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CURRENT WORLDWIDE STATUS RARE EARTH TECHNOLOGY

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ABSTRACT

The paper discusses the status of the rare earth industry worldwide, including the mining of bastnasite and the manufacture of various rare earth chemicals, metals, and alloys. Worldwide reserves and current production by company location are mentioned.

The operations of two major USA firms, Molycorp and Rhone-Poulenc are discussed in some detail.

The availability, extraction and application of the rare earths from concentrates, tailings, and residues are reviewed, with special emphasis on the anticipated growth in consumption of neodymium in permanent magnets is covered on a worldwide basis.

Secondary residues, mine tailings, and red muds are covered in some detail. Sources of rare earth minerals, either as by-products from residues such as red muds is compared to sources of rare earths from mineral concentrates such as bastnasite and monazite.

INTRODUCTION

China and the United States of America are self-sufficient in the production of the rare earth elements and are major exporters of rare earth concentrates and compounds to the rest of the world. The rare earth elements, having atomic numbers 57 through 71, are known as the Lanthanide Series. The light rare earth group are elements with atomic numbers 57 through 63, and the heavy rare earth group are with atomic numbers 64 through 71.

Table 1 lists the abundance of the rare earth elements compared to the more common elements based on several geological sources. This table indicates that a number of the rare earth elements are much more common on the crust of the earth compared to lead, molybdenum, antimony, arsenic, bismuth and others. This review excludes yttrium with atomic number 39, an element which is generally included in the literature as a rare earth element, even though it is not a lanthanide.

The more common minerals containing rare earth elements are summarized in Table 2, with the major commercial ones being monazite which is a phosphate mineral, and bastnasite which is a carbonate mineral. Attempts have been made to recover rare earth elements as byproducts from the mining of pyrochlore and apatite, but these are not being run commercially today. There are vast reserves of rare earths associated with phosphate rock, but they are not being extracted at this time.

In the United States the large rare earth deposit at Mountain Pass, California operated by Molybdenum Corporation of America (Molycorp), allows the United States to be self-sufficient in rare earths. The recovery of bastnasite as a byproduct in The People's Republic of China from the large iron ore deposit in Inner Mongolia permits China to be self-sufficient in the production of the rare earth elements. Both the United States and China are able to take care of all their domestic requirements and export to the world market.

RESERVES AND PRODUCTION

A summary of the world rare earth reserves is listed in Table 3 and shows that China has the largest reserves of rare earths followed by North America, mainly the United States of America. In addition, other rare earths are recovered from mineral sand mining operations in Australia, South Africa, South America, and other locations.

For over 20 years, the production of bastnasite has been the world's major source of rare earths. Previously the monazite mineral was the principle source of rare earths. Monazite is generally recovered as a byproduct mineral from the production of ilmenite, zircon, rutile, and other heavy mineral operations, and therefore, does have some production limitations. Since the monazite is associated with thorium, uranium, and other radioactive minerals, the mining operators have some difficulties with environmental authorities in certain locations.

Bastnasite and Monazite are readily soluble in acids. The most common acid being used today is sulfuric acid. Monazite is also leached with sodium hydroxide in a number of plants. Once the rare earth elements are placed in solution, the flow sheets are similar. Figures 1 and 2 point out the location of the major bastnasite and monazite deposits in the world today.

Except for the large bastnasite deposit in China, all the other deposits including the bastnasite deposit in the USA and the monazite deposits around the world are near the coastlines, and are associated with beach sand type environments.

During 1984 the lanthanides or rare earths were in abundant supply and it was anticipated that there would not be any shortages of any of the elements for the immediate future. The minerals are available, but in some instances the processing capability to treat the minerals will have to be expanded to meet the projected world needs of the purified elements, such as neodymium. Table 4 summarizes by country, the type of mineral, and current output of rare earth oxide (REO) and indicates that the world production is currently at about 37,000 metric tons REO per year. The main producers are the United States, Australia, China, India, Brazil, and several other countries. (1)

The predominant source today of the rare earths is the bastnasite mineral with monazite second. These two minerals make up the major source of rare earths, with minor amounts from other minerals such as xenotime for yttrium as shown in Table 5. Monazite mining takes place in Florida as a byproduct of the ilmenite and zircon

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production, while the bastnasite is the main mineral produced in one mine in California. In addition to domestic production, the United States is currently importing 3,300 metric tons of monazite per year from Australia, Malaysia and South Africa, along with various products. These products are mischmetal, alloys, oxides, rare earth chlorides, and others amounting to another 3,300 metric tons per year. At the same time, the United States exported in the form of concentrates 4,300 metric tons in 1984.

The companies producing the rare earth minerals are listed in Table 6 with Australia the major producer of monazite. (2)

The world's largest single producer of the rare earths is Molycorp at Mountain Pass, California, under the control of Union Oil Company. Molycorp have their own mine, mill, and chemical processing facilities.

The second largest producer of rare earths is The People's Republic of China at Baotou, Inner Mongolia with its byproduct mineral operation. The Rare Earths come from the tailings of their iron ore mine, which tailings contain approximately 240,000 tons of rare earth oxides per year. The rare earths are recovered in a bastnasite concentrate. In a private communication at the Baotou Laboratory, I learned that the mixture contains approximately 30% as monazite and the other 70% as bastnasite. The Chinese Rare Earth Company is producing the bastnasite and monazite mixture in Baotou, Inner Monoglian Autonomous Region. In addition, China has a Guangdong Mine in the Guangdong Province producing monazite

and a high grade xenotime. There is a Guangxi Mine in the Guangxi Province producing a monazite and low grade xenotime. Some rare earth concentrate is recovered from residual clays in the Longnan Plant at Longnan, Jiangxi Province. There is a similar operation at the Xunwa Plant at Xunwa Jiangxi Province recovering byproduct concentrates from their clay operations. The major source is the byproduct minerals from the iron ore mining operation.

The other producers mine principally monazite with some xenotime concentrates. All of these other operations produce the rare earths as a byproduct mineral since the main mining operation recovers ilmenite, zircon, and rutile, in Australia, Florida USA, India, and Sri Lanka.

Monazite and xenotime are recovered as byproduct minerals from tin operations in Malaysia, Thailand, and Indonesia. A small amount of monazite is recovered as a byproduct in Zaire.

In order to compare the different qualities of the bastnasite concentrates produced in the USA at Molycorp, and in China at Baotou, reference is made to Table 7. The comparison clearly points out the fact that the Chinese bastnasite is a byproduct of the iron ore mining, since it is high iron content. The phosphorous content indicates that some monazite which is a phosphate mineral, is contained in the bastnasite. The lanthanum oxide contents are quite similar. There is a considerable difference in cerium oxide content with the Chinese concentrate being of higher grade. The Chinese bastnasite also contains more neodymium oxide and europium oxide than the USA bastnasite.

OPERATION AT MOUNTAIN PASS, CALIFORNIA, USA

The two major processors of bastnasite concentrates and monazite concentrates in the USA are Molycorp and Rhone-Poulenc. The flow sheet for Molycorp can be found in Figure 3. The process consists of crushing and grinding followed by flotation to produce a concentrate. The concentrates are then dried, followed by acid leaching, washing, filtration, and calcination producing a high grade bastnasite concentrate. The Mountain Pass technical operations were discussed in detail by Dickerson. (3)

The Mountain Pass Mine which is the largest mine in the world, is a carbonatite ore associated with potash-rich syenite and shonkinite. The orebody, known as the Sulphide Queen carbonatite, is a north-striking sill with a maximum width of 700 feet and an original surface exposure of 2,400 feet. In the area of active mining the sill is about 200 feet wide. The ore typically contains 40% calcite, 25% barytes and/or celestite, 10% strontianite, 12% bastnasite (the major rare earth containing mineral in the deposit), 8% silica, and minor amounts of other minerals. The average rare earth oxide content (REO) in the run of mine ore is 3-10% REO. The mine is an open pit operation. The REO content of the bastnasite mined at Mountain Pass is fairly uniform, with only occasional variation. Cerium, lanthanum praseodymium, and neodymium represent 95-96% of the total REO content.

Ore is broken by drilling and blasting and it is blended before going to the flotation plant to give a consistent feedstock,

close to an average REO content of 7%. About 1,500 tons of ore are processed each day. A total of 6 million tons of ore have been processed in the 35 year history of the mine. However, production in recent years has been much greater than that in the early days of the mine. Output in 1984 was the highest ever recorded, and twice as much ore was mined as in the first 13 years of operations. Reserves at the mine are sufficient for at least 20 years production, and there is still a significant content of rare earths in tailings, which could possibly be utilized at some time in the distant future.

Demand for rare earths has been increasing, and in the early 1970's MolyCorp installed a new flotation plant. The old flotation plant was renovated in 1983, and it can be brought into service if back-up capacity is required. It can also be used for testing purposes, as a sort of large scale pilot plant in the development of improved processing methods. Ore is crushed and ground to minus 100 mesh (90% minus 200 mesh) which gives good liberation for recovery in the flotation cells. Concentrates from the flotation cells typically contain about 60% REO and an enriched concentrate with about 70% REO is produced by acid leaching, which dissolves carbonate gangue.

After concentration of the ore by flotation, the material is roasted, which drives off CO₂ and converts the cerium to +4 valency. The other rare earth elements remain in the +3 valency in which they occur in the ore. The roasted concentrates are

then leached with acid which dissolves most of the material except the cerium.

The cerium concentrate left after the leach is the first commercial product from the processing of the ore. The separation is not complete, but cerium represents 80-90% of the REO content and the concentrate is sold as-is often for further processing, either at Molycorp's York, Pennsylvania plant or by other companies. The solution obtained from the leaching of the roasted concentrate is then fed through the solvent extraction plant at the site. The initial solvent extraction step separates the light rare earths (La, Nd, Pr) from the heavier rare earths (Sm, Eu, Gd). Some of the light rare earth products are fed through another solvent extraction step to adjust the amount of lanthanum and the product is sent to the company's plant in Louviers, Colorado for further processing. The rest is sold in the form of lanthanum hydrates, mainly for the production of fluid cracking catalysts. The heavy rare earths go through two further solvent extraction steps. The first separates an europium oxide product, and the second separates samarium from gadolinium. The products are extremely pure and extraction plants are virtually sterile in their cleanliness. Terbium oxide and yttrium oxide are also produced.

OPERATION AT FREEPORT, TEXAS, USA

The Rhone-Poulenc rare earth process has been described in detail by Spooner (4) and Poirier (5).

This company processes mainly monazite in France where a sodium hydroxide pressure leach is applied, followed by filtration, washing, and recovery of a mixed rare earth hydroxide. A byproduct sodium phosphate is recovered and sold. The mixture of rare earth hydroxides is processed at their plant in La Rochelle on the Atlantic Coast of France, and at their plant in Freeport, Texas which was started in 1981. The plant in France has more than 1000 mixers/settlers for solvent extraction of the rare earth with a capacity of 5000 tons rare earth oxides per year (5). The plant in Freeport, Texas with an eventual capacity of 4000 tons/year rare earth oxides receives the mixed rare earth hydroxide where it is further processed by acid leaching and various steps of liquid extraction. The French process is flexible enough to utilize all three types of raw materials, namely, monazite, bastnasite, and xenotime. The xenotime contains only 10.6% of the light rare earths, and 89.4% of the heavy rare earth elements. This is totally different than the bastnasite which normally contains 93 to 99% of the light rare earth elements, and only 1 to 2% of the heavy rare earth elements.

The monazite contains about 93% of the light rare earth elements broken down between 23% La_2O_3 , 46.5% CeO_2 , 5.1% Pr_6O_{11} , and 18.4% Nd_2O_3 . The monazite is reacted with sodium hydroxide

to remove the non rare earth elements, and the fraction of rare earth mixtures. The rare earth hydroxides are normally leached with nitric acid and the solution is polished, finished, and sent to the liquid solvent extraction section for the production of the various rare earth oxides on an industrial scale. The flowsheet and the actual separation of some of the products is shown in Figure 4. Rhone-Poulenc has the capability to produce various rare earth products up to 99.999% purity.

The plant in France has a capacity of 5,000 metric tons per year of rare earth oxides. The plant in Freeport, Texas is gradually reaching 4000 metric ton capacity. Rhone-Poulenc has been heavily involved in the supply of samarium for the samarium cobalt permanent magnets.

In the Rhone-Poulenc process, they can use hydrochloric acid, also sulfuric acid, but use primarily nitric acid. The solution of rare earth nitrate is filtered to remove the insoluble non rare earths which are primarily silicate and phosphate and transported to the second phase of the process which separates them from the rare earth elements.

The separation is the most complex and critical phase of the rare earth process. Rare Earths have very similar atomic structures with completely filled external electron shells and partially filled internal $4f$ shells. These similar structures give rise to similar chemical properties. Historically, this made the separation of the individual rare earths difficult.

A number of chemical and physical properties have been identified, however, which can be employed in separation processes for all or a portion of the rare earths. Probably the most obvious approach is selective oxidation or reduction. Seven of the fourteen rare earths have dual valence states.

Since changes in valence states are accompanied by substantial changes in properties, selective oxidation or reduction has proven to be an effective and economical technique of separation. The oxidation or reduction can be accomplished thermally, electrolytically or chemically. Today, Molycorp commercially uses thermal oxidation to produce cerium (+4) in their bastnasite mixture. The trivalent rare earths in the mixture are then dissolved in mineral acid and separated from the acid insoluble cerium (+4). Molycorp also commercially separates europium from trivalent elements by the chemical reduction and precipitation of a europium (+2) sulfate salt.

Historically, other processes have been utilized. Earlier this century, fractional crystallization was used. In this process two rare earths can be separated by multiple recrystallizations of suitable salt forms. The limiting factor for this technique is that it takes several thousand successive crystallizations to achieve 99.9% purity. Later, ion exchange separation was used. Effective separation of specific rare earth complexes on ion exchange resins is possible but must be carried out in a very dilute system. Both of these processes have proven

uneconomical and technically restrictive for large scale, industrial separation and are not widely used today.

Liquid-liquid extraction is based on a physicochemical property of the relative solubility of rare earth elements in selective solvents. The process starts with two liquids. One is an aqueous solution of mixed rare earths. The second is a carefully chosen water immiscible solvent. A solvent is selected which has a greater affinity for one specific rare earth ion than the others. The technology for the development of the proper solvent is critical and highly proprietary. A solvent is an organic mixture containing an extracting agent, modifiers and the carrier. The extracting agent complexes with the desired rare earth ion to form a rare earth complex. They are typically organic phosphates, acids or amines and they make the desired rare earth element soluble in the organic phase.

Again, the extracting agent must have a greater affinity for one rare earth than others. The modifiers are chemicals which prevent emulsions and a third layer from forming. Modifiers are also added to enhance the rate of extraction and the final equilibrium position. The carrier is also a critical part of the solvent. The carrier acts first to dilute the system to facilitate good mixing with the aqueous phase. It also helps keep the complexed rare earth ions in the organic phase, enhances the systems thermal and chemical stability and improves the phase separation.

Separation is achieved by blending the aqueous rare earth containing phase with the solvent phase and then allowing them to separate in a mixer-separation cell similar to a continuous separatory funnel. The initial separation effect is slight but by repeating this mixing and separating operation over and over, the desired rare earth ion can be separated from the other rare earths to a purity of 99.9%. The separated rare earths are then converted into water soluble nitrates and go to the finishing step of the process.

The liquid-liquid extraction process for separating rare earths has been developed to a high degree of sophistication. With the proper design of the mixer-separator (known in the industry as batteries), the proper operating conditions and the proper choice of solvents, all the rare earth elements can be separated via this technique. The high degree of automation, solvent recycling and analytical control of the liquid-liquid extraction process make it the most economical route to separate rare earths. At Rhone-Poulenc, all of the rare earths (with the exception of one small mixed rare earth chloride line) are separated into the individual elements with purities of 95% or higher.

The finishing step entails converting the separated rare earth nitrates into various raw materials. For rare earth permanent magnets, where the rare earth element must ultimately be reduced to metallic form, the traditional starting materials are chlorides

for electrolytic reduction and fluorides and oxides for metalothermic and electrolytic reductions. The chlorides are produced from the nitrate into a carbonate or oxide and then reacting it with hydrochloric acid. The fluorides can be made by processes which are analogous to the chloride route. The oxides are produced by calcining any rare earth sale at about 1000 degrees C.

Today, Rhone-Poulenc continues to use monazite with a backup source of a Kenyan carbonatite that runs 10% REO in the ore. They have the following heavier oxide quantities for sale annually: 120 tons Sm_2O_3 ; 3.5 tons Eu_2O_3 ; 85 tons Gd_2O_3 ; 8 tons Tb_4O_7 ; 26 tons Dy_2O_3 ; 4.5 tons Ho_2O_3 ; 6.5 tons Er_2O_3 ; 0.65 tons Tm_2O_3 ; 3 tons Yb_2O_3 ; 0.3 tons Lu_2O_3 ; 100 tons Y_2O_3 .

One of the products from the processing of the mineral is the production of rare earth chloride. China is producing two grades of rare earth chloride: (1) Grade AA - a non depleted europium oxide, and (2) Grade A - a depleted europium oxide. Reference is made to Table 8 which compares the rare earth chloride being produced in China with the rare earth chloride being produced in the United States by Molycorp.

The differences in the lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide, should be noted. The rare earth chloride is shipped in solid cast form, lump form, flake form, and in the USA in solution form to the consuming plant.

INDUSTRIAL APPLICATION OF RARE EARTHS

The location of the major USA companies processing rare earths into chemicals, metals, and alloys are shown in Figure 5. These firms and others are producing various products for application in the electronics, glass, alloys, and ceramics industries summarized in Table 9.

METALLURGY

There are two firms in the United States, Ronson Metals Corporation and Reactive Metals & Alloys Corporation, producing mischmetal, flint, and silicides. The alloy of the light rare earth metals in the same ratio as the natural mineral is called mischmetal, and it is the main constituent of flints. Mischmetal is still used today as an additive in cast iron, to achieve the nodulisation of graphite. It is also used to improve the resilience of steel by decreasing the sulfur content.

Mischmetal is produced by first drying the commercially available rare earth chloride to an anhydrous rare earth chloride state. The hydrated rare earth chlorides contain about 30% by weight of water of crystallization. These chlorides are made by evaporating neutral rare earth chloride solutions to the point where the evaporated solution contains 44 to 46% rare earth oxide. The boiling point of such solutions is about 135 degrees C. The evaporated rare earth chloride solutions are allowed to solidify by cooling and then packed in steel drums for shipment to the consumers. It is essential that the metal producers dehydrate the rare earth chloride prior to electrolysis of the fused chloride.

On heating the chloride, water evolves until the water content is diminished to a point where the mass begins to solidify. Heating is continued until most of the water is driven off together with some hydrochloric acid resulting from the hydrolysis of the rare earth chloride. A porous solid nearly anhydrous rare earth chloride is obtained. Generally the anhydrous rare earth chlorides will contain up to about 10% water insoluble basic chlorides resulting from the hydrolysis of the chloride during dehydration.

To produce the mischmetal, the anhydrous chlorides are fused with sodium potassium and calcium chlorides in an iron pot which serves as the anode. External heat is applied until fusion occurs. Electrolysis with graphite anodes suspended vertically in the pot generates enough heat to keep the chlorides molten after the electrolysis starts. The temperature of the fusion during electrolysis is kept above the melting point of the metal which is about 750 degrees C, so that the metal collects in a pool at the bottom of the pot from which it may be drawn and cast into ingots. Electrolysis is generally done at temperatures of about 800 to 900 degrees C. As metal is drawn, additional amounts of rare earth chloride are added to the pot and electrolysis is continued until the melt accumulates sufficient impurities to result in a poor quality metal or lower yields. Cathode current densities are in the range of 3 to 4 amperes per square decimeter. The resulting mischmetal is cast into special sizes and sent to the steel mills.

Extrusion presses are used to produce flints from mischmetal for the cigarette lighter industry. The largest use of the mischmetal is in the lighter flints and in the steel industry for desulfurization of steel, and in various aluminum and magnesium alloys. Mischmetal produced by electrolysis is generally remelted with iron to produce an alloy containing about 50% rare earths with the iron making the product resistant to low temperature oxidation. Small additions of magnesium and copper can also be made and the alloys then cast or today mostly extruded to form the familiar flint.

A rare earth silicide is produced in a submerged arc furnace by direct reduction of purified bastnasite concentrates. Quartz iron ore, or scrap and a reductant is added to produce roughly an alloy one-third mischmetal, one-third silicon, and one-third iron. These silicides have been used for the production of the high strength low alloy steels. The silicides are generally lower in density, have higher melting points above 2200 degrees F as compared to mischmetal.

Yu and Chen compared the use of rare earths versus calcium injection technology for the treating of steel.(6) The rare earths addition to steel and the micro alloying effect of rare earths as well as the role of the rare earths in thermo plasticity and oxidation resistance was covered with special emphasis on the method of addition of the rare earths for desulfurization of the steel by plunging the rare earths into the ladle.

GLASS INDUSTRY

Several of the rare earths have attractive colors and are used for glass coloring. Neodymium, praseodymium, erbium, and cerium compounds have been used for many years for artistic or technical glasses. The neodymium, erbium and cerium also give good results for crystal decolorizing. The lanthanum, yttrium and gadolinium oxides increase the refractory indexes of glasses. They find important applications in camera lenses which contain up to as much as 40% of lanthanum oxide.

As far as glass polishing, the cerium oxides have replaced iron oxides for glass polishing. The cerium oxide is put into a slurry form and is used for lense polishing, polishing bevels on mirrors, and decorative glass. For example, plate glass, TV front plates, lenses, and precision optics all need large quantities of these cerium based polishing oxides. Over 10% of the total rare earth oxides recovered in the world are used in these applications.

CERAMICS

Considerable amounts of praseodymium oxide are used in the production of a stable bright yellow pigment which is widely used as insoluble stain for ceramics, particularly on tiles. Also the praseodymium oxide and the zirconium silicate matrix is extensively used for yellow stain in enamels. This pigment is stable at high temperature and has replaced a large part of the tin vanadium yellow stains. In opacification, cerium oxide

is used for opacification of enamel in vessels, by virtue of its high chemical resistance, and is also used for artistic tiles.

CATALYSIS

The main application for rare earths in terms of tonnage is the catalytic cracking industry, mainly in the refining of petroleum. This application consumes about a fourth of the total rare earths in the form of rare earth mixtures. The most common and large tonnage item is the lanthanum oxide. The oxides are used in hydrogenation, dehydrogenation, and oxidation reactions. These catalysts give much better results than the standard silica alumina catalysts producing less coke and less of the light fractions.

NUCLEAR INDUSTRY

Gadolinium is the element having the largest cross section for thermal neutron absorption. It is used as a burnable poison in nuclear reactors or in reprocessing plants for nuclear fuel treatment. In fast neutron reactors, europium is the most efficient element available at this time.

TELEVISION AND CATHODE RAY PHOSPHORS

The rare earth elements continue to play an important role in the cathode ray tube phosphor industry, in particular colored television tubes. Europium, cerium, terbium, and yttrium are used in these applications. Europium oxide continues to be the main compound. It was first introduced as a color TV phosphor in 1964 by Sylvania, and is the source of the bright red color.

Rare earth phosphors such as lanthanum terbium oxybromide or gadolinium terbium oxysulfide have a high efficiency on the intensifying screens of the x-ray tubes. The use of the rare earth compounds allows the same image quality and at the same time decreases the x-ray exposure considerably. This is important as it limits the damage that x-rays cause to humans. It also allows a decrease in the silver content of film which is an important economic consideration in view of the varying price of silver.

A more detailed discussion on numerous industrial applications of the rare earth elements can be found in the ACS Symposium.(7)

Various methods of applying the rare earths have been patented.(8)

Rare earths are used for various medicinal and pharmaceutical purposes, rubber, photography, space technology, oils and lubrication, instrumentation, polymers, and other industries.(9)

PERMANENT MAGNETS

The consumption of rare earths continues to grow each year in this field. The industry has evolved from the production of compounds and alloys of limited purity to the production today of high purity oxides and metals. One of the areas of expansion is in the field of permanent magnets.

During the past 15 years the samarium cobalt permanent magnets have grown substantially. One of the major producers of samarium oxide is Rhone-Poulenc who only sold 5.5 tons in 1975 and it reached 155 tons in 1978, and is considerably higher today.

With their development, the magnetism was 5 to 10 times greater than those of the usual magnets.

The recent development of the neodymium iron boron alloy and its tremendous growth potential deserves special attention.

A detailed report was published on the fundamental role that magnetic materials play in many of the electronic and electrical systems used by modern society. (10) It reviews the status of magnetic materials in their current engineering applications and identifies technical issues whose resolution would lead to improved performance in such applications as well as for new applications of these materials. Emphasis is placed on more research in the areas of rare earth permanent magnets, amorphous magnetic materials and recording media.

Special attention is placed on permanent magnets. The strength of these magnets is measured by its energy product which has increased more rapidly over the past decade than at any time in history through the introduction of rare earth - cobalt (RE-Co) compounds.

Recently it has been discovered in Japan and independently by General Motors in the USA, that Boron helps form ternary compounds with iron and neodymium which have magnetic properties superior even to those of RE-Co. This discovery was accidental - Boron was being introduced as a glass former in a rapid quench process. The energy product of these magnets are so large that they are expected to revolutionize the design of motors.

A permanent magnet is used to create a steady magnetic field in some region of space. It produces the same effect as an electromagnet but requires no external source of power after its initial magnetization. The field of the permanent magnet may be used to exert a force on a current carrying conductor, to deflect a moving charged particle, to induce an electromotive force in a moving conductor, or to exert a force on a magnetized or magnetizable body.

The usual measure of quality for permanent magnets is the maximum energy product $(BH)_{max}$, defined as the largest inscribed rectangle in the second quadrant of the hysteresis loop plotted as B versus H shown in Figure 6. The usual units (cgs) for $(BH)_{max}$ are megagauss-oersteds (MGOe); the SI units are kilojoules per square meter (KJ/M^2). Other important parameters, shown in Figure 6, are the remanent induction B_r and the coercive field or coercive force H_c .

An ideal permanent magnet has a constant magnetization equal to the saturation magnetization M_s in any practical applied field. Pure iron would have an energy product of 107 MGOe if it could be made into an ideal permanent magnet of 100 percent density.

Strnat et al (11) demonstrated that a series of rare earth - cobalt compounds made a superior magnet due to its high magnetization and strong uniaxial anisotropy in single domain particles. By about 1970 the first of these rare earth permanent magnets became commercially available in the form of $SmCo_5$. These materials have energy products of about 20 MGOe.

During the last five years, the Japanese manufacturers have used the compound $\text{Sm}_2\text{Co}_{17}$ with energy products above 25 MGO_e being achieved.

The latest addition is the $\text{Fe}_{14}\text{Nd}_2\text{B}$ composition announced by Sumitomo Metals and General Motors in 1983. The base compound is tetragonal rather than hexagonal. Energy products are 30 to 45 MGO_e.

The major drawback is a low curie temperature (300 degrees C) which causes magnetic properties to be strongly temperature dependent. The curie temperature can be raised by replacing iron with cobalt. The Sumitomo magnets are made by a process very similar to that used for SmCo_5 , so no major investment in new production facilities is required. General Motors made a similar composition starting from a rapidly solidified ribbon sample.

Figures 7 and 8 show the improvements in permanent magnet materials that have occurred over the last eighty years. Table 1 lists the major classes of permanent magnet materials in commercial use.

The rare earth permanent magnet production (mainly samarium cobalt alloy) in 1982 in the non communist world was estimated at 1 million pounds with a sales value in finished magnets of 80 million dollars per year and growing each year. The number of USA magnet producing companies is about 15 with 9 of them major firms and the world total is about 100.

The large uncertainty related to cobalt prices and availability stimulated the General Motors company to investigate the rare earth alloys as permanent magnet materials. Cerium and lanthanum, although more abundant than praeodymium and neodymium, do not possess the intrinsic magnetic properties necessary for the development of high coercive force.

Scientists Coate and Herbst discovered small additions of Boron to a Nd-Fe alloy using rapid solidification. They discovered the unique crystal structure of the $\text{Nd}_2\text{Fe}_{14}\text{B}_1$ inter metallic phase responsible for its excellent properties.

Delco Remy, one of the 14 automotive divisions of General Motors, has built a new 160,000 square feet factory in Anderson, Indiana, 30 miles northeast of Indianapolis to produce these magnets for motors.

The new factory will produce three families of magnets: (1) MQ-I, an epoxy bonded with energy products in the 7 to 9 MGO; (2) MQ-II in the 13 to 15 MGO range; and (3) MQ-III, an anisotropic material with an energy product as high as 40 MGO_e.

The new plant will be in operation this year. The first magnets, which substantially reduce the size and weight of the automotive cranking motors, will be introduced in the 1986 Corvette and Buick Somerset car models.(12)

Coate and Lee (13) patented the bonded neodymium boron iron magnet by assigning the patents to General Motors Corporation in the USA and Europe. The magnets are made from an alloy melted and spun into ribbon particles.

Kukita (14) reported on a neomax magnet which is a sintered magnet with a tetragonal crystal structure composed of Nd-Fe-B alloy which reached a (BH)max of up to 35 MGO; the world record in commercial production. The density of neomax is 7.4 grams/cm³ which is lower than rare earth cobalt magnets by 13%, enabling lighter weight applications such as new motors, office automation equipment, and audio equipment.

Batoux (15) estimated the use of Nd-Fe-B alloy in new magnets will increase the efficiency by ten times (BH)max and will reduce by ten times the volume. He further states that by 1990 the new Nd-Fe-B magnets will have 12% of the market and a sales volume of 200 million dollars annually. This value is based on a price of \$5 to \$7 per kilogram for Nd in oxide or salt, \$15 to \$20 per kilogram for Nd in alloy supplied to permanent magnet producers, and \$60 to \$85 per kilogram for the Nd-Fe-B magnets.

Falconnet (16) reviewed neodymium availability and markets, and stated the Nd high reserves can easily take care of increased consumption. For 1983 he reported production of 1500 tons REO from bastnasite, 1700 tons REO from monazite, and 700 tons REO from rare earth chloride for a total of 3900 tons REO. Neodymium nitrate or chloride in the amount of 2000 tons REO is available from Rhone-Poulenc, Molycorp and Treibacher. In 1983 a total of 520 tons of Nd₂O₃ was consumed with 400 tons in ceramic capacitors, 100 tons in TV and glass coloring, and 20 tons various applications.

SUMMARY

The rare earth industry continues to develop rapidly in the USA and it is anticipated that the consumption of rare earths will continue to increase with the consumption in 1985 exceeding 1984 and each year afterward even higher. The demand for rare earths used in permanent magnets was strong and created a temporary shortage of samarium oxide. The newly developed neodymium magnet is expected to be produced at substantially larger numbers in the next five years. The consumption of rare earth compounds used in television, x-ray intensifying applications, and lighting phosphors will increase each year.

It is anticipated that the demand for the lanthanides in mischmetal and ferro alloys will continue to drop in the USA due to the reduction in steel production from over 100 million tons per year to approximately 70 million tons per year in 1985. Demands for the rare earths in the other uses is expected to remain at the same levels.

We anticipate in the United States that there will be an average annual increase in the consumption of rare earths in the order of three percent per year for the remainder of this century.

Rare earths used in alloys for hydrogen storage, fuel cells, and heat exchangers, and in cryogenic refrigeration will increase as this could be a source of high purity hydrogen and energy efficient heat pumps in the future.

The United States is expected to continue to be a leader in technological developments, and China is expected to become a major source of rare earths as it develops and processes its vast deposits.

57	58	59	60		62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

--	--	--	--	--	--	--	--	--	--	--	--	--	--	--

Light
Heavy

THE LANTHANIDE SERIES

<u>Rare Earth Elements</u>			<u>Common Elements</u>		
<u>Symbol</u>	<u>Atomic Number</u>	<u>Abundance g/MT</u>	<u>Symbol</u>	<u>Atomic Number</u>	<u>Abundance g/MT</u>
Sc	21	5	Be	4	6
Y	39	28.1	B	5	3
La	57	18.3	N	7	46.3
Ce	58	46.1	Co	27	23
Pr	59	5.5	Cu	29	70
Nd	60	23.9	Ga	31	15
Pm	61	0	Ge	32	7
Sm	62	6.5	As	33	5
Eu	63	1.06	Br	35	1.6
Gd	64	6.4	Mo	42	2.5 - 15
Tb	65	0.9	Ag	47	0.1
Dy	66	4.5	Cd	48	0.2
Ho	67	1.2	Sn	50	40
Er	68	2.5	Sb	51	1
Tm	69	0.2	I	53	0.1
Yb	70	2.7	Pb	82	16
Lu	71	0.8	Bi	83	0.2

ABUNDANCE OF ELEMENTS IN IGNEOUS ROCKS OF CRUST
OF THE EARTHS

TABLE 1

GADOLINITE	$\text{Be}_2\text{FeY}_2\text{Si}_2\text{O}_{10}$
CERITE	$\text{CaCeSi}_3\text{O}_{13}$
XENOTIME	YPO_4
BASTNASITE	CeFCO_3
MONAZITE	$(\text{Ce},\text{Y})\text{PO}_4$
APATITE	$(\text{CaCe})_5(\text{P},\text{Si})\text{O}_4\text{O}_3(\text{O},\text{F})$
PYROCHLORE	$(\text{NaCaCe})_2\text{Nb}_2\text{O}_6\text{F}$
FERGUSONITE	$(\text{Y},\text{Ce},\text{U},\text{Th},\text{Ca})(\text{Nb},\text{Ta},\text{Ti})\text{O}_4$
SAMARSKITE	$(\text{Y},\text{Ce},\text{U},\text{Ca})(\text{Nb},\text{Ta},\text{Ti})_2\text{O}_6$
EUXENITE	$(\text{Y},\text{Ca},\text{Ce},\text{U},\text{Th})(\text{Nb},\text{Ta},\text{Ti})_2\text{O}_6$
ALLANITE	$(\text{Ca},\text{Ce},\text{Th})_2(\text{Al},\text{Fe},\text{Mn},\text{Mg})_3\text{OH}$
FLUOCERITE	CeF_3

MINERALS CONTAINING RARE EARTHS

TABLE 2

METRIC TON REO

China	38,000,000
United States	5,200,000
Brazil	73,000
Canada	197,000
India	2,500,000
Malaysia	35,000
Thailand	1,000
Other Market Economy Countries	950,000
Other Centrally Planned Economy Countries	<u>500,000</u>
WORLD TOTAL	47,656,000

WORLD RARE EARTHS RESERVES

TABLE 3

<u>COUNTRY</u>	<u>TYPE ORE</u>	<u>RARE EARTH OXIDE CONTENT MT</u>
USA	Bastnasite	16,300
	Monazite	1,000
Brazil	Monazite	1,000
China	Bastnasite	6,000
India	Monazite	2,200
Australia	Monazite	8,000
Malaysia	Monazite/Xenotime	200
Thailand	Monazite	80
Market Economy Countries	Monazite	170
Centrally Planned Economy Countries	Monazite	1,500
WORLD TOTAL		36,550

1984 WORLD MINE PRODUCTION

TABLE 4

	<u>MT REO 1984</u>
BASTNASITE	22,300
MONAZITE	12,000
OTHERS: RE CL ₃ Solutions, Concentrates, Xenotime	2,250
TOTAL	36,550

PRODUCTION OF RARE EARTH MINERALS

TABLE 5

REO MT/YEARAUSTRALIA

Allied Eneabba Ltd	Monazite	3,400
Associated Minerals	Monazite	2,500
Cable Sands Pty Ltd	Monazite	200
Westralian Sands	Monazite	1,500
Rutile and Zircon Mines (Newcastle) LTD	Monazite	400

BRAZIL

Nuclebras de Monazita e Associados Ltda	Monazite	1,100
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INDIA

Indian Rare Earths Ltd	Monazite	2,000
Kerala Minerals & Metals Ltd	Monazite	200

INDONESIA

PT Tambang Timah	Monazite/Xenotime	85
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MALAYSIA

Beh Minerals Sdn	Monazite	180
	Xenotime	10
Bidor Malaya Tin Semdoroam Berhad	Monazite	10

THAILAND

Various Tin Mining Companies	Monazite	80
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THE PEOPLE'S REPUBLIC OF CHINA

Various	Bastnasite	6,000
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USA

Molycorp	Bastnasite	16,300
Associated Minerals Ltd.	Monazite	1,000
Humphreys Mining	Monazite	0

ZAIRE

Sominki	Monazite	40
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MAJOR RARE EARTH MINERAL PRODUCERS

TABLE 6

CHEMICAL ANALYSIS OF BASTNASITE CONCENTRATES

Molybdenum Corporation
of America, USA

The China Rare Earth Company
Baotou, Inner Mongolia, China

La ₂ O ₃ - 29.0 %	27.0 %
CeO ₂ - 44.0 %	50.0 %
Pr ₆ O ₁₁ - 4.0 %	5.0 %
Nd ₂ O ₃ - 10.0 %	15.0 %
Sm ₂ O ₃ - 0.8 %	1.1 %
Eu ₂ O ₃ - 0.11 %	0.17 %
Gd ₂ O ₃ - 0.15 %	0.4 %
Tb ₄ O ₇	
Dy ₂ O ₃	
Ho ₂ O ₃ 0.12 %	1.0 %
Er ₂ O ₃	
Tm ₂ O ₃	
Yb ₂ O ₃ - 0.01 %	0.30 %
Lu ₂ O ₃ - 0.01 %	
ThO ₂ - 0.5 %	0.15 - 0.22 %
Y ₂ O ₃ - 0.1 %	0.3 %
BaO - 3.3 %	0.15 - 0.22 %
Fe - 0.5 %	5.0 - 7.0 %
P - 0.62 %	3 - 5 %
S - 0.95 %	0.15 %
SiO ₂ - 3.0 %	0.4 %
CaO - 2.2 %	1.8 %
F - 7 %	5.0 - 7.0 %
H ₂ O - 0.5 %	1.0 %

TABLE 7

**RARE EARTH CHLORIDE
(Lanthanide Chloride)**

<u>Specification</u>	<u>China</u>		<u>USA</u>
	<u>Grade AA</u>	<u>Grade A</u>	
REO	45.00%(min) 47.00%(typical)	45.00%(min) 47.00%(typical)	46.00%(min)
La2O3/REO	27.00%(approx)	27.00%(approx)	15-16%
CeO2/REO	50.00% "	50.00% "	22-23%
Pr6O11/REO	5.00% "	5.00% "	1.7%
Nd2O3/REO	15.00% "	15.00% "	5.3%
Sm2O3/REO	1.00% "	1.00% "	
Fe2O3	.07% "	.07% "	.02%
ThO2	.03% "	.03% "	
BaO	0.8 % "	0.8 % "	
CaO	3.0 % "	3.0 % "	3.0%
SO4	0.1 % "	0.1 % "	
PO4	.01% "	.01% "	
Eu2O3/REO	.17% "	.05% "	
Radioactivity	1 x 10 ⁻³ microcuries/gram.max.		
Na2O			0.5%
Packaging:	In steel drums of 200 kgs net each.		
Physical			
Description:	Solid Cast or lump form available.		Flake or Solid Cast
Origin:	Inner Mongolia, The People's Republic of China		Molycorp

TABLE 8

INDUSTRY**APPLICATION****A. Electronics**

Y_2O_3 ; Eu_2O_3

Color television and
mercury vapour lighting

Gd_2O_3 ; La_2O_3 ; Tb

Phosphors for x-ray screens,
and low pressure mercury lamps
(fluorescent tubes)

Sm_2O_3 ; Nd

Permanent magnets

B. Glass

La_2O_3 ; CeO_2 , Nd_2O_3
 CeO , and other rare earths

Melt additions
Polishing

C. Alloys and Ceramics

La, Ce, Pr, Neodymium
(mischmetal)

Flints, steel and cast iron

Pr_6O_{11}

Ceramic pigments

CeO_2

Ceramic opacifiers

**VARIOUS APPLICATIONS OF RARE EARTHS
IN ELECTRONICS, GLASS, ALLOYS AND CERAMICS**

TABLE 9

<u>Types</u>	<u>Introduced</u>	<u>Use</u>	<u>Use Trend</u>
Martensitic steels	1820 - 1930	Small	Declining
Alnico alloys	1930s	Large	Declining
Remalloy (Fe-Co-Mo)	1930s	Very small	Replaced by Fe-Cr-Co
PtCo	1930s	Very small	Fast declining
Cunife, Cunico	1930s	Small	Declining
Vicalloy	1940s	Very small	Steady
ESD Fe-Co	1950s	Small	Steady
Ferrites (oxides)	1950s	Large	Fast growing
RE-Co alloys	1970s	Small	Fast growing
Fe-Cr-Co alloys	1979	Medium, replacing Alnico 5, Cunife	Modest growth
Mn-Al-C alloy	1979	Small, replacing some Alnicos	Steady, stable
Fe-Nd-B	1983	Currently Very small	Rapid growth expected

HISTORY OF VARIOUS ALLOYS IN PERMANENT MAGNETS

TABLE 10



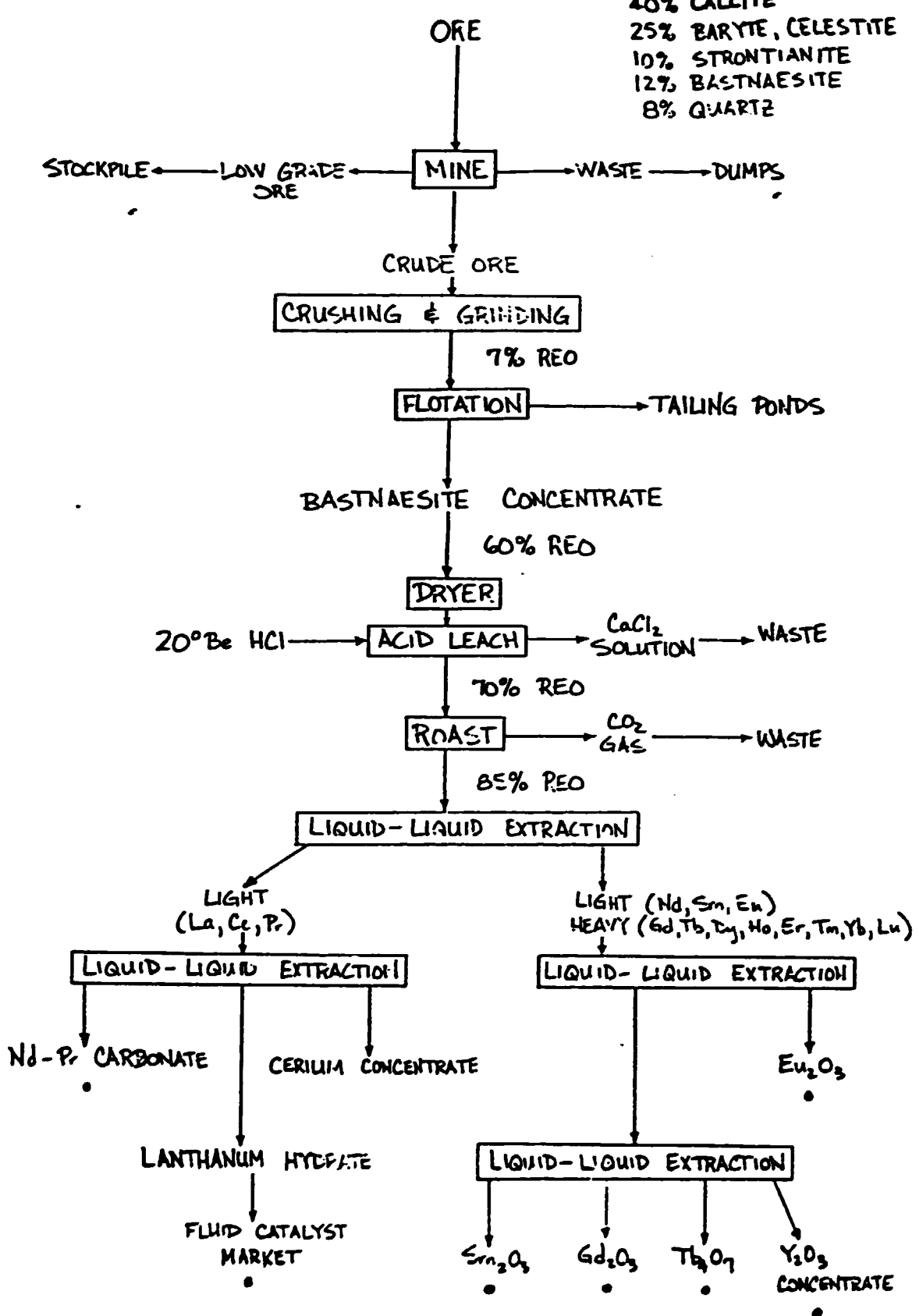
LOCATION OF WORLD BASTNASITE DEPOSITS

FIGURE 1

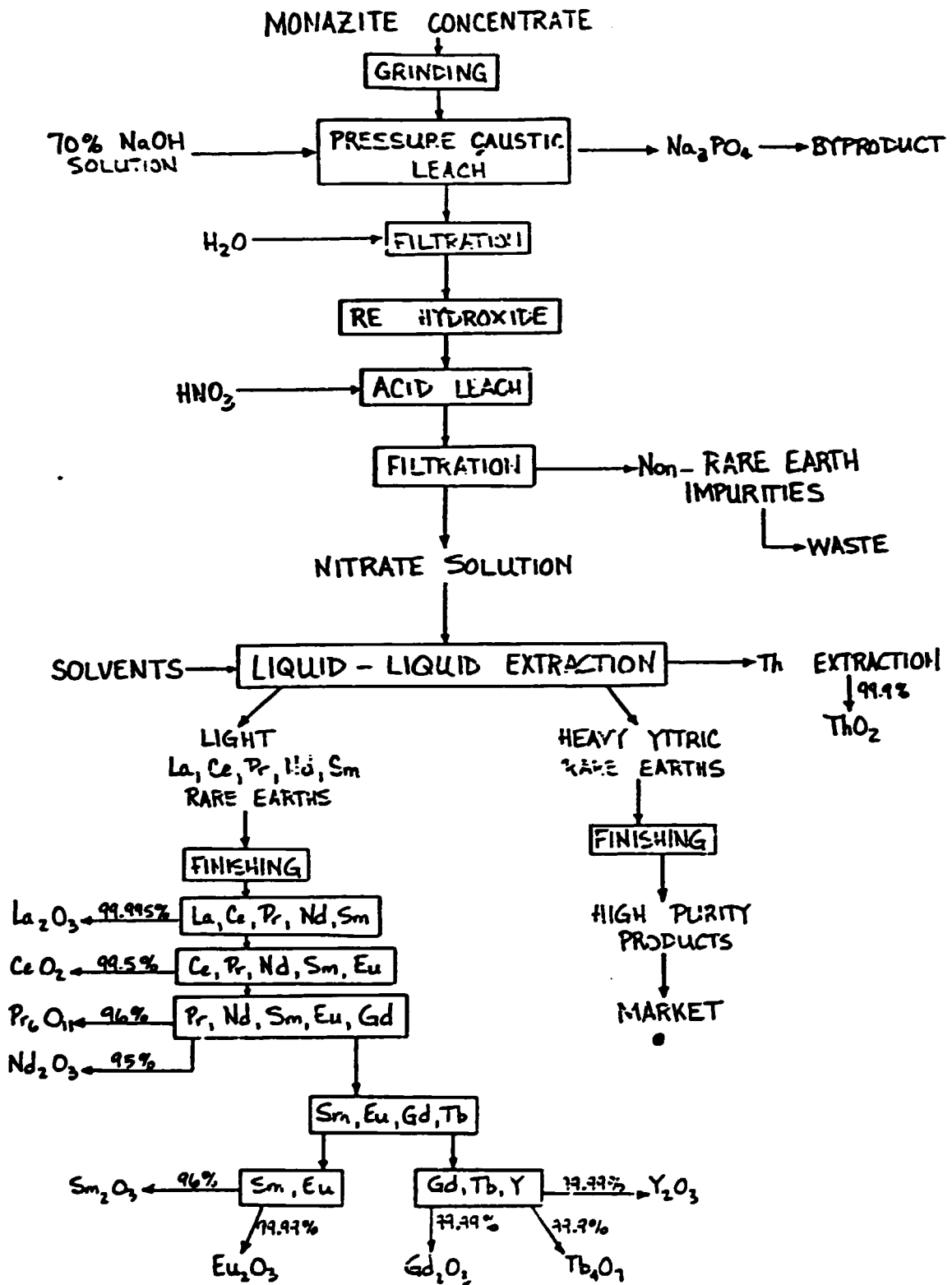


LOCATION OF WORLD MONAZITE DEPOSITS

FIGURE 2



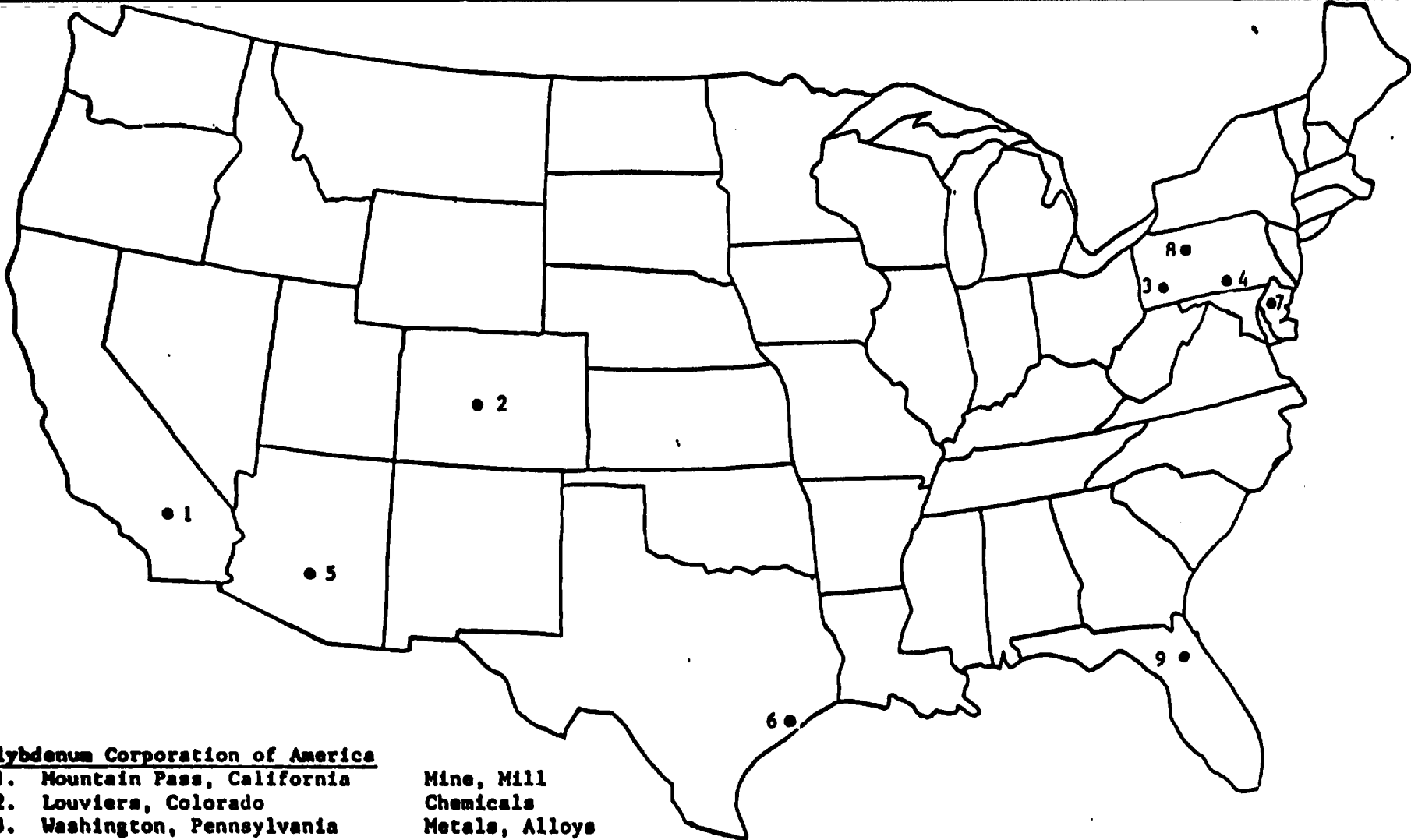
MOLYCORP MOUNTAIN PASS OPERATION
PRODUCT FLOW
FIGURE 3



RHÔNE - POULENC RARE EARTH PROCESS

FIGURE 4

FIGURE 5



Molybdenum Corporation of America

- 1. Mountain Pass, California Mine, Mill
- 2. Louviers, Colorado Chemicals
- 3. Washington, Pennsylvania Metals, Alloys
- 4. York, Pennsylvania Metals, Alloys

Research Chemicals Company

- 5. Phoenix, Arizona Compounds & Metals

Rhone-Poulenc Inc. - Chemicals Division

- 6. Freeport, Texas Chemicals

Ronson Metals Corporation

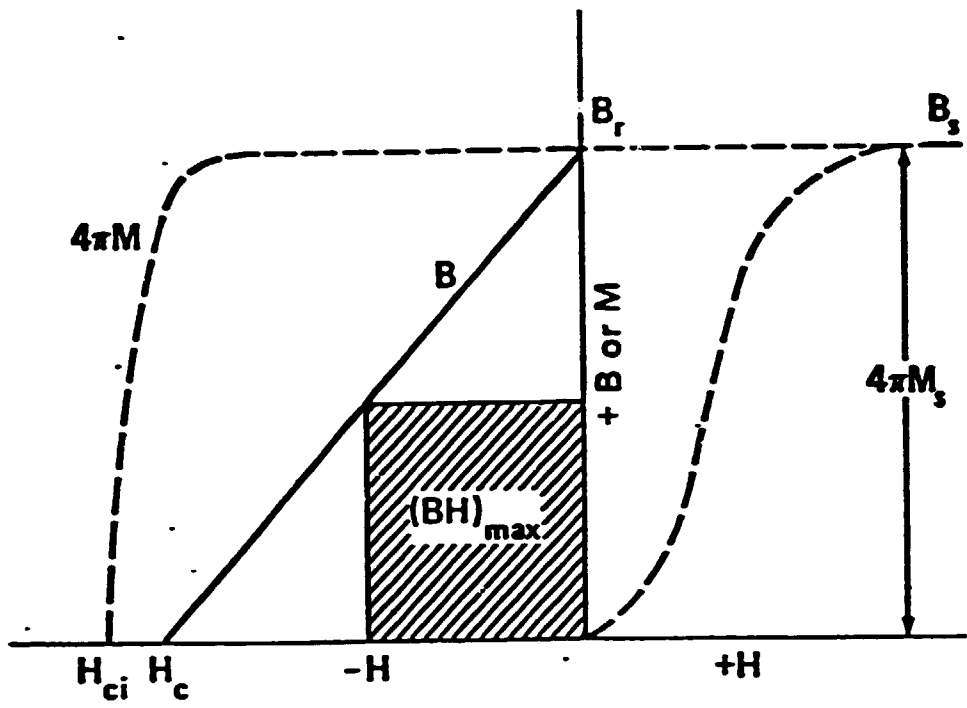
- 7. Newark, New Jersey Mischmetal, Flint

Reactive Metals & Alloys Corporation

- 8. West Pittsburg, Pennsylvania Mischmetal, Silicides

Associated Minerals Ltd, Inc.

- 9. Green Cove Springs, Florida Mine, Mill



$$(BH)_{\max} = \frac{(B_s)^2 A^2 P^2}{4}$$

- $4\pi M_s$ = INTRINSIC SATURATION INDUCTION
- A = ALIGNMENT FACTOR
- P = PACKING DENSITY

FIGURE 6

HYSTERESIS LOOP ASSOCIATED WITH A PERMANENT MAGNET

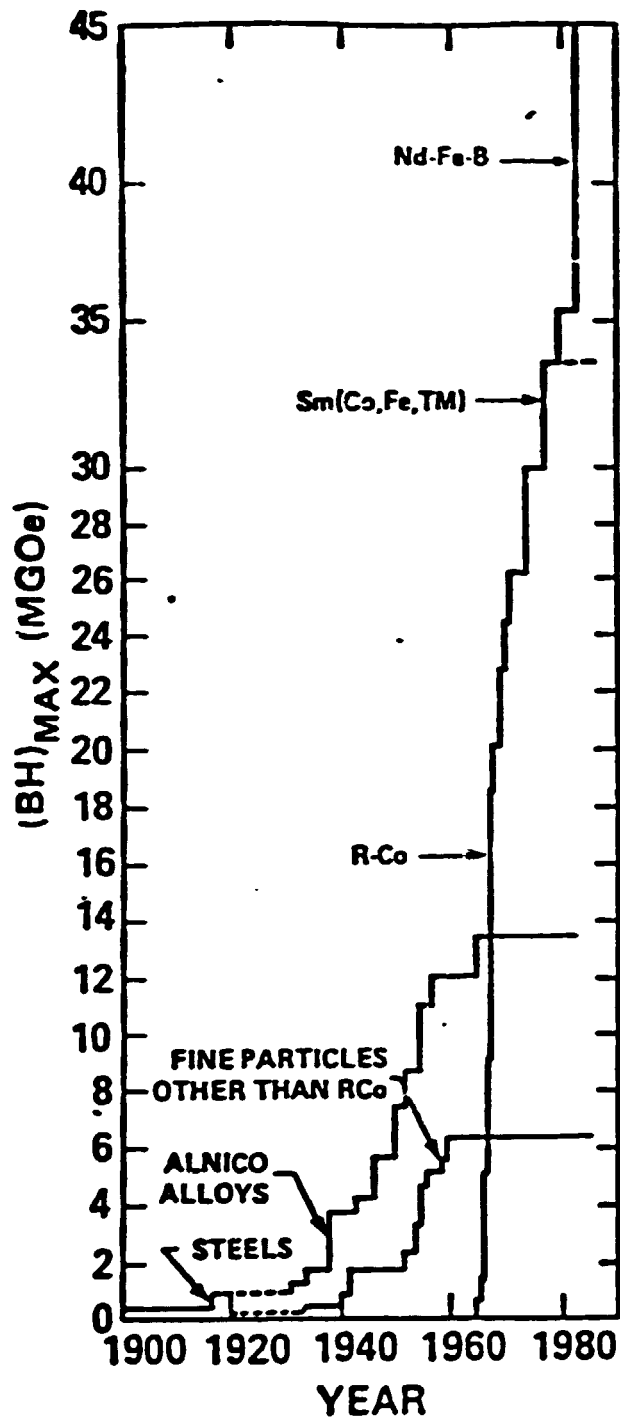


FIGURE 7

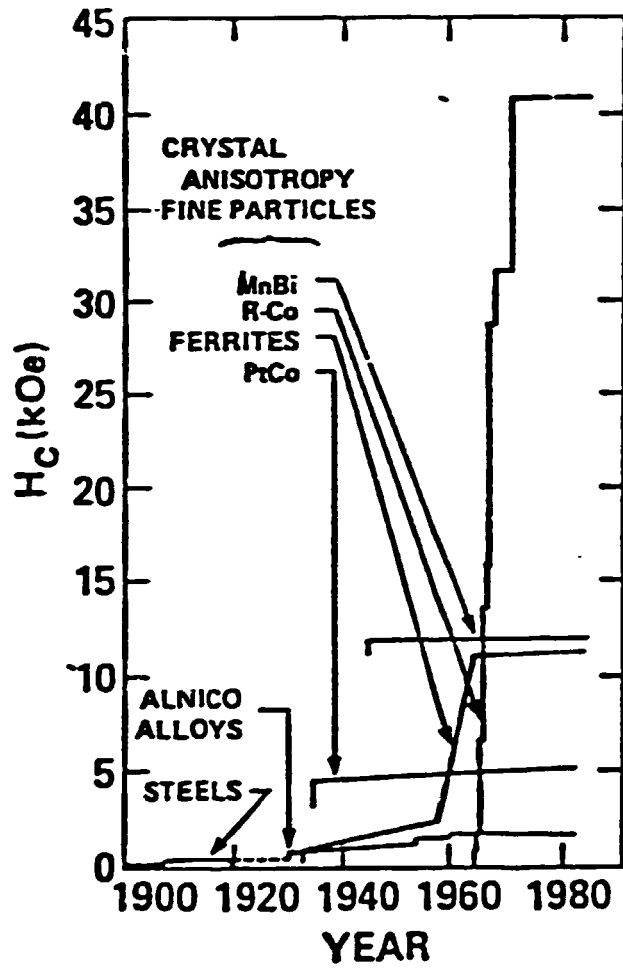


FIGURE 8

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