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Cerium-based polishing compounds: discovery to manufacture

James B. Hedrick
US Bureau of Mines, 810 Seventh Street N.W., MS 5209, Washington, DC 20241 (USA)

Shyama P. Sinha
AdTech Systems Research Inc., 1342 North Fairfield Road, Beavercreek, OH 45432-2698 (USA)

Abstract

An overview of cerium as a polishing compound from discovery to manufacture is presented. The historical record of cerium began with its discovery in 1803. Although other grinding and polishing compounds were known from the 15th century, cerium's use as a glass polish did not begin until the 1930s. The mining, refining and recovery of cerium is reviewed with emphasis on the refining process. Cerium concentrates and compounds are manufactured into various grades of polishing compounds. Basic manufacturing processes are examined including calcining, milling and particle size classification. Following the mine-to-manufacture sequence, prices are traced from the ore, concentrate and oxide through to the polishing compound. Prices and principal applications for various polishing compounds are listed. Demand for US manufactured cerium polishing compounds has increased. Shipments doubled between 1985 and 1991. World demand is expected to continue to increase, especially in the rest of the world.

One of cerium's important applications is as a polishing compound. Cerium oxide, in conjunction with water, polishes by both mechanical and chemical means. World demand for cerium-based polishing products has continued to increase. US producers shipped over 2000 metric tons of product in 1991.

1. History of cerium

Cerium was discovered independently by three scientists in 1803. The mineral, cerite, from which it was discovered, was described several years earlier in 1751 by Swedish chemist and mineralogist, Axel F. Cronstedt. Cronstedt called the mineral "tungsten (heavy stone) of Bastnas", based on its high specific gravity and the locality from which it was collected, the Bastnas Mine at Riddarhyttan, Vestmanland, Sweden. The "heavy stone" was examined independently in 1782 by Carl W. Scheele and Juan Jose de Elhuyar who both determined that it contained no tungsten [1]. Neither scientist, however, was able to isolate the new element.

It was 21 years later, in 1803, that M.H. Klaproth, and collaborators Jons J. Berzelius and Wilhelm Hisinger independently separated a new substance from the mineral. Klaproth named the substance, ochroite, based on the light yellow brown color of the new compound [2]. His contemporaries, Berzelius and Hisinger, believed their discovery to be a metallic oxide and named it cerous oxide, noting the existence of two separate salts of differing colors and properties [2]. Berzelius and Hisinger derived the element's name, cerium, and the name of the mineral from which it was isolated, cerite $(Ca,Ce)_9(Mg,Fe)Si_7(O,OH,F)_{28}$, from the recently discovered asteroid, Ceres (Roman goddess of agriculture and the harvest).

2. History of polishing

Although the earliest references to grinding and polishing came in the 15th century, it was not until 1901 that grinding and polishing were determined to be different processes. Lord Rayleigh, who observed the variation, proposed that the difference was caused by the backing material. Another mechanism, proposed by G.T. Beilby in 1903, noted that the surface flow and the mobility of surface molecules were the main processes. Beilby's theory found greater support and additional studies confirmed the importance of chemical processes.

The use of cerium oxide as a polishing compound is not credited to any individual. Prior to World War 2, cerium oxide was not recognized as a superior polishing product for glass and was not available in commercial quantities. Its use was first reported in the

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European glass industry around 1933 [3]. Cerium oxide's use spread to the North American continent around 1940–1941 when the Canadian optical industry started using it. Its development was accelerated during the 1940s by wartime demand for a fast and efficient polish. In the 1950s and 1960s, demand for televisions created a rapid increase in demand for faceplate polishes. Advances in technology have attained polishing accuracy at the angstrom level [4].

3. Mining

Cerium is recovered from the rare earth ore minerals monazite, bastnasite and loparite. In the United States, monazite was produced as a by-product of titanium and zirconium minerals by RGC (USA) Minerals Inc., at Green Cove Springs, FL. Bastnasite was produced domestically as a principal product by Molycorp, Inc., at Mountain Pass, CA.

Most monazite was mined by surface placer methods from unconsolidated sands. Leading producers are Australia, Brazil, China, India, Indonesia, Malaysia, Thailand and the United States.

Bastnasite is mined from hard rock deposits. Production in China is a by-product of iron ore mining while US production is solely for rare earths. Ore is recovered by drilling and blasting. At the mill, bastnasite is crushed, screened and processed by flotation to produce a concentrate.

Loparite is mined as a by-product of phosphate rock in the Commonwealth of Independent States (CIS). Loparite is the leading source of rare earths, including cerium, for the CIS [5].

Economic deposits of cerium are located throughout the world. Principal world reserves are located in China, the CIS, the United States and Australia (see Table 1). Cerium reserves in China and the United States are primarily contained in bastnasite with lesser amounts in monazite. The CIS's reserves are mostly in loparite while those in Australia are predominantly in monazite, secondary monazite and cheralite [6].

World mine production capacity is about 84 000 metric tons of equivalent rare earth oxide per year. Based on mine capacity and the cerium content of the major ores, it is estimated that 41 000 tons of cerium oxide could be produced annually. Leading mine producers of cerium ores are the United States, China, Australia and the CIS (see Table 1).

4. Ore refining

The principal cerium ores are monazite, bastnasite and loparite. Cerium compounds are generally separated from the other rare earths and thorium early in the refining process. Countries with cerium-refining capacity are the United States, China, France, the CIS and Japan. Three US companies process cerium-containing ores, concentrates and compounds; Molycorp, Inc. at Mountain Pass, CA, Rhône-Poulenc Basic Chemicals Co. at Freeport, TX and Davison Specialty Chemical Co. at Chattanooga, TN.

TABLE 1. World reserves, reserve base and mine capacities

Country	Reserves[a,b]	Reserve[a,b] Base	Mine production capacity[c]	Potential cerium recovery[a]
United States	5900000	6320000	28000	14000
Australia	2700000	2400000	11000	5100
Brazil	130000	150000	2300	1000
Canada	420000	460000	–	–
China	24000000	22000000	22000	10800
Commonwealth of Independent States	9600000	10600000	8500	4300
India	500000	600000	4500	2100
Malaysia	9000	11000	4300	2000
Sri Lanka	3700	4000	1700	900
Thailand	500	500	280	100
Zaire	500	500	1000	500
Other Countries	9500000	9700000	170	100
Total (rounded)	53000000	52000000	84000	41000

[a] Metric tons of cerium oxide. Cerium oxide contents from US Bureau of Mines, Annual Reports for 1990 and 1991, by James B. Hedrick. A cerium oxide content of 46% was used if analytical data were not available. Potential cerium recovery based on mine production capacity.

[b] Definitions from Resource Reserve Definition. US Geological Survey Circular 831, 1980.

[c] Metric tons of rare earth oxide.

4.1. Monazite

Monazite concentrate is processed with either sulfuric acid or sodium hydroxide. The sodium hydroxide process is preferred since it removes the phosphates more readily [7]. In the sodium hydroxide process, monazite concentrate is finely ground and reacted with a hot concentrated sodium hydroxide at 140–150 °C. Insoluble hydroxides of the rare earths and thorium are formed while trisodium phosphate and excess sodium hydroxide remain in solution. The insoluble hydroxides are rinsed, recovered by filtration and the thorium removed. Thorium hydroxide, being less basic than the rare earth hydroxides, is separated from the rare earths based on differences in solubility.

4.2. Bastnasite

Bastnasite concentrate is produced by flotation. After crushing and grinding, it is conditioned for flotation by heating, adjusting the pH and adding organic depressant and collector chemicals. Hot froth flotation follows with the flotation concentrate leached, thickened and drum filtered. Bastnasite concentrate is then processed with hot concentrated hydrochloric acid to form a rare earth chloride solution.

4.3. Loparite

Loparite is decomposed in hot concentrated (85%) sulfuric acid in the presence of ammonium sulfate. The rare earths and thorium precipitate as double sulfates and are removed by filtration and rinsed. The remaining solution of sulfates of titanium, niobium and tantalum is removed for separate processing. The double sulfates of rare earths and thorium are converted to carbonates followed by dissolution in nitric acid. Thorium is precipitated by raising the alkalinity of the solution through the addition of sodium hydroxide or ammonium hydroxide.

5. Cerium refining

Commercial production of cerium oxide and compounds is by solvent extraction (SX), selective precipitation and ion exchange (IX). Most grades of polishing compounds are produced from standard-grade cerium compounds.

5.1. Solvent extraction (liquid–liquid extraction)

In SX, cerium is separated from a thorium-free rare earth solution using differences in solubility. The solvent, tri-n-butyl phosphate (TBP), is added to an aqueous rare earth nitrate solution to selectively extract cerium in its ceric state. Cerium is stripped from the TBP, precipitated with oxalic acid and ignited to produce cerium oxide.

5.2. Selective/fractional precipitation

Separations by selective precipitation depend primarily upon basicity differences. These differences can only operate when equilibrium between the solid phase and the solution is complete. Cerium is separated commercially based on its reduced basic property in the tetravalent state. Being less soluble than the trivalent rare earths, Ce^{IV} may be selectively precipitated from a mixed rare earth solution by adjusting the pH. Cerium may also be enriched in a mixture of rare earth oxides by treating with nitric acid (pH 3–4). The more soluble trivalent rare earths are dissolved causing concentration of the less soluble Ce^{IV}.

Selective hydrolysis is another way of concentrating Ce^{IV}. Hydrolysis to a basic nitrate or sulfate is effected by diluting and boiling a concentrated solution containing the trivalent lanthanides and Ce^{IV}. A high purity cerium is obtained, but a complete separation cannot be achieved by this method.

5.3. Ion exchange (displacement chromatography)

The preferred methods for refining cerium are solvent extraction and selective precipitation. Cerium is generally not produced by ion exchange because of its low solubility in ethylene-diaminetetraacetic acid (EDTA) solutions.

In IX, cerium is separated from the other rare earths based on differences in adsorption and selective elution. In a typical process, thorium-free rare earth solutions are run through multiple columns of synthetic ion exchange resins. A mixed rare earth solution is introduced into the initial loading column and exchanges with cations on the synthetic resins. The loading resins are designed to have an affinity for rare earth ions. Typical resins are sulfonic polymer beads containing monovalent hydrogen or ammonium cations. Cerium and the other rare earth cations in the solution displace the hydrogen or ammonium cations on the resins (three H^+ or NH^{4+} ions for each rare earth +3 ion). After loading, the resins contain a mixed distribution of rare earths. Unadsorbed ions are flushed from the column.

Removal of cerium or the other rare earths from the loading resins (elution) is effected by an organic eluting agent, such as hydrogen EDTA, ammonium EDTA or other hydrogen-bearing eluting agents [8]. In the process, an EDTA eluting agent is pumped into the loading column at a pH of about 8. $EDTA^{H-}$ ions or EDTA-like agents form complexes with the rare earths to form a mixed rare earth EDTA solution. Protons (H+) and/or NH^{4+} ions are readily replaced regenerating the original resins. This solution continues down the loading column into the next stage, the separation column. Partial separation occurs in the loading column as the heavy rare earths have a greater affinity for EDTA than the light rare earths. Typical formation constants for heavier rare earth EDTA complexes are 10^8–10^9 while those for the lighter rare earths EDTA are 10^7 [9].

In the separation column, the rare earth EDTA solution interacts with copper ion resins. Copper has a higher affinity for EDTA than the rare earth ions so the copper ions go into solution, displaced by the rare earths. Lutetium elutes off the loading column first due to its smaller ionic radius, coordination bonding with EDTA and charge density (ratio of valence state to ionic radius). Separation is improved by heating and the process is normally run between 60 °C and 100 °C.

6. Manufacture

Cerium-based polishing compounds are produced internationally. Seven companies manufacture cerium polishing compounds in the United States (see Table 2). Leading foreign producers are Austria, China, the CIS, France, Japan and the United Kingdom. Polishing compounds are manufactured from cerium concentrate and cerium compounds, mainly cerium carbonate and cerium hydrate. Factors influencing the quality of the final product include calcination time and temperature, purity of the feedstock, impurities from processing, crystallite size, particle size and distribution, agglomeration, milling and classification, water hardness, pH, and dissolved solids.

Cerium concentrate is produced from bastnasite concentrate. Calcined bastnasite concentrate is leached with concentrated hydrochloric acid for conversion to soluble rare earth chloride. The cerium is oxidized to the ceric state during calcining, precipitated and passed through a countercurrent decantation and thickening circuit, resulting in a filter cake composed of about 70% rare earth oxide, of which 90% is ceric oxide. This precipitate is reprocessed and dried to a saleable cerium concentrate [10]. The concentrate is suitable for standard-grade polishing, however, additional processing, such as size classification and additives, is needed to produce a higher grade polish.

Cerium hydrate is produced from a rare earth chloride solution. The slow addition of chlorine and sodium hydroxide oxidizes the cerous cations to the ceric state and the chloride anion is replaced by the hydroxide. Microcrystalline ceric hydroxide forms as a precipitate [11]. The ceric hydroxide precipitate is washed, recovered by filtration and calcined to a cerium oxide polishing product.

Cerium carbonate is also produced from rare earth chloride. The controlled addition of sodium carbonate yields an alkaline rare earth carbonate solution that in contact with air promotes the formation of $\mathrm{Ce^{IV}}$. Ceric carbonate precipitates as a coarsely crystalline product that is recovered by filtration. Calcination produces a fine-grained cerium oxide polishing powder.

Cerium oxide produced by solvent extraction, ion exchange or selective precipitation, is used in the production of a few "high cerium" polishing compounds. A high cerium content, however, is not the primary factor in producing a quality polishing product. Calcination time and temperature, particle size, reactivity, additives and particle impurities are critical elements affecting a polish's efficiency.

7. Products and applications

A wide range of polishes are produced internationally. Various grades are manufactured for specific applications. Most material is sold in powdered form with lesser amounts of slurried polishes marketed for precision applications.

Cerium polish is used to polish flat glass for windows and mirrors, cathode-ray tube (CRT) faceplates for television and computer monitors, prescription glass for eyeglasses, industrial optical glass for cameras, camcorders, television cameras, binoculars, and copy machines, photomask substrates for integrated circuits, and precision optical glass for microscopes, filters, prisms and telescopes. Cerium is also used to polish quartz crystal, granite and faceted gemstones.

TABLE 2. US producers of cerium-based polishing compounds

Company	Plant location	Product markets	Size
Cercoa Incorporated, a subsidiary of Ferro Corp.	Lake Park, FL	Standard to precision	Large
Davison Specialty Chemical Co., a subsidiary of W.R. Grace	Chattanooga, TN	Standard to precision	Medium
Hastings Development Corp.	Princeton, NJ	Precision to ultra-precision	Small
Micro Abrasives Corp.	Westfield, MA	Standard to precision	Small
S and D Technical Services	Hudson, OH	Precision	Small
Solution Technology Inc.	Matthews, NC	Precision	Small
Transelco Division of Ferro Corp.	Penn Yan, NY	Standard to precision	Large

TABLE 3. Cerium ore, concentrate and oxide prices

Year	US dollars per kilogram of rare earth oxide contained				US dollars per kilogram of cerium oxide contained			
	Bastnasite concentrate 60% REO		Monazite concentrate 55% REO plus thoria		Cerium concentrate 60% ceric oxide		Cerium oxide 95%–96% purity	
	Actual dollars	1991 constant dollars[a]	Actual dollars	1991 constant dollars[a]	Actual dollars	1991 constant dollars[a]	Actual dollars	1991 constant dollars[a]
1981	2.25	3.34	0.83	1.23	3.09	4.58	9.92	14.71
1982	2.43	3.39	0.75	1.05	3.09	4.31	9.92	13.85
1983	2.43	3.26	0.71	0.95	3.09	4.14	9.92	13.31
1984	2.43	3.12	0.64	0.82	3.09	3.97	9.92	12.75
1985	2.54	3.15	1.09	1.35	3.09	3.83	9.92	12.30
1986	2.54	3.07	1.06	1.28	3.09	3.73	9.92	11.98
1987	2.54	2.97	0.90	1.05	3.09	3.61	9.92	11.61
1988	2.54	2.86	1.15	1.30	3.09	3.48	9.92	11.17
1989	2.76	2.98	1.19	1.28	3.42	3.69	9.92	10.71
1990	2.87	2.97	1.19	1.23	3.64	3.77	11.57	11.99
1991	2.87	2.87	0.93	0.93	5.07	5.07	12.13	12.13
1992	2.87	NA[b]	0.42	NA	5.07	NA	12.13	NA

Bastnasite, cerium concentrate and cerium oxide princes from Molycorp, Inc., a subsidiary of Unocal Corp. Monazite prices from Metal Bulletin (London), converted from Australian dollars.

[a] From implicit price deflators for "Gross Domestic Product" by the Council of Economic Advisors, based on 1987 = 100.

[b] NA, not available.

TABLE 4. US polishing compound prices, 1993

Polishing compound	Type	Principal applications	Cost per kilogram[a]
Cerium oxide	Powder	CRT faceplates, Rx and glass lenses, flat glass	4.74–12.00
Cerium oxide	Slurry	Precision, photomasks, massive optics	15.00–38.00
Zirconium oxide	Powder	Glass lens manufacture	7.72–14.05
Zirconium oxide	Slurry	Precision, semiconductors, camera lenses, plastics	7.62–20.30
Ferric oxide (red rouge)	Powder	Metals: brass, copper, silver, gold	4.12–7.50
Colloidal silica	Slurry	Semiconductors, silicon optics	1.54–3.21
Aluminum oxide	Powder	Lapidary, contact lenses, aircraft windows, IR optics	7.72–72.00
			Cost per liter[a]
Cerium oxide	Slurry	Precision, photomasks, massive optics	19.81–44.91
Aluminum oxide	Slurry	Plastic and polycarbonate lenses, aircraft windows	4.50–7.33
Zirconium oxide	Slurry	Precision, semiconductors, camera lenses, plastics	8.05–25.08

[a] Prices for standard package quantities. Individual prices may differ depending on product, grade, market conditions, and quantity purchased.

TABLE 5. Shipments of Ce-based polishing compounds
(metric tons of rare earth oxide)

Year	US producer shipments	Annual change in shipments	Annual percent change
1985	1072	W[a]	W
1986	1184	112	10.4
1987	1241	57	4.8
1988	1388	147	11.8
1989	1628	240	17.3
1990	1834	206	12.7
1991	2109	275	19.8
1992	W	W	W

[a] W, withheld to avoid disclosing company proprietary data.

8. Prices

Prices for polishing compounds vary widely depending on the grade and quantity purchased. Standard grade cerium polish is available for less than double the price of the cerium ore, bastnasite concentrate. Prices for the two principal ores and the intermediate products, cerium concentrate and cerium oxide, are shown in Table 3. Polishing compound prices for 1993 are shown in Table 4.

9. Market trends

US produced shipments of cerium polishing compounds have increased every year since 1985 (see Table 5). Demand has increased primarily in the rest of the world. Principal uses are in polishing CRT screens, flat glass and prescription lenses. Reduced demand for precision polishing is expected in the United States due to decreased government spending for defense applications. US demand is expected to continue to shift to foreign markets to take advantage of low-cost labor and favorable tax provisions.

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