. Other uses consist of lasers, electronic components, jewelry, paint and lubricants, nuclear control rods, plus nuclear detectors and counters (Rare Earth Elements, 2003). Rare earth phosphors are applied in the manufacture of televisions and other cathode ray tubes, computer monitors, fluorescent lighting, radar, and X-ray intensifying film (USGS, 2003c). REE are suitable for the medical field such as magnetic resonance imaging (MRI) plus surgical and dental lasers, while also reporting in dyes, fertilizers, and for storing holographic images. The gross sales of phosphors including pigments accounted for about 36% of the overall rare earths €901.5 million (US$830 million) market worldwide in 2000 (X-rates, 2003). Additional areas of consumption include microwaves, propulsion jets, data storage, optical fibres, textiles, mirrors, and electron microscopes (Roskill, 2001). The attributes of rare earths such as being environmentally benign and their unique properties allow many useful applications. Another area of use is the manufacture of nickel-metal hydide (Ni-MH) rechargeable batteries. Bounds (1998) described the incorporation of rare earths within catalytic converters, exchange-coupled magnets, and the evolution of rechargeable batteries. Apart from their reduced size, nickel-rare earth rechargeable batteries are environmentally friendly due to the replacement of heavy metals such as cadmium, lead and mercury. The industrial application of rare earth transition metal intermetallics (eg., SmO_5 and $Nd_2Fe_{14}B$) has allowed development of commercial items such as personal computers (eg., notebooks) and Walkmans that we take for granted in our daily activities (Bounds, 1998). Performance additives assist in the production of clean energy and minimum impact on the greenhouse effect (Rhodia, 2002a).

The 2002 world mine production of rare earths amounted to 85,500 metric tonnes which represented a marginal increase from the previous year. This figure translates into 119,000 tonnes when expressed as rare earth oxides (USGS, 2003a). The overall world resources of contained rare earth elements (REE) are estimated at about 100 million tonnes located in China (43%), the CIS (19%), the USA (13%), Australia (5%) and India (1%). Australia's REE reserves are comprised of 80% in mineral sand deposits and 20% in hardrock deposits. The total world reserves of rare earths range from 88 to150 million tonnes depending upon the definition of reserves. Countries such as France and India represented the major import sources of rare earths in the form of chlorides, nitrates, various compounds and concentrates. The variety of rare earth-bearing ore species such as bastnäsite, monazite and ionic ores in the People's Republic of China provide it with a unique position in the global market place (Smart, 1999). Expensive rare earths in 2001 included europium oxide (€279-447, ie., US$250-400), terbium metal (€302-358), and ytterbium metal (€279-425) expressed in Euros per kilogram for large orders. The prices compiled by Metal Statistics (2002) for rare earths sold by the USA in 2001 varied according to small or large quantities. For example, cerium oxide (maximum purity of 99.999%) varied from 13-37€/kg while large tonnage orders ranged from 3.4-36€/kg. August 2003 prices for dysprosium metal and terbium metal were 71.7-127€/kg and €300-619 respectively for material greater than 99% purity (Market Prices, 2003). Less expensive rare earths include lanthanum metal (12-33.5€/kg) and holmium oxide (134-213€/kg). It is noteworthy that the most expensive rare earths are scandium metal and lutetium oxide which commanded a price of 1,956-13,413€/kg and 531-2,235€/kg respectively in global markets (Market Prices, 2003).

September 2003 prices for ytterbium metal were 195€/kg while lower priced rare earths were neodymium metal (5.7€/kg), praseodymium metal (6.0€/kg), and samarium metal (10.0€/kg) according to Metal Pages (2003). A significant difference exists for metals priced FOB China and that quoted through channels such as Rare Earths Marketplace (Market Prices, 2003) which publish on the basis of CIF U.S. port prices. For example, cerium oxide's pricing structure ranged from 10.7-29.6€/kg for Market Prices during August while the commodity was listed at 1.6€/kg for Metal Pages during mid September 2003. It is appropriate to mention the principles of value adding which affect price structure. For example, one kilogram of Chinese bastnäsite (aka bastnaesite) theoretically costing €2.7 actually contains rare earth oxides valued at €26.9 which represents a ten-fold increase. Hence, individual rare earths in their elemental state would fetch a value of €29.6 thereby contributing an additional 10% to the value of the oxides (Smart, 1999). The U.S. applies a modest tariff expressed as a percentage on imported rare earths which is in proportion to the value (ie., ad valorem) and tailored to each country of origin.

A lag time exists to obtain the latest pricing information for rare earths and specialty metals without incurring charges on several home page sites featured on the Internet since the figures are sometimes1-2 months or more behind the most recent data. Hence, it is sometimes difficult to cite realistic costs due to the lead time required to obtain relevant data concerning rare earths and related product forms. Paid daily access via a subscription to recognized sources such as Metal-Pages is advantageous to participants. Commercial publications such as one entitled "The Economics of Rare Earths and Yttrium" and costing about €2,125 are readily available to serious aficionados of the subject (Roskill, 2001). Apart from present pricing structure, the bulk of the 2001 vintage report may still be relevant in today's competitive culture since it describes production of rare earths in some 36 countries whilst about 48 major producing companies are profiled. The extensive Roskill report is anticipated to present a good overview of the worldwide industry albeit it does not include the significant changes in Asian production within the past two years such as in the Baotou region of northern China. It is significant that Hedrick (2001) has drawn information from some 70 sources and compiled a summary of the world rare earth situation with respect to global supply and demand and other related issues. Although the publication focussed on U.S. conditions prevailing in 2000, it highlighted activity in 12 other countries. After more than a decade of gathering rare earth data for the U.S. Geological Survey, this individual may be regarded as a reliable source of information. Apart from InfoMine's reports, other publications in the public domain include reports marketed by the USGS Minerals Information Services (eg., minerals yearbook), Indian Institute of Metals (TIFAC) and Saxman (2000). At present, no shortfall exists for a continuous supply of rare earth ores which are expected to adequately meet anticipated demand for several hundred years. This particular paper entitled "Rare earths: the unseen metals" presents a comprehensive overview of the diversified global rare earths industry and selected references thereby assimilating pertinent facts in a single publication.

2. RARE EARTHS

Table 1 illustrates 18 "rare earth elements" comprised of 15 metallic elements in the lanthanide series and three other metals with similar characteristics. Yttrium, which occurs with the lanthanides, plus scandium and thorium are normally included in the overall group since they exhibit similar chemical properties. The mineral bastnäsite (aka bastnaesite) contains a small amount of yttrium within the fluorocarbonate of cerium. Global estimates of unmined yttrium are as high as 610,000 tonnes. Ancient and recent placer deposits are a large source of yttrium coupled with ion-adsorption ore (ie., weathered clay deposits), carbonatites and uranium ores. Additional reserves consist of sedimentary phosphate deposits, apatite-magnetite rocks, monazite-bearing deposits, and deposits of columbium-tantalum minerals. For example, the specific uranium ore species at Blind River, Ontario in Canada is a potential source of yttrium. An entrepreneur is investigating development of a large carbonatite deposit in the Sudbury, Ontario region as both a fertilizer for nutrient-poor soils and as a mineral additive in livestock feed (Ross, 2003). The deposit contains about 65% igneous calcite (calcium carbonate), 10% apatite (phosphate rock) and is relatively low in impurities such as uranium-bearing minerals. The REE category is divided into two portions. Light rare earths consist of metals with atomic numbers from 57-63 (lanthanum to europium) while the heavy rare earths include those with atomic numbers from 64-71 inclusive (gadolinium to lutetium). The first four elements of the lanthanides are designated as light or ceric rare earths. The latter elements are referred to as the yttric or heavy rare earths (Bounds, 1998).

Table 1
Rare earths elements (Smart, 1999)

Element	Atomic No.	Element	Atomic No.
Scandium (Sc)	21	Yttrium (Y)	39
Lanthanum (La)	57	Cerium (Ce)	58
Praseodymium (Pr)	59	Neodymium (Nd)	60
Promethium (Pm)	61	Samarium (Sm)	62
Europium (Eu)	63	Gadolinium (Gd)	64
Terbium (Tb)	65	Dysprosium (Dy)	66
Holmium (Ho)	76	Erbium (Er)	68
Thulium (Tm)	69	Ytterbium (Yb)	70
Lutetium (Lu)	71	Thorium (Th)	90

3. SOURCE OF SUPPLY

As a general rule, rare earths normally occur in various compounds as trivalent cations in carbonates, oxides, phosphates, and silicates (Hedrick, 2001). The main minerals containing rare earths consist of bastnäsite, monazite, xenotime, and ion-adsorption clay. The latter two minerals are important sources of yttrium and other heavy rare earths albeit that they represent a small part of overall production (USGS, 2003a). Bastnäsite ($CeFCO_3$) contains 60-70% rare earth oxides (REO) such as lanthanum and neodymium. The mineral occurs as a mixture with dolomite breccia with syenite intrusives, carbonatite, pegmantite veins, and amphibole skarn. Bastnäsite, which is mined in hardrock deposits such as in China and California, USA, is the primary source of light rare earths. Bastnäsite was obtained from the Bastnäs mine in Sweden. Additional minerals hosting rare earths include beryl, cassiterite, columbite, garnet, muscovite, wolframite and the aluminum phosphate minerals. Scandium is a trace constituent of ferromagnesium minerals such as biotite and pyroxene and ranges in concentration from 5-100ppm equivalent scandium oxide (Hedrick, 2003). Scandium reports as a by-product within Chinese operations. To date, southern China is the only known source of ionic ores which have displaced xenotime as the main source of europium and yttrium. Yttrium, which is a soft and malleable silvery metal, has a similar density to titanium. The global demand for yttrium increased about four percent in 2001 as compared to the previous year (Hedrick, 2001). Monazite is rare earth phosphate [(Ce, La,Y,Th)PO_4] which is recovered as a component of heavy mineral sands as found in Australia and Madagascar. Pegmantites in the Befanomo area of Madagascar were reported to contain scandium (Hedrick, 2003). The high specific gravity of monazite facilitates its concentration by wind and water and it is commonly associated with illmenite, rutile and zircon as a constituent of heavy mineral sands (Smart, 1999). Thorium is a major constituent of this mineral and imparts radioactive properties to the monazite mineral containing 50-78% REO. The yttrium phosphate called xenotime (YPO_4 or $Y_2O_3.P_2O_5$) includes cerium, erbium, and thorium in its 54-65% concentration of REO. It is associated with pegmantite and igneous rocks and often is a component of heavy mineral sands which host other valuable materials such as uranium and rutile which is a minor source for TiO_2 pigment. Xenotime is commonly located in placer deposits. Other minerals hosting rare earths include (i) zircon which is a zirconium silicate ($ZrSiO_4$) with thorium, cerium and yttrium (ii) apatite which is a calcium fluorophosphate with cerium and (iii) allanite containing cerium and yttrium in its 5-20% REO (Rare Earth Elements, 2003). Some varieties of zircon contain up to 4% hafnium oxide. Rare earths occur in the species hagatalite as found in Hagata, Iyo Province, Japan. It should be emphasized that commercial products are in the form of rare earth concentrates which represent about 95% of global usage while the remainder consists of individual rare earth compounds.

China is the largest producing country for a wide range of rare earth elements. Ion-adsorption clay minerals are only located in the southern regions. Some of China's resources are iron deposits, tin, and tungsten which host rare earths and these are located in the provinces of Fujian, Guangdong, Guangxi, Jiangxi, and Zhejiang (Hedrick, 2003). Jiangxi province hosts the world's largest tungsten-dominated production base for rare earths. Apart from being a major source of tungsten, this province also produces electrolytic copper, niobium and tantalum. The country has officially designated ten non-ferrous metals in its production targets which resulted in a 33% growth. In 2002, the production of rare earth metals and mixed rare earth oxides from Jiangxi amounted to 3,091 (40% increase) and 4,255 (17.2% increase) tonnes respectively. The projected full year 2003 revenues for Jiangxi's non-ferrous metal industry are estimated at €1.48 billion which is about 22% greater than the year 2002. Over 170 state-owned producers actively engage in REE production. Joint ventures with foreign groups and small privately owned facilities also contribute to China's burgeoning rare earths industry. However, the rare earth industry is restricted in China thereby requiring government approval for foreign investment (CCBC, 2003). The People's Republic of China is a formidable competitor due to low labor rates and an ample supply of raw resources. During 2002 China produced 90,000 tonnes of rare earth mineral ores which represented a 19% increase year-on-year. The separated and smelted rare earth products from China amounted to 80,000 metric tonnes in 2002 which translated into a significant one year growth rate of 50 percent. Although China's annual overall rare earth output is approximately 80,000tpa its rare earth capacity is rated at 180,000tpa (China, 2003). Apparently, local producers in China are still eager to expand beyond this potential level of output which is almost double the current world demand. During the year 2003 a total of eight new rare earth facilities were commissioned in China. It is worth illustrating the long corporate names assigned to producers of rare earths in China such as (1) Jinxiungmao Rare Earths Co. which is a subsidiary of (2) Gansu Rare Earths Corporation (3) Baotou Huamei Rare Earth Products Co. Ltd. and (4) Sangfeng in Baotou City within Inner Mongolia. The home page for China Rare Earths (CRE) contains a two page listing of articles ranging from the present and spans a two year period which highlights rare earths and non-ferrous activity worldwide. Abstracts are taken from the "Metal-Pages" publication which has locations in London, UK, and Beijing, China. A one page summary in point form is provided in a "read only" format for each newspaper article. Unfortunately, the website is not user friendly since the English version is apparently encoded to prevent printing of any page flashed on the computer monitor's screen. Despite this shortfall, one can quickly acquire a brief outline of global activity whilst the vast majority of articles feature news items within China.

Considerable rare earths activity is in evidence within the Baotou region of Northwest China (China, 2003). It is worth noting that Inner Mongolia is considered the center of rare earth production in China with proven reserves of 40 million tonnes which represent 90 percent of the known resources in the People's Republic of China. The production base at Baotou in the Nei Mongol region in fact contains about 80 % of the world's rare earth reserves (E&Mj, 2003). Baotou City, situated in China's Inner Mongolia Autonomous Region, registered €163.7 million in production value for rare earths produced in the first half of 2003 which represented an increase of 108 percent. Baotou is ranked as one of the world's largest rare earth production centres due to its abundant resources. It was reported that Baotou intends to further expand development of its rare earth resources (China, 2003). Construction of a new rare earth separation line was completed in May 2003 for Baotou Damao Rare Earth Co., Ltd. in the Inner Mongolia Autonomous Region. The nameplate capacity of 125,000tpa is expected to be reached in 2008 with a capex of €40 million.

It was reported by China Rare Earths in August 2003 that another company in the same area, Baotou Rare Earth Hi-Tech Co. Ltd., expanded its capacity of rare earth oxides from 6,000 to 15,000tpa in 2003 by means of its three main plants (China, 2003). At present, supply exceeds demand under current market conditions. More than 90% of the neodymium recovered is sold domestically due to the poor demand on international markets. Meanwhile, China's Baotou Huamei Rare Earth Hi-Tec Co. has launched a project to produce 40,000 metric tonnes of rare earths contained in concentrates. This company is a subsidiary of China's largest producer of rare earths. Baotou Rewin Rare Earth Metal Materials Co. doubled its annual capacity from 500tpa in 2002 to 1,000tpa (tonnes per annum) for neodymium and praseodymium products. Chinese smelters presently obtain 5.8-6.0€/kg of neodymium metal. It was reported by Metal-Pages on August 6, 2003, that this company may increase throughput to 3,000tpa (China, 2003). China at mid 2003 has already produced 13,000 tonnes of neodymium metal whereas 2002 output amounted to only 8,000 tonnes.

One company in the USA, Molycorp, Inc., actively mined rare earths contained in bastnäsite at Mountain Pass, CA. Molycorp is a wholly owned subsidiary of Unocal Corporation. Although this recovery facility is temporarily closed, it is expected to resume separation operations in 2004 (USGS, 2003c). In the interim, Mountain Pass continues to produce bastnäsite and cerium concentrates. Resumption of regular operations in California may cause a decline in prices. Two other American companies include Santoku America, Inc. with facilities in Tolleson, AZ, and the Grace Davision organization in Chattanooga, TN, which refines rare earths from chlorides and other compounds to produce catalysts for petroleum cracking. Although scandium is not mined in the United States it has three scandium processors consisting of (i) Sausville Chemical Co. in Knoxville, TN (ii) Boulder Scientific Co, located in Mead, CO, and (iii) Aldrich, LLC in Urbana, IL (Hedrick, 2001). At present, seven other firms fabricate rare earth products within the USA. Magnequench International, Inc. (MQ) operates nine rare earth production facilities such as three in the U.S., one each in China, Germany, Japan, Singapore, Switzerland and the United Kingdom. American domestic applications included glass polishing and ceramic applications (39%), automotive catalytic converters (22%), permanent magnets (16%), petrochemical catalysts (12%), alloys and metallurgical additives (9%), rare earth phosphors for televisions and computer monitors, lighting, radar (1%) and miscellaneous (1%) according to Metal Statistics (2002). Catalytic converters incorporate rare earths such as cerium oxide (CeO_2) to control carbon monoxide and hydrocarbon emissions while reducing the NO_x levels (Bounds, 1998). The United States of America is a net importer of rare earths upon exporting about 30% of what it imported to some 20 countries in the form of finished rare earth products. The U.S. consumption of 15,600 tonnes of rare earths received as metals, compounds and oxides, represented a value of over €1.12 billion in 2001(X-rates, 2003). The U.S. exported both inorganic and organic rare earth compounds primarily to Algeria, Argentina, the Republic of Korea and Taiwan.

Georges Urbain founded the Rare Earths Company (Société des Terres Rares) at the beginning of the 20th century which was the precursor of the present modern global firm. Rhodia Electronics and Catalysis, Inc. (formerly Rhodia Rare Earths) is a major producer of rare earths which are mainly processed at La Rochelle in France as their flagship facility. Although the plant was constructed in 1947 for the manufacture of rare-earth based performance products it has been upgraded to become the most advanced in the world. The La Rochelle site initiated the treatment of solid waste in effluent during 2001 to recover over 25% of rare earth oxides from recycled materials (Rhodia, 2002a). The company operates four research centres such as Rhodia Recherche at Aubervilliers, France. During 2003 Rhodia was restructured to be comprised of four operating divisions to service eight strategic marketing areas. The company presently employs 24,500 people worldwide. The consolidated net sales in 2002 amounted to €6.617 billion (Rhodia, 2002b). The Rhodia Group consolidated its assets and presently operates 179 companies in many countries (Rhodia, 2002b). By virtue of key locations such as in China, France, Japan and the USA, Rhodia demonstrates an international presence on five continents through its industrial plants, application laboratories and research centres. The company is a leading global manufacturer of rare earth oxides and salts, automotive emissions control, batteries, electronics, glass and chemical catalysis, luminescence, material coloration and magnetism (Rhodia, 2003). Rhodia's headquarters are located at Cranbury, NJ, and it operates a plant at Freeport, TX, in the United States of America. The company also has a joint venture with Santoku Metal Industry Co. Ltd. in Japan which manufactures alloys and metals for high performance batteries and magnets from salts and oxides of rare earths. In late 1999 Santoku acquired Rhodia's plant activities at Phoenix, AZ (Rhodia, 2003). At the beginning of 2003 Aventis owned 25.2% of Rhodia's capital stock. Aventis, which employs 71,000 people in its core business (ie., the pharmaceutical sector), has its corporate headquarters in Strasbourg, France. Silmet Grupp is an Estonian rare earths producer which has shut down operations for three months until possibly October 2003 due to a slump in the world market which has a cyclical nature.

The rare earth production in Japan is entirely derived from imported raw ores and intermediate materials containing various amounts of REE. The mineral thortveitite [$(Sc,Y)_2Si_2O_7$] was reported in the vicinity of Kobe, Japan (Hedrick, 2003). Showa Denko (SDK), which is a Japanese specialty chemicals producer also involved in the Baotou area of China, announced that it is merging its rare earth and electronic materials into a single division (China, 2003). The rare earths section of Showa Denko produces SmCo alloys, master alloys, and NdFeB magnet alloys (China, 2003). As a point of interest, Showa's electronics section produces AlGaAs, AlInGaP, GaAs, GaP, and InP wafers and crystals. During 2003 the writer published separate technical papers, via Elsevier Science Ltd., on gallium and indium production worldwide which also closely interact with the global electronics sector. Anan Kasei at Osaka (Japan) which began operations in December 1993, as an affiliate of Santoku (33%), maintains a joint venture with Rhodia Electronics and Catalysis, Inc. (67%) at the operations in Kobe, Japan (Hedrick, 2001). Rhodia has a majority stake (55%) in a Mongolian producer which owns a facility alongside the world's largest bastnäsite resource at Baotou. Rhodia Rare Earths S.A (France) controls the joint venture with Baotou Rhodia Rare Earth Co., Ltd. at Wanshuiquan, Baotou in Inner Mongolia, China. The two Mongolian provinces combined represent the largest geographic area amongst the 29 provinces in the People's Republic of China. Baotou Rhodia Rare Earth Co. Ltd. produces rare earth chloride and oxide, rare earth metals and compounds, and NiMH powder which are exported (Rhodia, 2003). This firm which was founded in 1997 achieved its ISO-9002 certification in 1999 to be in line with the quality standards advocated by the Rhodia Group. Rhodia's holds a 45% stake in the joint venture with its two Chinese partners which include the Beijing Founder Group Co., Ltd. and Liyang Licheng Economic General Industrial Co., Ltd. Rhodia also operates the Rhodia (China) Co. Ltd. facilities in Shanghai and the Liyang Rhodia Founder Rare Earths Co. in the Jiangsu province of China. Rare earth processors in India extract constituents from mineral sands as by-products during separation of ilmenite, rutile, and zirconium minerals. Traditionally, ilmenite and rutile serve as feedstock for the production of titanium and/or titanium dioxide pigment. The three main companies in India include, V.V. Minerals, India Rare Earth Ltd., and Kerala Minerals and Metals Ltd. (Hedrick, 2001).

Within the CIS (Commonwealth of Independent States) rare earths are regarded as strategic metals and the data is confidential (Roskill, 1998). Analysts at Roskill observed that the rare earths sector in the former Soviet Union, which collapsed in December 1991, requires considerable foreign investment to attain previous production levels. The InfoMine Research Group in Moscow publishes information about rare earths in the CIS which is periodically updated to present day status upon purchasing a report (Troitsky, 2003). The proven reserves are estimated at about six million tonnes of REO in the CIS (Metall, 2003). Bastnäsite occurs in gold sands of the Barsovka River near Kyshtym in the Ural Mountains of Russia which divide Europe and Asia. Light rare earths are primarily recovered from the Lovozero deposit in the Murmansk oblast (ie., region) of Russia. Although AO Sevredmet Kombinat went into receivership on March 15, 2000, another company was formed to continue recovery operations. The loparite concentrator operated by the new public firm, Lovorezero Mining Company (LMC), targets to produce 5,150 tonnes per year of rare earth carbonates which satisfies 96% of Russia's domestic demand. The loparite concentrate is shipped to Solikamsk followed by further separation and refining in Estonia, Kazakhstan, and Krygyzstan (Hedrick, 2001). Rare earth resources are reported in the apatite and uranium-bearing deposits of the Kola Peninsula in Russia and Kazakhstan respectively (Hedrick, 2003). Kazakhstan is the 9th largest country in the world and occupies an area five times the size of France. Scandium is recovered in the Ukraine as a by-product of processing iron ore at Zheltye Voda. Rare earth metals were reported in the Donetsk region of the Ukraine. Cerium and ytterbium were mined from the Kutessay II deposit in Kyrgyzstan from 1958-1992 (E&MJ, 1999). The processing plant near the city of Bishkek imports ore from China to produce rare earth oxides and metal products. Other potential deposits in Kyrgyzstan include Aktuz, Jangart, Kenkol, and Kuperlisay. Levine (1997) indicated that rare earths are produced from the Aktyuz and Orlovka deposits in Kyrgyzstan (formerly Kirghizia) while uranium is recovered from the Kara Balta complex. The Kyrgyz Chemical and Metallurgical plant had been insolvent for several years and produced the entire group of lanthanides in conjunction with 16 rare metals. The production facility tolled raw materials and exported 98% of its output beyond the CIS boundaries while only 2% reported to the Russian Federation. It was surprising that six armed men stole 2,460kg of europium oxide in 20 kilogram boxes from the Orlovka enterprise in Kyrgyzstan during mid 2003. Fortunately, this material can not be used in weapons of mass destruction (WMD). Europium oxide is only used to absorb neutrons in the atomic industry. After the disintegration of the USSR in late 1991 the production of rare earths dwindled while other facilities were mothballed due to lack of financial support. It is anticipated that considerable cash flow is needed to modernize existing processing equipment in order to become competitive with the proliferation of low cost producers in China albeit that labor rates in many CIS countries are comparative to that experienced in China.

Monazite is recovered as a by-product of heavy mineral sands in both the east and west coasts of Australia. Western monazite was used as feedstock for Rhodia Rare Earths (formerly Rhône-Poulenc) for its REE refinery at La Rochelle, France, until 1994 when it began importing bastnäsite material from China and the USA. Hardrock resources containing rare earths presently are not developed in Australia and are located in the Mount Weld carbonatite deposit which is estimated to contain 23.6% rare earth oxides within the 1.3 million tonnes close to surface ore body. During June 2001 the Lynas Corporation divested itself of gold holdings and entered the rare earths business. After joint ventures and acquisitions such as from Anaconda Nickel Ltd., Lynas obtained 100% control of the tenements for the ore body consisting of about 20km^2 in overall size. The company was incorporated in 1983 and had its roots in Lynas Gold NL followed by later name changes. Lynas Corporation Ltd. owns the richest deposit of rare earths in the world at Mt. Weld which is located 35km south of Laverton in Western Australia. Cerium represents 46% of the rare earth oxides distribution in the unique extensive deposit. Apart from the significant quantity of cerium the deposit includes appreciable amounts of lanthanum and neodymium, minor amounts of praseodymium and samarium plus traces of other metals (Lynas, 2002). At present, one mine in China supplies over 70 percent of the light rare earths marketed globally. The high-grade deposit containing light rare earths at Mt. Weld is expected to reach production levels in the latter half of 2004. The tenements also contain substantial recoverable niobium (Nb) and tantalum (Ta) which were estimated at over 400,000 and 29,000 tonnes of metal respectively. The Australian deposit hosts the second largest niobium deposit after Araxá in Brazil. It is expected that recovery of Nb and Ta will proceed in parallel as a twin operation to recovery of rare earths. Niobium and tantalum are virtually interchangeable over the broad spectrum from capacitors for mobile phones to production of high-strength steels. One portion of the Mt. Weld deposit consists of the Central Lanthanide Deposit (CLD) which is conservatively estimated to contain 917,000 metric tonnes of rare earth oxides (REO) whilst using a 4% REO cut-off grade. The mine life was projected in excess of 20 years (Lynas, 2002). The Mt. Weld complex is purported to represent the richest source worldwide for this group of rare earths. The design capacity of the planned concentrator is treatment of 200,000tpa ore to produce about 20,000 tonnes per year of flotation concentrate. Established access to Chinese excess capacity by means of partner processing plants enables final separation to individual oxides without incurring the large capital cost attributed to greenfield separation plants. The company has already registered its own RED brand (Rare Earths Direct) and targets to achieve a global benchmark with respect to quality and continuity of supply. Lynas is strategically positioned to capture an important share of the growing rare earths global market. Australia's Lynas Corporation recently received environmental approval to transport a mildly radioactive concentrate from its rare earth mine at Mt. Weld in Western Australia. After upgrading on site about 13,000tpa of rare earth oxides are to be shipped to China for further processing (China, 2003). Other deposits in Australia include the Cummins Range carbonatite and the Brockman deposit which contains other metal values such as gallium, hafnium, niobium, tantalum, and zirconium. Olympic Dam's copper-uranium deposit contains approximately 0.5% contained REE within a fine grained bastnäsite and monazite mixture. Queensland hosts several rare earth deposits such as North Stradbroke Island, Bribie, the Caloola Coast, Coonarr, the Fraser Islands and Moreton. A potential deposit exists at the Mary Kathleen tailings impoundment area which grades about 3% REO. It is located near the Mt. Isa area as the result of uranium ore extraction but presents a difficult recovery procedure compounded by the residual radioactivity in the discarded tailings. Some rare earth resources in Australia include the nickel and cobalt deposits in Syerston and Lake Innes. Producers in each of the 35 countries known to recover one or more of the many rare earths may be divided in the following main geographic areas (Roskill, 2001; Ann-Marie, 1998):

- North & South America - Brazil, Canada, Greenland, Guyana, United States
- Europe & the Middle East - Austria, Egypt, Estonia, Finland, France, Germany, Norway, Poland, Turkey, United Kingdom
- Africa, Asia & the Far East - Burundi, China, India, Kenya, Malaysia, Malawi, Mozambique, North Korea, South Africa, South Korea, Sri Lanka, Taiwan, Thailand, Vietnam, Zaire, Zimbabwe
- C.I.S. - Kazakhstan, Kyrgyzstan, Russian Federation, Ukraine

4. RECOVERY PROCESSES

Solvent extraction and ion exchange processes are two principal methods used to separate rare earth chemicals and achieve purities of five nines quality (ie., 99.999 %). Separation is difficult because all rare earth elements are quite similar and exhibit minimal difference in the outer electron configuration. Vacuum calciothermic reduction of rare earth salts such as fluorides and chlorides is employed to produce individual metals. Electrolytic techniques are applied to produce cerium, lanthanum, praeseodymium, mischmetal and neodymium. An argon atmosphere is used in the distillation of Europium, samarium, thulium, and ytterbium due to their low boiling points (Metall, 2003). The following four main steps with minor variations to suit each facility are typically employed to extract rare earths from REE feedstock:

- Following crushing, grinding and classification of rare earth-bearing ores, the desired minerals are concentrated by means of gravity, magnetic separation and flotation techniques.
- Addition of hot concentrated caustic soda to produce rare earth elements (REE) as salts of carbonate, halide or nitrate in a hydrometallurgical leaching stage represents one approach. Another method involves the addition of concentrated sulphuric acid to crack the rare earths in a high temperature process thereby producing an intermediate product via carbonate precipitation. The term "cracking" denotes the process whereby the rare earths mineral (eg., carbonate or phosphate) is converted to a form more readily soluble in weak acid solutions.

- Dissolution of the rare earths carbonate in acid followed by solvent extraction (SX) to separate individual rare earths into groups and individual elements is an accepted practice such as in Australia (Lynas, 2002). Rare earths concentrate and/or carbonate are easily transported as an intermediate product to supply a remote facility. Calcining of the residual filter cake in a heated kiln to produce REE oxides constitutes another procedure.
- The reduction of the REE oxides to produce rare earth metals in a saleable form completes the four stages of extraction (Smart, 1999). The finishing of oxides into specialty compounds is a companion process to thermal reduction.

5. DISCUSSION

The annual demand for rare earth metals in developed countries featuring high-tech applications has reached an 8% growth rate during the past years. Roskill (2001) forecasted an annual growth rate in the range of 4 to 9% during the next several years. The global market for rare earths is expected to amount to about €1.24 billion by the year 2004 (Lynas, 2003). The Lynas Corporation based in Sydney, NSW, Australia, forecasts rare earths consumption to increase from 70,000-100,000tpa at an annual rate of 7% by the year 2008 (Lynas, 2002). The People's Republic of China is capable of providing 85 to 95% of the world's annual output of rare earths. China apparently has produced in excess of 75,000 tonnes of rare earth oxides per annum contained as ore while its domestic consumption approaches 20,000tpa of REO. Apart from the economic slowdown in Asia, the realized prices of rare earths in the Chinese market continue to be low since these are fueled by a weak demand from major consuming countries such as Japan and the United States. Total world demand for rare earths is anticipated to exceed 100,000 tonnes in 2004 due to the increased growth in areas such as rare earth magnets and autocatalysts required by more stringent regulations to control emission levels. It was indicated by China (2003) that rare earth prices are now half the value realized 2-3 years ago. Some analysts attribute this decline as a result of China dumping excess material on the market. A conundrum exists since the production of rare earths slated for environmentally benign applications are hindered by environmental compliance issues such as experienced with raw material sources consisting of ionic adsorption clays in China and bastnäsite in California, USA. It was reported by Roskill (2001) that rare earth stockpiles have decreased. Albeit that this apparent reduction in a supply of minerals may trigger new greenfield projects and/or expansions of present facilities, it is recognized that significant overcapacity exists within secondary processing capability. Prices have stabilized at a three year low for rare earths products. Previous inventories, which accumulated prior to collapse of the high-tech market, notably impacted the worldwide market and these are now being depleted. A turn-around in demand led by an economic recovery in the United States may have a positive effect on realized prices since the Asian and European economies follow the American pattern in tandem (Lynas, 2003).

Until recently, an uneven playing field existed in global markets. The state owned monopoly on rare earths was disbanded in 2001 within China while asset ownership was decentralised to a provincial level. Reform is well underway in China. As an example, this feature has allowed Lynas to use surplus processing capacity in China to toll treat material from the rich Mt. Weld deposit in Australia (Lynas, 2002). Due to the sole proprietorship of a one-of-a-kind mineralized property Lynas is poised to capture a significant share of the light rare earths market within the international forum and disseminate products destined for a myriad of end uses through its customers. The non-ferrous industry is changing within China. For example, the Aluminium Corp. of China (Chinalco - parent company of Chalco) plans to purchase several copper and rare earth metal companies during 2003 (China, 2003). The rare earth metals sector in China is presently in the process of a major re-organization since domestic demand has significantly declined whilst many mines have increased capacity during the past two years. During 2003, the Chinese government aims to limit the domestic production of separated rare earth products to 76,000 tonnes while exports will be restricted to 40,000 tonnes. The State authorities intend to curb rampant production expansion while protecting the countries rare earth resources. The output of rare earth products originating from North and South China will be capped at 52,000 and 24,000 tonnes respectively. The government of China has approved the creation of distinct rare earth groups to strengthen control over exploration, production, and exportation. The restructuring involves the formation of the Northern Group comprised of major rare earth companies in the Inner Mongolia Autonomous Region, plus Gansu, Sichuan, and Shandong provinces. The Southern Group will include enterprises in Shanghai and the provinces of Guangdong, Hunan, Jiangsu and Jiangxi which will mainly produce heavy rare earths. Baotou Steel and Iron Corp. in Inner Mongolia will dominate the northern group which predominantly produces light rare earth metals which are applied in the petrochemical sector plus in steel and non-ferrous production. It appears that only the "big two" in China will be allowed to exploit rare earths resources and/or export. It is noteworthy that the transformation of the Chinese rare earths industry involves over 170 rare earth producers in 17 provinces and autonomous regions (China, 2003).

Rhodia Rare Earths, Inc., changed its name on January 1, 2001 to Rhodia Electronics and Catalysis INC. During 1999 the company had been called Rhône-Poulenc. Rhodia Electronics and Catalysis (E&C) is investigating the feasibility of establishing a REE plant at Pinjarra near Perth, WAU (ACTED, 2003). Although plans are presently on hold, the project remains a long-term option for the Rhodia Group according to Civiello (2003). The plant nameplate capacity was 15,000tpa of rare earths contained in a nitrate concentrate. The proposed facility was to be located adjacent to its former gallium chloride plant which extracted gallium as a by-product from the bauxite liquors derived from Alcoa's alumina works at Pinjarra. Currently, Alcoa supplys a bleed stream of the caustic leach solution from its aluminum refinery to GEO Gallium S.A. in Salindres, France. During September 1999, GEO Specialty Chemicals, Inc. acquired all the gallium assets of the Rhodia organization (Deutsche, 2003). Rhodia is a leader in specialty chemicals worldwide and develops value-added products and services for the beauty, clothing, foodstuffs and healthcare markets apart from its contribution to the environment and transportation industries. The Rhodia Group controls the formulations, characteristics, physical and chemical properties of rare earth compounds to adapt products to each field of application.

In 1997, Advanced Material Resources (AMR), headquartered in Toronto, Canada, announced their intent to construct a rare earth processing plant in Thailand to service regional manufacturers of permanent magnets. The 1999 vintage facility manufactures bonded magnetic powders and magnets for the electronic and automotive industries (AMR, 2003). The Canadian company, which was established in 1993, is listed as AMR Technologies Inc. at its regional sales offices in Barbados, Korea, Thailand, the United Kingdom and USA. AMR owns controlling interests in two joint ventures in China: Jiangyin Jia Hua Advanced Material Resources Co., Ltd. and Zibo Jia Hua Advanced Material Resources Co., Ltd. (CCBC, 2003). AMR quadrupled the production capacity at its Chinese plants within a six year period. Australia currently is not a producer of rare earths although the heavy titanium-bearing and black minerals sands operations in Western Australia to recover ilmenite for TiO_2 pigment production generate the world's largest supply of monazite and xenotime. At present, processing operations do not proceed beyond the concentrate stage. Despite the high level of radioactivity in monazite (6-7% ThO_2) no concern apparently exists for an assured long-term source of raw supply of rare earth feedstock. Uranium tailings at Port Pirie in South Australia contain an estimated 1,500 tonnes of many rare earth oxides (REO) remaining from treatment of davidite concentrates.

Olympic Dam's ore body on the Gawler Craton usually contain 2,000 and 3,000ppm of lanthanum and cerium respectively. The Olympic Dam copper deposit in South Australia was discovered by Western Mining Corporation (WMC) in 1975 and the plant produces refined copper, uranium, gold and silver. Rare earth-bearing minerals are often associated with uranium and base metal mineralization. Hence, Australia has the potential to become a recognised player in the global supply of rare earths as a commercial commodity conditional upon future demand and pricing scenarios. Australia's vast topography has untapped resources for REO feedstock originating from several sources such as Mt. Weld, mineral sands, and uranium waste enriched with valuable impurities.

The control of chemical purity of recovered rare earths is dependent upon efficient separation and purification processes. Product morphology consists of assigned grades for particle size, surface area, texture and pore size. Considerable research is being carried out to investigate potential new uses for rare earth materials incorporated into special alloys and compounds (Hedrick, 2001). One leading edge application involves the next generation of infrared (IR) detector which traditionally require cyrocoolers. A detector composed of lead-scandium-tantalum trioxide appears promising once manufacturing techniques are resolved to produce a thin film detector that is not supported by a substrate. Both gadolinium and permanent magnets composed of neodymium-iron-boron promise future application for magnetic refrigeration once further research is conducted. Metallocenes are being examined for new catalysts (Bounds, 1998). PPG Industries developed a water-based yttrium coating to provide a lead-free surface primer and corrosion resistance. Although lead has been banned in paints since January 1971, an exemption exists for soluble lead pigments up to 1,000ppm used in electrodeposition coatings. The special properties of rare-earth based products enables miniaturisation of electronics, plus development of flat-screen technologies, new lighting and signaling sytems. Another future application involves a rare earth laser crystal that continuously emits a three colour beam (blue, green, and red). China (2003) reported that Sumitomo Metal Mining in Japan has developed a means of incorporating minute particles of lanthanum compound in window glass exposed to direct sunlight to reduce room temperature by 5°Centigrade. The technique blocks out infrared light with a wavelength greater than 1000Nm but allows passage of 80% of the visible light. Sumitomo plans to provide a service to coat the windows of hotels and office buildings (China, 2003). Sumitomo Chemical developed a blue phosphor that retains its brightness ten times longer than current materials in plasma panels. Europium, which emits blue light, is combined with calcium, magnesium and silicon as a potential replacement for existing phosphors comprised of Eu/Ba/Al/Mg. Plasma screen televisions wear out quickly because the blue phosphors decrease in brightness as compared to LCD televisions. The Japanese firm intends to produce 10-20 tonnes per annum of the new phosphors at its Ehime factory and targets to develop sales in this market at the level of about €33.5 million by the year 2005 (China, 2003). The philosophy of the Lynas Corporation is supply of high-quality products combined with customer interaction to enable customers to apply rare earths as key ingredients of the nanotechnology age (Lynas, 2002). As a point of information, the Rare Earths 2004 conference is scheduled for November 7-12, 2004 in Kasugai, Nara, Japan. Another forum for exchange of ideas and discussions of leading edge technology consists of conferences scheduled in the year 2004 for Chicago, IL, and Geneva, Switzerland, during April and August respectively.

6. CONCLUSIONS

- Although rare earths are normally invisible to the average consumer in various products, they contribute an important role with respect to the world's economy.
- It is noteworthy that the metallic "rare earth elements", which are relatively abundant in the Earth's crust, are adaptable to a myriad of uses ranging from improving the quality of life to specialty items such as high technology electronics.
- The combination of existing plant operations at primary and secondary producers featuring improved extraction recoveries coupled with ongoing global exploration and development will ensure a sustainable supply of the ubiquitous rare earths for many years.

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