RARE EARTHS

A. Commodity Summary

The rare earth elements are comprised of scandium, yttrium, and 15 lanthanide elements, of which, cerium, lanthanum, and neodymium are the most abundant. While rare earth elements are found in several minerals, almost all production comes from less than 10 minerals, primarily monazite and bastnasite. Since the scandium industry is, for the most part, separate and distinct from the yttrium and lanthanide industries it is the subject of a separate commodity summary (see the chapter on scandium).

The United States is a major producer and consumer of rare earth ores and compounds which are used in petroleum fluid cracking catalysts, chemical and pollution-control catalysts, metallurgical applications, glass and ceramics, permanent magnets, phosphors, and electronics.  

In 1993 two domestic mines, Molycorp, Incorporated and RGC (USA) Minerals Incorporated, produced rare earths. Twenty facilities produce rare earth materials. Exhibit 1 presents the names, locations, and products of the facilities involved in the production of rare earth materials.

B. Generalized Process Description

1. Discussion of Typical Production Processes

Most production of rare earth elements is from the minerals monazite and bastnasite. Processing of these ores is by sulfuric and hydrochloric acid digestion. The compounds recovered from these processes must be processed further to produce and recover rare earth metal compounds. Processes include fractional crystallization and precipitation, solvent extraction, ion exchange, and reduction. Exhibits 2 through 6 present typical process flow diagrams for the production of rare earths.

Bastnasite is produced only by Molycorp at Mountain Pass, California. It is produced as a mineral concentrate and consumed captive at this facility. Monazite is produced by Associated Minerals at Green Cove Springs, Florida as a byproduct of beach sand mining for titanium and zircon minerals.

2. Generalized Process Flow

Mining

Because rare earth elements are often associated with the radioactive elements uranium and thorium, many rare-earth deposits are discovered during exploration for these elements.

At Mountain Pass, Molycorp mines rare earth ore in an open pit approximately 100 m deep. Blast holes drilled at 3 to 4 m spacing are routinely assayed for total rare earth oxides and other elements by X-ray fluorescence methods. Approximately 300 kilotons per year are mined with a stripping ratio of 5:1. The ore is crushed and blended in stockpiles that contain about 40 kt and fed to a mill located less than

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### EXHIBIT 1

**SUMMARY OF RARE EARTHS PROCESSING FACILITIES**

<table>
<thead>
<tr>
<th>Facility Name</th>
<th>Location</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Associate Minerals</td>
<td>Green Cove Springs, FL</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Crucible Materials</td>
<td>Elizabethtown, KY</td>
<td>Rare earth magnets</td>
</tr>
<tr>
<td>Delco Remy Division of General Motors</td>
<td>Anderson, IN</td>
<td>Rare earth magnets, neodymium-iron-boron magnet alloys</td>
</tr>
<tr>
<td>Hitachi Magnetics</td>
<td>Edmore, MI</td>
<td>Rare earth magnets</td>
</tr>
<tr>
<td>IG Technologies</td>
<td>Valparaiso, IN</td>
<td>Rare earth magnets</td>
</tr>
<tr>
<td>Moly-corp</td>
<td>York, PA, Louviers, CO, PA</td>
<td>Neodymium-iron-boron magnet alloys</td>
</tr>
<tr>
<td></td>
<td>Washington, PA, Mountain Pass, CA, Canton, OH</td>
<td>Uncertain, Bastnasite mine, Uncertain</td>
</tr>
<tr>
<td>Mountain Pass Mine &amp; Mill</td>
<td>Mountain Pass, CA</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Neomet</td>
<td>West Pittsburgh, PA</td>
<td>Neodymium-iron-boron magnet alloys</td>
</tr>
<tr>
<td>Nord Resources</td>
<td>Jackson, NJ</td>
<td>Uncertain</td>
</tr>
<tr>
<td>Reactive Metals &amp; Alloys Corp.</td>
<td>West Pittsburgh, PA</td>
<td>Mischmetal</td>
</tr>
<tr>
<td>Research</td>
<td>Phoenix, AZ</td>
<td>Uncertain</td>
</tr>
<tr>
<td>RGC (USA) Mineral Inc.</td>
<td>Green Cove Springs, FL</td>
<td>Byproduct monazite</td>
</tr>
<tr>
<td>Rhone-Poulencc Chemicals Co.</td>
<td>Phoenix, AZ, Mineville, NY, Freeport, TX</td>
<td>Neodymium-iron-boron magnet alloys</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Uncertain, Uncertain</td>
</tr>
<tr>
<td>W.R. Grace</td>
<td>Chattanooga, TN</td>
<td>Uncertain</td>
</tr>
</tbody>
</table>

100 m from the pit. Moly-corp’s mine was the leading producer of rare earths in both the United States and the rest of the world in 1992. In 1993, mine production decreased from the 1992 level of 22,713 tons to 16,465 tons of rare earth oxides.

Almost all mining of heavy mineral sands from surface placer deposits is done by floating cutterhead or bucket wheel dredges that concentrate the heavy minerals on board and discharge the unwanted tailings back into previously mined areas. An onboard wet mill separates the heavy minerals from the lighter weight fraction through a series of wet gravity equipment that includes screens, hydroclones, spirals, and cones. Wet mill mixed heavy mineral concentrate is sent to a dry mill to separate the individual heavy minerals and produce a concentrate. Dry mill processing includes a combination of scrubbing, drying, screening, electrostatic, electromagnetic, magnetic, and gravity processes. Gravity methods include the use of jigs, spiral and cone concentrators, and shaking tables. Sizing and concentration

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commonly is performed at the mine site by trommels, shaking screens, and gravity separation. Many dredges have such facilities on board or utilize floating preconcentration plants. Monazite can be separated from zircon by electrostatic methods such as electromagnetic or gravity methods. Xenotime is usually separated from monazite by precise gravity methods. Some deposits may require acid leach treatment and calcining to eliminate iron oxide or other grain coatings.

Some sand deposits, too difficult to mine by dredging, are mined using dry methods. Ore is stripped with scrapers, bulldozers, and loaders. Sands recovered by these techniques are crushed, screened, and processed by the wet mill equipment described above.

**Recovery**

**Monazite Ore Processing**

As Exhibit 2 shows, rare earth metals are recovered as oxides from monazite ore by sulfuric acid digestion. The ore undergoes grinding, spiraling, or other similar operations for the initial coarse purification of the ore. Magnetic separation removes the magnetic ore constituents which can be processed separately or discarded as waste. The refined ore is then digested with sulfuric acid at 200-220°C. Rare earth sulfates and thorium sulfates are then dissolved and removed from the waste monazite solids by filtration. Rare earth elements are then precipitated as oxalates or sulfates. These precipitates undergo caustic digestion or roasting to form rare earth oxides which are finally recovered by filtration. The resulting filtrate is discarded as waste.

**Bastnasite Ore Processing**

As shown in Exhibit 3, to recover rare earth chlorides from bastnasite ore, the ore is crushed, ground, classified, and concentrated to increase the rare earth concentrations. Tailings produced during these operations are discarded as waste. The concentrated bastnasite undergoes an acid digestion to produce several rare earth chlorides; hydrochloric acid is used to digest the bastnasite. The resulting slurry is filtered, and the filter cake is further digested with sodium hydroxide to produce rare earth hydroxides. This rare earth hydroxide cake is chlorinated, converting the hydroxide to chlorides. Final filtration and evaporation yields the solid rare earth chloride products. The wastes produced include a sodium fluoride filtrate, which can be recovered for further processing, and filter cake which is discarded.

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7 Ibid.
EXHIBIT 2  Graphic Not Available.

RECOVERY OF RARE EARTHS FROM MONAZITE BY THE SULFURIC ACID PROCESS

EXHIBIT 3

RECOVERY OF RARE EARTH CHLORIDES FROM BASTNASITE ORE

Graphic Not Available.

Purification/Concentration

Flotation

Flotation is used at Mountain Pass to make a bastnasite concentrate containing about 60% rare earth oxides. This concentrate is either used on site as feed for chemical separation of rare earth elements, leached to produce a 70% rare earth oxide concentrate, or shipped as is.

Extraction

Extraction of rare earth elements from monazite and xenotime is accomplished by dissolution in a hot concentrated base or acid solution. At Rhone-Poulenc Inc. plants, which process most of the world's monazite, rare earth elements are extracted in a concentrated solution of sodium hydroxide at 140 to 150°C. After cooling, hydroxides of rare earth elements and thorium are recovered by filtration, and thorium is separated by selective precipitation or dissolution. At Mountain Pass, bastnasite is calcined to drive off CO₂ and fluorine, and leached with hydrochloric acid to dissolve most of the trivalent rare earth elements. The residue is sold as a polishing abrasive.¹

The rare earth hydroxides and chlorides recovered from sulfuric and hydrochloric acid digestion must undergo further processing to produce and recover individual rare earth metal compounds such as fluorides, nitrates, carbonates, oxides, and pure metals, for a variety of applications. Processes include fractional crystallization, fractional precipitation, solvent extraction, ion exchange, and reduction.

Fractional Crystallization and Precipitation

In fractional crystallization, one or more rare earths in a mixture are precipitated by changing the salt concentrations in solution through evaporation or temperature control. Fractional precipitation involves adding a precipitating agent to selectively remove a metal from solution. These two processes generally produce waste salts and salt solutions requiring treatment and disposal. If organic precipitation is used, then organic containing waste fractions may be produced as well.²

Solvent Extraction

To separate individual rare earths in a mixture from each other, an aqueous solution containing rare earth salts is sent countercurrent to an immiscible organic stream which selectively extracts one rare earth from the others. Several stages of extractions are needed to separate each rare earth metal. Each organic stream is then scrubbed with an aqueous stream to transfer the rare earth element into an aqueous phase. Since all of the products are aqueous solutions, the spent solvents leave the process as wastes.³ Exhibit 4 presents a process flow diagram for solvent extraction.

Ion Exchange

Ion exchange produces highly pure rare earths in small quantities. For separating a lanthanide mixture, a cation exchange resin is flushed with a solution such as cupric sulfate to prepare the resin for ion exchange. A solution containing the lanthanides is then passed over the ion exchange resin. The lanthanides displace the cation on the resin surface. This step produces an aqueous waste containing the cation which was exchanged, and small amounts of rare earths. At this stage, the lanthanides have been

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³ Ibid.
EXHIBIT 4

RARE EARTH SEPARATION BY SOLVENT EXTRACTION

Graphic Not Available.

deported on the resin as a mixture. To separate individual rare earth elements, a chemical solution containing a complexing agent, such as NH$_4^+$EDTA, is passed over the resin. The EDTA has a high affinity for rare earths, and the lanthanides are complexed with the EDTA and displaced by NH$_4^+$ on the resin. Each lanthanide has a different affinity for EDTA, and individual lanthanides can be separated and recovered as a result of these varying affinities. Relative to the amount of product generated, large quantities of waste solutions are generated during the process. The waste solutions may be acidic, basic, or neutral, and will contain the metals displaced from the resin during ion exchange, as well as the complexing agents used.\footnote{11} Exhibit 5 presents a process flow diagram for ion exchange.

**Calcium Reduction**

High purity rare earth metals can be produced by the metallocermic reduction of rare earth halides. This process is used when 99.99% purity is required. After converting the rare earths into fluorides, they are reduced to the metallic state through contact with calcium or barium at high temperatures.\footnote{12}

Ten of the rare earths (lanthanum, cerium, praseodymium, neodymium, gadolinium, terbium dysprosium,holmium, erbium, and lutetium as well as scandium, and yttrium) are produced by calcium reduction. The raw material form of these metals is the metal fluoride. The individual metal fluoride is placed with calcium metal into a reduction vessel where a heat-driven reaction produces pure rare earth metal and calcium fluoride. The metals are further purified by melting in a vacuum to remove impurities. Casting is dependent upon the form in which a buyer wants the metal. Non-contact cooling water is used to cool both the reduction vessels and the melting and casting equipment. A process flow diagram for calcium reduction is presented in Exhibit 6.

**Mischmetal**

**Mischmetal Production**

Wet rare earth chlorides or hydrated rare earth compounds must be stripped of their water before electrolytic reduction can take place in order to prevent decay of the graphite anode during electrolysis. The anode could be decayed by the reaction of the liberated oxygen in the electrolyte with the carbon anode to form carbon dioxide. Batch or continuous mode dryers may be used. Both gas heat and electric heat have been used to run the dehydration furnaces.\footnote{13}

Dry rare earth chlorides are reduced to mischmetal in electrolytic cells. Batch process electrolysis reduces the rare earth salts to metal in 8 to 12 hours. Excess slag is removed and may be sold for its rare earth chloride content. Following reduction, the mischmetal is cast into bars or ingots for future uses.\footnote{14} Exhibits 7 and 8 present process flow diagrams for mischmetal production.

\begin{footnotes}
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EXHIBIT 5
LANTHANIDE SEPARATION BY ION EXCHANGE

Graphic Not Available.

EXHIBIT 6
CALCIUM REDUCTION PROCESS

Graphic Not Available.

Mischmetal Reduction

Mischmetal is an alloy typically composed of cerium, lanthanum, neodymium, praseodymium, other rare earth metals, and iron. Mischmetal processing reduces the oxide form of the rare earth metals (samarium, europium, and ytterbium) to an elemental form. In this reaction, the mischmetal acts as a reducing agent and is oxidized to a mixture of rare earth metal oxides. The process is performed at a low pressure and a temperature below the melting point so that the metals vaporize or sublime. The pure metal is condensed and collected in a crystalline mass of high purity. These solids may be crushed into powder or melted and cast if a solid product form is desired.

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

None identified.

4. Beneficiation/Processing Boundaries

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in Section B.

EPA determined that for rare earths and mischmetal, the beneficiation/processing line occurs between ore preparation and acid digestion when the ore is vigorously attacked with concentrated acids, resulting in the physical destruction of the ore structure. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations, irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents below the mineral processing waste streams generated after the beneficiation/processing line, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C. Process Waste Streams

Rare earth element ores and commodities, as well as byproducts and waste materials from rare earth processing, are naturally radioactive, due to contained thorium.

1. Extraction/Beneficiation Wastes

Tailings and magnetic fractions are possible waste streams from the extraction and beneficiation of rare earths.

2. Mineral Processing Wastes
Existing data and engineering judgement suggest that the materials listed below do not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate these materials further.

**Off-gases from dehydration.** From the furnaces are treated by water or alkaline scrubbers to remove particulates and acid. The treated gases are vented.\(^\text{15}\) Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent hydroxide cake.** Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent monazite solids.** Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent offgases from electrolytic reduction.** Off-gases from electrolytic reduction include chlorine gas, carbon monoxide and carbon dioxide gases from the carbon in the graphite anodes, and hydrochloric acid fumes. These gases are contacted with water to both cool the gases and to absorb particulates and hydrochloric acid vapors. The partially cleansed gases are then contacted with sodium hydroxide solution, resulting in the formation of sodium hypochlorite. After a sufficient hypochlorite concentration is attained, the solution may be sold as a byproduct.\(^\text{16}\) Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Spent sodium fluoride.** Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Waste filtrate.** Existing data and engineering judgement indicate that this waste does not exhibit any characteristics of a hazardous waste. Therefore, the Agency did not evaluate this material further.

**Waste solvent.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 2,000 metric tons/yr, 1,000,000 metric tons/yr, and 2,000,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of ignitability. This waste may be recycled and is classified as a spent material.

**Spent Lead Filter Cake.** This waste may be stabilized with a polysilicate material and then reinserted into the process for extraction of additional cerium. Tailings containing carbonates are used to precipitate iron. The resulting lead filter cake may exhibit the characteristic of toxicity for lead. This waste may be recycled to extraction/beneficiation units and is classified as a byproduct. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 3,300 metric tons/yr, 4,200 metric tons/yr, and 5,000 metric tons/yr, respectively.

**Lead Backwash Sludge.** Existing data and engineering judgement indicate that this waste does not exhibit characteristics of a hazardous waste. Therefore, the Agency did not evaluate the material further.

**Waste Zinc Contaminated with Mercury.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 200 metric tons/yr, 45,000 metric tons/yr, and 90,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of toxicity for mercury. This waste may be recycled and is classified as a byproduct.

**Solvent Extraction Crud.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 200 metric tons/yr, 45,000 metric tons/yr, and 90,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic ignitability. This waste may be recycled and is classified as a spent material.


\(^{16}\) Ibid.
Spent surface impoundment liquids are a likely waste stream from rare earth production. Surface impoundment liquids were generated at a rate of 477,000 metric tons per year in 1991. Waste characterization data are presented in Attachment 1. This waste is not expected to be hazardous.

Spent surface impoundment solids. This waste stream was generated at a rate of 100 metric tons per year in 1991 and may be toxic for lead. This waste is not expected to be hazardous. Waste characterization data are presented in Attachment 1.

Lanthanide Production

Spent ammonium nitrate processing solution is a possible waste stream from lanthanide separation. The 1991 waste generation rate for the sector was 14,000 metric tons per year. This waste may exhibit the characteristic of corrosivity. Attachment 1 presents waste characterization data.

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18 Ibid.

19 Ibid.
Graphic Not Available.

EXHIBIT 8
Mischmetal Production Process

Graphic Not Available.

Cerium Production

**Process wastewater.** This waste stream may be toxic for lead as well as contain detectable levels of ammonium. This wastewater may also be corrosive. The 1991 waste generation rate for the sector was 7,000 metric tons per year.\(^{20}\) Waste characterization data are presented in Attachment 1. This waste may be recycled and is classified as a spent material.

Mischmetal Production

**Spent scrubber liquor** from wet air pollution control is generated from mischmetal production. Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 500,000 metric tons/yr, and 1,000,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity. This waste may be recycled or discharged to wastewater treatment. This waste is classified as a spent material.

**Wastewater from caustic wet air pollution control.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 100 metric tons/yr, 500,000 metric tons/yr, and 1,000,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristics of toxicity for chromium and lead and corrosivity. Scrubber liquor is recycled and the bleed stream is discharged to treatment. This waste is classified as a spent material.

**Spent electrolytic cell quench water and scrubber water.** Waste characterization data are presented in Attachment 1. This waste is not expected to be hazardous.

**Electrolytic cell caustic wet APC sludge.** Although no published information regarding waste generation rate or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 70 metric tons/yr, 700 metric tons/yr, and 7,000 metric tons/yr, respectively. We used best engineering judgement to determine that this waste may exhibit the characteristic of corrosivity. This waste is recycled and is classified as a sludge.

**Spent sodium hypochlorite filter backwash.** The caustic wet air pollution control system following the water quench or water scrubber is designed to recover chlorine present in the gas stream. Sodium hydroxide is circulated through the scrubber and the reaction with chlorine forms sodium hypochlorite. When a 12 to 15% sodium hypochlorite concentration is attained, the solution is drawn off and sold for industrial use. This waste is not expected to be hazardous.

D. Ancillary Hazardous Wastes

Ancillary hazardous wastes may be generated at on-site laboratories, and may include used chemicals and liquid samples. Other hazardous wastes may include spent solvents (e.g., petroleum naptha), acidic tank cleaning wastes, and polychlorinated biphenyls from electrical transformers and capacitors. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, waste oil (which may or may not be hazardous), and other lubricants. Pinion gear grease is an ancillary waste. At Molycorp, this waste contains 50% aromatic oils, 35% petroleum asphalts, and 0-10% 1,1,1 trichloroethane.

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\(^{20}\) Ibid.
BIBLIOGRAPHY


