CERIUM

A GUIDE TO ITS ROLE
IN
CHEMICAL TECHNOLOGY

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Cerium : A Guide to its Role in Chemical Technology

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PREFACE

You-who are reading these words-may well be sitting under a fluorescent light, with reasonable probability own a vehicle, and most likely regularly watch television. These consumer durables, symbols of modern technology, all depend on chemistry for their creation and performance. This brochure describes-among other topics-how *cerium,* in various guises, contributes to those technologies, to lighting, to the automobile, and to television. These uses, and many other practical applications, illustrate the crucial and varied roles of *cerium* in chemical technology.

Molycorp, with its unique lanthanide deposit near Las Vegas, Nevada, U.S.A., is the world's prime producer of *cerium* derivatives. It has produced, and continues to produce, a range of cerium-based materials to meet market demand. The element, the dominant member of the often-overlooked lanthanide series, is essential to many industries.

This brochure aims to be an introduction to *cerium,* to sources, to production and especially to uses. It is intended to be a guidebook rather than a comprehensive study. The references provided will, it is hoped, give guidance to those readers who wish to explore more deeply some of the topics discussed. New uses will no doubt come from such exploration. In addition, for those of you educating the next generation of chemists and writing the next editions of chemistry textbooks, up-to-date information about *cerium* is hereby available. Please use it.

All data and information are furnished in good faith and believed to be reliable. However, no warranty of merchantability, of fitness for any use, nor any other warranty, express or implied, is made regarding the accuracy of the data contained herein, the results to be obtained from the use of materials mentioned or the hazards connected with such use. Nothing contained herein shall be construed as a recommendation for use in violation of any patent and no responsibility is assumed by Molycorp, Inc., with respect to any claim of infringement of a patent in such use.

INTRODUCTION

Cerium is the most abundant member of the series of elements known as *lanthanides* or *rare earths,* the elements in the Periodic Table in which the inner 4f electron shell is being filled.

Current (1990) IUPAC nomenclature rules[1] approve the term *lanthanide* as a collective name for the 15 elements from 57 (La) through 58 (Ce) to 71 (Lu), the 4f elements. This brochure uses that term and the symbol *Ln* to mean any lanthanide. In addition the label *light* will be used for the elements 57 to ≈63 and the label *heavy* for ≈64 to 71. (The division is somewhat arbitrary and varies with context.) On occasion the term *rare earths is* also used; IUPAC approves *rare earth metals* as a collective name for the elements 21 (Sc), 39 (Y), plus 57 (La) to 71 (Lu). *(Earth* is an alchemy term for what are now known to be oxides and, as is pointed out later, these elements are not truly *rare.)*

Cerium is characterized chemically by having two stable valence states, Ce^{4+}, *ceric,* and Ce^{3+}, *cerous,* and this property underlies several technological uses. The ceric ion is a powerful oxidizing agent but when associated with the strongly coordinating ligand, oxygen, is completely stabilized and indeed cerium oxide, $Ce^{4+}O_2$, (also called ceria) is the form of cerium most widely used.

First isolated as an impure oxide in 1803, the element was named after the earliest recognized asteroid *Ceres* that, in turn, was named for the patron saint of Sicily, the roman goddess of food plants. The recognition that Cerium was a unique element, and its relationship to other elements, were factors in the gradual development of the Periodic Table concept. The separation and identification of all the individual 4f elements, cerium included, caused considerable confusion one hundred years or so ago but helped lead eventually to our understanding of atomic structure.

Cerium

Element	
Chemical Symbol	Ce
Atomic Number	58
Atomic Weight	140.12
Electron configuration	$[Xe]4f^2 6s^2$
Electronegativity	1.1
Valencies	3 and 4
Ionic radius for (3+)	114 pm
8-coordination (4+)	97 pm
Magnetic moment	2.4 μB
metal	
Crystal Structure	Fcc
Melting Point	798°C
Boiling Point	3443°C
Electrode Potential $Ce(s) \Rightarrow Ce^{3+} + 3e^{-}$	2.34 V
Density	$6.77\ g/cm^3$
Metallic Radius	182 pm

One hundred years ago, too, in 1891 outside the Opern cafe in Vienna, cerium made its first major contribution to chemical technology. This successful installation of gas lights, using the Welsbach gas mantle based on a thorium- and cerium-oxide impregnated fabric, was soon followed by the rapid widespread adoption of this form of illumination. Cerium still contributes to lighting, now in several ways, but today is also to be found in automobiles, televisions and many more technologies.

This brochure emphasizes applied technology. It covers resources and production followed by summaries of the essentials of chemical behavior upon which cerium's uses are based. (The primary literature, and reviews of that literature[2], should be consulted for more detail.) The variety of applications are then discussed and related to the physical and chemical properties of cerium.

RESOURCES and RECOVERY

ABUNDANCE

The solar abundance of the element[3] along with the abundance in the earth's crust[4] are in the tables. The enhanced stability of nuclei with certain proton, Z, and neutron, N, counts, where both Z and N are "magic numbers", explains the dominance of the isotope ^{140}Ce where Z = 58 (atomic number) and N = 82. (Of the naturally occurring isotopes ^{142}Ce is radio-active but with a half life greater than the age of the earth.) Cerium is the most abundant element of the lanthanide series, a consequence of the inherent greater abundance of the light- as opposed to the heavy- lanthanides combined with the "odd-even rule" (even atomic-numbered elements being generally more common than their odd-numbered neighbors).

Cerium

Abundance in the solar system

(relative to 106 atoms of Si)

Isotope	*abundance*	*per-cent*
136	0.0022	0.19
138	0.0029	0.25
140	1.026	88.5
142	0.129	11.1

Geochemical processes can but just modify the inherent patterns of solar system abundance. The light lanthanides, when compared to their heavy analogues, have an enhanced distribution in the crust. This enrichment is most pronounced for lanthanum and tails off relatively smoothly towards lutetium, the last lanthanide. In consequence the greater abundance of cerium compared with other lanthanides is even more enhanced in the earth's crust than in the solar system.

Cerium ranks around 25th in the listing by abundance in the earth's crust of all the naturally occurring elements. (Despite the label "rare" applied to the 4f element series Ce is not especially rare when compared, for example, to the "well-known" members, Ni and Cu, of the first transition series.)

If exploitable resources are to exist then fractionation processes will have had to improve on the inherent abundance. For the lanthanides though, two fractionation processes, differentiation through magmatic recystallization and hydrothermal activity, tend to oppose each other. In consequence there are but few major lanthanide deposits recognized. Certain rocks of igneous origin, however, formed by melting and recrystallization, can include minerals enriched in the lanthanides and yttrium.

Crustal Abundance

Z		ppm
58	**Ce**	**60**
57	La	30
59	Nd	28
28	Ni	75
29	Cu	55

Furthermore, apart from the gross differentiation between light and heavy lanthanides, none of the fractionation processes has produced other than a partial separation *between* individual members of the lanthanide series. Consequently there are *no* minerals that are sources for cerium *alone;* in particular all the lighter lanthanides occur together in any potential deposit and, for pure cerium products, a clean separation from adjacent lanthanides will be necessary.

MINERAL RESOURCES

Although cerium, the most abundant lanthanide, has been found in many minerals[5] it is usually present as a trace element rather than as an essential component. Furthermore, of those minerals in which it is an essential structure defining component, only a few occur in economically significant deposits. The net result is that there are just two minerals that supply by far the bulk of the world's cerium :

Bastnasite and **Monazite.**

These two minerals both contain, as far as the lanthanide fraction is concerned, predominantly light-lanthanides and furthermore both have very similar cerium contents.

Source Minerals

Relative Lanthanide Proportions

(w.r.t. total Ln = 100 %)

	Bastnasite	***Monazite***
	LnFCO3	(Ln,Th)PO4
Ce	≈49	≈47
La	≈33	≈22
Nd	≈12	≈18
others	≈6	≈13

Bastnasite

Bastnasite, a light-Ln fluoride carbonate, $LnFCO_3$, occurs in an unusual type of magma-derived deposit in which the concentration of the Ln-elements has been especially enhanced. Carbonatite magmas are produced when mantle rocks melt deep in the earth's crust in the presence of large amounts of carbonate ion. This type of magma can occasionally rise to the surface to produce a variety of alkaline igneous rocks. If fluoride ion is introduced during the ascent the final stage of the emplacement can be specific lanthanide-containing fluoro-carbonate minerals such as Bastnasite.

Bastnasite has been identified in various locations on several continents. The largest recognized deposit occurs, mixed with Monazite and iron-ores, in a complex mineralization at Baiyunebo in Inner Mongolia, China. This deposit is open-pit mined and the Bastnasite obtained as a by-product of the iron-ore mining. The only other current commercial Bastnasite source is Molycorp's Mountain Pass, California, U.S.A., deposit where the average Ln oxide content of the ore is ≈9%. This U.S.A. deposit is the only resource that is mined *solely* for its content of cerium and other lanthanides.

Monazite

Monazite, a light-lanthanide thorium phosphate, $(Ln,Th)PO_4$ is found in many countries. It is an accessory mineral in granites and, because of a high specific gravity, on weathering of those primary rocks tends to segregate out in placer deposits. Monazite-bearing placers, in association with other heavy minerals such as ilmenite, zircon and rutile, have been identified in many beach and dune sand deposits throughout the world. Those other minerals are usually the economic driving force for exploiting the deposits and hence monazite is almost always derived as a by-product of the production of titanium- and zirconium-containing minerals.

Several countries supply monazite, or monazite derivatives, onto the world market. Extensive deposits along the coast of Western Australia are worked for ilmenite and are the major source of world monazite. Other regions of Australia, along with India, China and Brazil also supply the mineral.

Phosphate

Phosphate-containing rock, mined widely throughout the world in large quantities for its fertilizer value, in certain regions contains a few per-cent of lanthanides, e.g. the apatite deposits in the Kola peninsula on the Russian/Finnish border. Other Ln containing minerals are also present, e.g. loparite, a Nb-mineral. The Ln-content is recoverable from the various processing residues and, for the CIS (and other ex-Soviet) block countries, this location has supplied a major part of their demand.

World reserves

World reserves of contained Ln oxide are estimated as ≈50,000,000 tonnes with ≈80% of this in China, at Baiyunobo, ≈1O% in the U.S.A., mainly at Mountain Pass, and ≈5% in India.[6] (One half of this total, reflecting the similar proportions of ceria in the lanthanide content of the two dominant source minerals, is *potentially* cerium oxide. Only a small portion though is actually recovered as a separated oxide.)

PRODUCTION

The production of cerium derivatives requires:

- ore beneficiation and production of a mineral concentrate,
- attack on that concentrate to create a suitable mixed-lanthanide precursor for later separation processes,

and then *either*

- direct production of a cerium-rich material,

or

- separation of the mixed-lanthanide precursor into individual pure lanthanide compounds, including compounds of pure cerium,

or both.

The choice depends on the relative market demand for the different products and obviously varies over time as demand changes.

The starting mineral determines how the suitable mixed-lanthanide precursor is formed and the process is different for the two minerals. In contrast the separation technology (liquid-liquid counter-current extraction, or solvent extraction SX) for preparing the individual lanthanides is essentially independent of the starting mineral and different feedstocks can ultimately be processed by the same separation routines and equipment.

Processing of Bastnasite

In the U.S.A. the ore is extracted by open-pit mining, crushed, ground and subjected to froth flotation. The bastnasite fraction is floated off and thereby separated from other minerals including barite, calcite, strontium containing materials and quartz. The resulting *basinasite concentrate is* a commercially available commodity, see analysis.

Basmasite can be converted directly, without separating out individual Ln's, to other derivatives such as sulphate or chloride, i.e. $LnCl_3$ / $RECl_3$, by dissolution in acid. Bastnasite -derived rare-earth chloride, for example, will have a composition very similar, differing only marginally in the proportions of the various lanthanides present, to the analogous rare-earth chloride produced from Monazite.

Bastnasite Concentrate
Typical Analysis

Ln content		*Non-Ln content*	
CeO2	30%	SrO	5%
La3O	20%	CaO	4%
Nd2O3	7%	BaO	1.5%
Pr6O11	2.4%	F	5.5%
other Ln	0.6%	SiO2	1.5%
		PO4	1%
Loss on ignition		Fe2O3	0.5
(Carbonate)	20%	SO4	1%

The step used at Mountain Pass, California, to crack, to "open", the concentrate for further processing is to :

- roast in air, and then
- leach with HCI

This produces :

- an insoluble portion, *cerium concentrate,* and
- a soluble fraction.

Cerium Concentrate
Typical Analysis

Ln content		*Non-Ln content*	
CeO2	**62%**	CaO	6%
Other Ln oxides	10%	other oxides	4%
loss on ignition	8%	F	10%

The insoluble cerium-rich portion, *cerium concentrate,* although predominantly $Ce^{4+}O_2$, is of poorly defined composition; a typical analysis is given.

The soluble fraction from the HCI leach is converted to a solid *lanthanum concentrate.* The *lanthanum concentrate,* essentially a mixed-lanthanide hydroxide chloride, still contains a small percentage of cerium and, because it is consumed in quantity in FCC catalysts for gasoline production (see below), accounts for a portion of the net consumption of cerium.

Lanthanum Concentrate
Typical Analysis

total Ln Oxides		80%
La_2O_3	46%	
CeO_2	12%	
other Lns	22%	
Cl		12%
loss on Ignition		Balance

An alternative process for "opening" Bastnasite is used in China :

- roasting with sulfuric acid, followed by
- an aqueous leach,

to produce a solution with the full natural ratio of the Ln elements. The Ln's are then precipitated either as a mixed sulfate or as hydroxide and eventually taken up in HCI.

The initial cerium -containing product will be, when the valuable heavies (Sm and beyond) have been removed, a light-lanthanide (La, Ce, Pr and Nd) rare earth chloride.

Processing of Monazite

Monazite is a by-product of the mineral-sands industry production of the economically more dominant minerals ilmenite, rutile and zircon. Gravity, electrostatic and magnetic separation are used to produce a monazite concentrate, marketed worldwide, in which the rare earth oxide content is ≈ 60 %. Monazite can be cracked by reaction with sulfuric acid, like bastnasite, to yield a mixture of sulfates but the usual process is with alkali[7]. (Whichever method is chosen the radioactive thorium must be completely removed.)

After beneficiation the monazite concentrate is finely ground and digested with an excess of caustic soda at ≈150 °C for several hours.

$$\mathbf{(Ln,Th)PO_4 \;+\; NaOH \;=>\; Na_3PO_4 \;+\; Ln(OH)_3 \;+\; Th(OH)_4}$$

The phosphate portion produces a soluble sodium phosphate while the lanthanides, along with thorium, form insoluble hydroxides (hydrated oxides) that can be recovered.

Rate Earth Chloride
a.k.a. Lanthanide Chloride
LnCl3.6H2O
Typical Analysis

total as Ln Oxides		≈46 %
CeO2	22 – 25%	
La2O3	11 - 16 %	
Nd2O3	5 - 9 %	
Pr6O11	2 - 3 %	
Chloride		≈31 %

The next step is hydrochloric acid attack, at ≈70 °C and pH 3-4, on the solids portion. The thorium remains insoluble and a crude thorium hydroxide can be filtered off. (Trace contaminants that do carry through into solution, such as uranium and lead as well as some thorium, are removed by coprecipitation with barium sulphate in a deactivation step.) The chloride solution containing the rare earths, the lanthanides, after concentration can be cast into solid form.

The rare-earth-chloride (REC1$_3$), like monazite concentrate, is a material traded commercially not only for further separation processes but also for the production of ferro-alloys such as mischmetal, see below. Addition of sodium carbonate to the REC1$_3$ solution precipitates a RE carbonate that can be converted to other mixed lanthanide derivatives, e.g. fluorides, nitrates and, by calcination, an oxide. (Whether made from Bastnasite or Monazite rare earth chlorides will have essentially the same composition.)

Production of Cerium Derivatives

A moderately pure, 90 - 95 %, cerium hydrate can be made from rare-earths contained in acid solutions by use of appropriate oxidants by taking advantage of the stability of the Ce(IV) state.

The cerium concentrate derived from bastnasite can be also upgraded to ≈96% cerium(III) by dissolution and reprecipitation as carbonate.

Ce(IV) can be extracted more readily into organic solvents than can the trivalent Ln(III) ions and, using liquid-liquid extraction systems, this provides a route to 99% and higher purity cerium compounds. The Ce(III) content of mixed-lanthanide, Ln(III), aqueous systems can be oxidized to Ce(IV) and the resulting solution then contacted with an organic extractant. The Ce(IV) is preferentially extracted into the organic phase from which it can, in a separate step, be recovered by reduction to Ce(III) and back extraction into the aqueous phase. Cerium can then be precipitated as, for example, a hydrate or a carbonate ; in either case calcination will produce the oxide.

Counter-current liquid-liquid extraction technology, commonly termed solvent extraction SX, is the chosen process for the commercial separation of the individual light lanthanides[8]. Each SX step, usually in nitrate solutions, with chelating extractants and organic solvents such as kerosene, will cut the Ln series into two parts. Consequently, as an alternative to the processes outlined above, cerium can be recovered from the second step, after the first step of lanthanum separation, in the general sequential SX processing of the Ln(III) series. Whichever process technology is used to obtain cerium compounds the precise details and operating conditions are usually proprietary knowledge.

Production Quantities and Materials

Worldwide the production of lanthanides yearly is about 70,000 tons[9] measured, as is customary, as contained Ln-oxide. The major sources are given in the table; data from the former U.S.S.R. grouping of countries has only just become available. The rise of Chinese production during the '80's has become a major factor in the global market picture for the lanthanides.

The production total implies, because bastnasite and monazite are the dominant resources, *potentially* about one-half, 35,000 tons, might be considered cerium oxide. It must be emphasized, however, that this amount of cerium oxide is **not** available. Only a small fraction of the ≈70,OOO tons is produced as *separated* relatively-pure individual Ln derivatives, cerium included; the bulk is consumed as concentrates and the like. Cerium is used in several forms other than pure oxide and a detailed breakdown by product is not possible.

Lanthanide Production by Country, ≈1990

(metric tons contained Ln oxide)

Australia	7,500
Brazil	2,500
China	25,000
India	2,000
Malaysia	2,000
Russia	8,500
United States	23,000

Cerium-containing Materials and their Applications		
Nature of Ce content in Material	***Example***	***Commercial Application***
major component of mixed-lanthanide composition	rare earth chloride, mischmetal	FCC catalysts Fe metallurgy
minor component of mixed-lanthanide composition	lanthanum concentrate, La-Ln chloride	FCC catalysts
dominant element in oxide-type composition	cerium concentrate	glass polishing, glass decolorizing
relatively pure compound >≈ 90 %	oxide, nitrate, metal	auto-emission catalysts, etc.
highly pure compound >≈ 99 %	oxide, salts	luminescence, catalysts

The various cerium-containing materials available commercially are summarized above.

CHEMISTRY

ELECTRONIC STRUCTURE AND OXIDATION STATES

The ground state of all the neutral Ln atoms is probably either $[Xe]4f^n5d^16s^2$ or $[Xe]4f^{n+1}6s^2$ where the increase in n from 0 to 14 corresponds to the change from La (Z=57) through to Lu (Z=71). Cerium is the second and most reactive member of the Ln series. It is very electro-positive and has predominantly ionic chemistry due to the low ionization potential for the removal of the three most weakly bound electrons. The energetics are such that for all lanthanides the most stable state is a trivalent one, Ln^{3+}, with $[Xe]4f^n$; i.e. for Ce^{3+}, $[Xe]4f^1$.

The 4f electrons are well-shielded inner orbitals not influenced by the external environment and hence the chemical behavior of all Ln^{3+} ions, including Ce^{3+}, is very similar. At the start of the Ln series though, the 5d orbitals are not much higher in energy than the 4f shell and with cerium a potential 4f - 5d charge transition accounts for the absorption by Ce(III) compounds in the u.v. just outside the visible.

The relative increased stability of empty $4f^0$, half-full $4f^7$ and completely full $4f^{14}$ shells, can, for certain elements, cause oxidation states *other than three* also to be reasonably stable, in particular Ce^{4+} with a $[Xe]4f^0$ configuration.

CERIUM(IV) CHEMISTRY and COMPOUNDS

The tetravalent cerium state, *ceric*, is (apart from Eu^{2+}) the only non-trivalent lanthanide ion stable in aqueous solution. The influence of the higher cation charge and a smaller ionic size make ceric salts much more hydrolyzed in aqueous solution than those of the trivalent lanthanides.

$$[Ce\ L_m\ (H_2O)\ ]^{n+} \quad + \quad H_2O \quad => \quad [Ce\ L_m\ (OH)\ ]^{\{n-1\}+} \quad + \quad H_3O^+$$

In consequence ceric salt solutions are strongly acidic. Basic salts tend to form from solution and there are no stable simple salts of weak acids. Ceric salts tend to be orange or red in color due to charge transfer interactions. The simple uncoordinated ceric ion, e.g. in a glass matrix or the oxide, absorbs in the ultraviolet portion of the spectrum but not in the visible; the details of the spectra though are very dependent on composition.

The fluorite structure, with its large crystal lattice energy, provides an exceptionally strong stabilizing influence for *tetra*valent cations and is adopted by CeO_2 (see below), preferentially stabilizing this oxide form rather than Ce_2O_3 with *tri*valent cerium. Some complex fluorides and oxides are also stabilized by a similar factor. Compounds of Cerium(IV), other than the fluoride, oxide and related materials, are less stable but can be prepared. Those most readily obtained include the sulfate, $Ce(SO_4)_2$, and certain "double" salts. Orange crystals of ceric sulfate can be obtained from solutions prepared by dissolving a reactive cerium precursor, such as the freshly precipitated hydrated oxide, in sulfuric acid in excess to prevent hydrolysis to basic insoluble salts.

The double salts, ceric ammonium nitrate and ceric ammonium sulfate (see below for more suitable names) are stable orange compounds prepared by dissolving freshly prepared (hence reactive) hydrate or oxide, in excess of the appropriate acid, adding the correct amount of ammonium salt, and evaporating down at low temperatures to cause crystallization. The tetravalent cerium is present in the *anion,* not the cation, of these salts. The crystal structure, with cerium(IV) at the center of the anion complexed, for example, by six bidentate nitrate groups, shows that the formal name is di-ammonium hexanitrato*cerate*. Similarly solid sulfate analogues are correctly - sulfatocerates, e.g.

$$(NH_4)_2\ [Ce(NO_3)_6] \quad : \quad (NH_4)_4\ [Ce(SO_4)_4].2H_2O \quad : \quad (NH_4)_2\ [Ce(SO_4)_3)]$$

The complex anions, along with other similar stable anionic species, exist in the aqueous solutions. The complex equilibria between these species and the dependence on pH means that the solution chemistry of Cerium(IV) is intricate.

Chlorocomplexes of Cerium(IV) are not as stable as nitrato or sulfato derivatives due to oxidation of Cl^- by Ce(IV). The simple tetrachloride $CeC1_4$ is unstable but salts of the $[CeCl_6]^{2-}$ ion can be stabilized with large cations such as $NEthyl_4$ and also neutral chlorocomplexes can be obtained with large chelating ligands.

Cerium in the tetravalent state is a strong oxidizing agent and can be reduced by, for example, oxalic acid, halogen acids, ferrous salts and hydrogen peroxide. The exact redox potential (E) for the reaction Ce(IV)/Ce(III) ranges from ≈1.3V (1N HCl) to ≈1.8V (6N $HClO_4$) and depends strongly on the electrolyte and on which small anionic groupings are complexed to the cerium ion.

$$\mathbf{E = 1.45 + 0.059 \log ([Ce^{4+}]/[Ce^{3+}])}$$

Despite the lower electrode potential for the H_2O/O_2 couple (1.23V), aqueous solutions containing Ce(IV) species are stable, probably for kinetic reasons. Water can nevertheless be oxidized to oxygen by Ce(IV) in the presence of catalysts such as Pt or RuO_2[10]. Cerium(IV) ion oxidation is a useful tool in organic chernistry[11] and can be used for quantitative volumetric oxidation reactions, "cerate oxidimetry", in analytical chemistry[12]. In addition, the oxidizing ability of Ce^{4+} offers possibilities in indirect electroorganic synthesis[13]; after reaction the Ce^{4+} is regenerated from the Ce^{3+} in a separate electrochemical step.

Cerium Oxide, CeO_2

The most stable oxide of cerium is cerium dioxide, CeO_2, also called *ceria* or *ceric oxide*. When cerium salts are calcined in air, or oxygen-containing environments, this *tetra*valent Ce(IV) oxide is formed. (The sesquioxide, Ce_2O_3, with *tri*valent Ce, can be prepared in strongly reducing conditions but is unstable in air, water and the like, readily converting to the dioxide.) Cerium (along with the other lanthanides) has one of the highest free energies of formation for an oxide. The oxide is soluble in mineral acids but can prove difficult to dissolve unless a trace of reducing agent such as hydrogen peroxide is added. (The hydrate is mentioned below under cerium(III) hydroxide.)

Ceria has the fluorite, CaF_2, structure, space group Fm3m, with 8-coordinate cations and 4-coordinate anions. It can be visualized as a cubic close-packed array of metal atoms with oxygens filling all the tetrahedral holes; the structure-determining OCe_4 coordination tetrahedra thereby share all edges in three dimensions.

CeO_2, when pure, is a very pale yellow probably due to Ce(IV)-O(-Il) charge transfer transitions. The color of the oxide is sensitive not only to stoichiometry but also to the presence of other lanthanides. A slight trace (≈0.02%) of Pr results in a buff color attributable to Ce(IV)-Pr(III) transitions. (With higher values of Pr (≈2%) the material becomes a potential red pigment.[14]) Grossly non-stoichiometric ceria samples are reported to be blue, related to Ce(IV)-Ce(III) transitions. In addition, as the oxide is usually produced by the calcination of a precursor salt, the observed color depends on the extent of that calcination.

Cerium Oxide, CeO_2

Chem. Abs. No.	1306-38-3
Formula Weight	172.1
Physical Properties	
Melting Point	≈2750,K
Density	$7.28\ gcm^{-3}$
Specific Heat	$\approx 460\ Jkg^{-1}K^{-1}$
Thermal Conductivfty	$\approx 12\ Wm^{-1}K^{-1}$
Thermal Expansion	$\approx 11\ 10^{-6}K^{-1}$
Refractive Index	≈2.1 visibie ≈2.2 infra-red
Young's Modulus	$\approx 165\ 10^{9}Nm^{-2}$
Poisson's Ratio	≈0.3
Hardness	≈5 - 6 mhos

It can exhibit large deviations from stoichiometry, CeO_{2-x} (x can be up to 0.3), at low oxygen partial pressures, $P(O_2)$. In air or oxygen, though, it stays close to stoichiometry and its defect structure is therefore controlled by doping.[15] When doped with divalent oxides (RO) or trivalent oxides (R_2O_3) the introduction of oxygen vacancies provides the charge compensation. For a trivalent dopant one oxide vacancy is produced for every two dopant ions. Solid solutions of ceria with, for example, trivalent ions such as Y or La, can readily be formed. The resulting oxygen vacancies are mobile and form the dominant point defect involved in transport behavior; oxygen diffusion is fast whereas cation diffusion is slow. The resulting *defect-fluorites* have good oxide ion conductivity and act as novel solid electrolytes above ≈600 °C.[16]

Ceria can be sintered (at≈1400 °C) to high densities, > 97 % theoretical, by the addition of trace amounts, < 1.0 %, of oxides such as TiO_2 or Nb_2O_5.[17] These additives work either by the formation of a transient liquid-phase intermediate, e.g. $CeTi_2O_6$ m.pt. 1350 °C, or by suppressing oxygen deficiencies, e.g. high valent Nb.

Cerate-type Perovskites

Some cerium-containing ternary oxides with the perovskite structure, $A^{2+}Ce^{4+}O_3$, display, at high and moderate temperatures, unusual ionic conductivity behavior. In particular acceptor-doped $BaCeO_3$ and $SrCeO_3$, after exposure to water-vapor at high temperatures, become proton conductors. The conduction mechanism is probably due to proton hopping between adjacent oxide ions. The property has potential applications in high-temperature fuel cells, hydrogen pumps and sensors.[18]

CERIUM(III) CHEMISTRY AND COMPOUNDS

Trivalent cerium, *cerous,* closely resembles (apart from its possible oxidation to Ce(IV)) the other trivalent lanthanides in chemical behavior. The early original literature[19], containing much descriptive chemistry, and current publications [2] can provide detailed chemical and physical property information.

Compound	***Ideal Formula***	***Formula Weight***	***% Oxide***	***% Element***
Acetate	$Ce(CH_3COO)_3.1½H_2O$	344.28	50.0	40.7
Carbonate	$Ce_2(CO_3)_3,3H_2O$	514.31	66.9	54.5
Chloride	$CeC1_3.6H_2O$	354.59	48.5	39.5
Fluoride	$CeF_3.H_2O$	215.12	---	65.1
Hydroxide	$[CeO_2.2H_2O]$	208.15	82.7	67.3
Nitrate	$Ce(NO_3)_3.6H_2O$	434,23	39.6	32.3
Oxalate	$Ce_2(C_2O_4)_3.9H_2O$	706.43	48.7	39.7
Sulfate	$Ce_2(SO_4)_3.8H_2O$	712.55	48.3	39.3

The simple cerous salts can be prepared by dissolving the oxide, or preferably a more reactive precursor, in the appropriate acid or, where appropriate, produced by precipitation from solution. Upon crystallization most salts are capable of forming a wide variety of hydrated species with the hydrates of the soluble salts tending to be hygroscopic. Basic salts, e.g. $Ce(OH)CO_3$, may be formed and can be contaminants in the solid salts.

Ce(III) forms a water-insoluble *hydroxide, carbonate, oxalate, phosphate* and *fluotide,* sparingly soluble *sulfate* and *acetate,* and soluble *nitrate* and *chloride* (and bromide). With the sparingly soluble sulfate and acetate an increase in temperature causes a decrease in solubility. In solution the salts are only slightly hydrolyzed. (The carbonate is readily prepared, easily handled, and is a convenient precursor for the preparation of other derivatives.) The stability of the tetravalent oxide means that, after intermediate hydroxy and oxy-species, CeO_2 is the end product of the calcination of most Ce(Ill) salts although, with halides, stable oxyhalides, CeOX, can be formed.

The bonding between the cation and the surrounding ligands is ionic with no directional character. In solution coordination numbers are uncertain and in solids the precise structure determined by the packing of the ligands.

The ionic salts in general are colorless as Ce^{3+} has no absorption bands in the visible. Trivalent cerium, however, is one of the few lanthanide ions in which parity allowed transitions between 4f and 5d configurations can take place. In consequence Ce(III) compounds do absorb strongly in the ultraviolet region just outside the visible.

Hydroxide

When freshly precipitated the hydroxide, $Ce(OH)_3$, is readily oxidized, by air or oxygenated water, through poorly defined violet-tinged mixed-valence intermediates, to the *tetra*-valent buff-color $Ce(OH)_4$. The precipitate can prove difficult to filter, is amorphous and, on drying, converts to the hydrated ceric oxide, $CeO_2.2H_2O$. This is a commercial material, "cerium hydrate", available in various purities, that behaves essentially as a reactive cerium oxide.

Carbonate

The carbonate, $Ce_2(CO_3)_3.nH_2O$, when prepared under ideal conditions, e.g. by decomposition of trichloracetate solution, tends to crystallize as the octahydrate, n = 8. The commercial product, prepared on a large scale by sodium carbonate addition, has a composition best represented by n ≈ 3. Temperature, pH and precipitation conditions as well as the drying process determine the amount of water in the solid; in addition the species $Ce(OH)(CO_3).xH_2O$ and $Ce_2O_2(CO_3)$ may also be present. Thermal decomposition will initially cause loss of crystallization water followed by the formation of hydroxy and oxy species and eventually, at ≈550 °C., CeO_2. The existence of discrete intermediates, however, is not always apparent because of the concommitant oxidation of Ce(III) to Ce(IV).

Nitrate

Cerium nitrate, $Ce(NO_3).6H_2O$, is the most readily commercially-available soluble salt of cerium and, since it decomposes to the oxide on calcination, it is used, for example, if a porous solid is to be impregnated with cerium oxide. The nitrate is very soluble in water, up to ≈65 wt.%, and also in a wide range of polar organic solvents such as ketones, alcohols and ethers.

Chloride

The hydrated chloride, $CeC1_3.nH_2O$, usually with n ≈6, on heating tends to form the oxychloride. The anhydrous chloride can be made from the hydrated salt by suppressing oxyhalide formation during thermal dehydration by the presence of hydrogen chloride or ammonium chloride. The anhydrous salt is soluble in a variety of organic solvents, e.g. alcohols and ethers. $CeC1_3$, m.pt. 817 °C, can be volatilized at high temperatures in vacuum particularly if $AIC1_3$ is also present; presumably transient double metal chlorides are formed.

Fluoride

Precipitation of the fluoride from aqueous solution by HF addition produces $CeF_3.nH_2O$, n ≈½, from which the anhydrous salt can be prepared by controlled dehydration. An alternative route to CeF_3, m.pt. 1432 °C, is the reaction of a suitable precursor, such as carbonate, with ammonium bifluoride, NH_4HF_2. The anhydrous salts, chloride and fluoride, are precursors for cerium metal production.

Carboxylates

Cerium carboxylates, water-insoluble, can be made[20] by double decomposition with precipitation, using water-soluble precursors, or by reaction of an insoluble precursor directly with the organic acid. Typical anions can be 2 ethylhexanoate (octanoate), naphthenate or stearate.

Sulfides, etc.

A variety of cerium sulfides have been characterized[21] including not only the compound Ce_2S_3, expected for a trivalent cation and a divalent anion, but also CeS and Ce_3S_4. Solid solutions between these species are possible. CeS[22], bronze in color with a metallic lustre, adopts the NaCl structure with Ce^{3+}, S^{2-} and one electron in a conduction band. This sulfide has a high electrical conductivity (in the metallic range), a high thermal conductivity, a high melting point (≈2715 K) and good thermal shock resistance.

The oxysulfide, Ce_2O_2S, is a high-melting stable compound that precipitates out when steel is treated with a cerium-based metal to control sulfide inclusions, see below. Its thermodynamic properties are well known and the Ce-O-S phase diagram has been determined[23].

Miscellaneous Compounds

Among the simple ionic salts the acetate, as commercially prepared, has ≈1½H_2O, has a moderate aqueous solubility (≈100 gms/l *decreasing* with temperature) and is an attractive precursor to the oxide. The sulfate can be made in a wide range of hydrated forms and has solubility behavior comparable to that of the acetate. Many double sulfates, with alkali metal and ammonium cations, are known with varying degrees of aqueous solubility. The phosphate, being equivalent to monazite, is very stable.

The oxyfluoride and oxychloride are stable high melting species often formed undesirably during the calcination of halide salts. CeOF, because of the comparable ionic size of F^- and O^{2-} as well as the Ce(III)/Ce(IV) interchange, can form fluoritestructure solid solutions with CeO_2; the materials have novel ionic conductivity.

Derivatives such as borides, carbides, nitrides and hydrides are best prepared by direct reaction between the elements. These metalloid-type compounds often show variable composition, are colored and sometimes semi-conducting.

METAL

In the bulk form the element is a reactive metal, prepared by the calciothermic reduction of the fluoride, CeF_3.

$$2CeF_3 + 3Ca \Rightarrow 2Ce + 3CaF_2$$

A slight excess of calcium is used and the exothermic reaction, carried out in a tantalum crucible, is initiated at ≈900 °C. After physical separation of the upper layer of immiscible fluoride slag, vacuum distillation removes unreacted volatile Ca. Cerium can also be made by the electrolytic reduction of fused chloride

Cerium (metal)

Thermal Conductivity	0.110 w/cm-K
Specific Heat, 25°C	6.44 cal/mol-K
Heat of Fusion	1305 cal/mole
Thermal Expansion	6.3 10-6 K^{-1}
Electrical Conductance	0. 13 µohms^{-1}

On a fresh surface the metal has a steely lustre but rapidly tarnishes in air due to the surface formation of oxide, and carbonate, species. For protection against oxidation the metal is usually stored in a light mineral oil. When made finely divided, e.g. on being cut, it can be strongly pyrophoric and, for this reason, is used, as the ferro alloy *mischmetal,* in lighter flints and ordnance. The metal reacts steadily with water, readily dissolves in mineral acids and is also attacked by alkali; it will react with most non-metals on heating.

Cerium metal has unique solid-state properties; it is the only material known with a solid-solid critical point. Three allotropes, α, β, γ, are stable at or close to ambient conditions, and have complex structural inter-relationships. One particular transformation, $\gamma$to α, with a major volume change, involves a modification of the electronic structure to a phase with a non-integer valence number of electrons.

Mischmetal

Mischmetal contains, in metallic form, the mixed-lanthanides in the same ratio that occurs in the resource minerals, and is produced by the electrolysis of fused mixed lanthanide chloride prepared from either bastnasite or monazite. Although the precise composition of the resulting metal depends on the composition of that chloride, the cerium content will always be close to 50 %.

An alternative commercial form of a metallic mixed lanthanide containing material is *rare-earth silicide.* This is produced in a submerged electric arc furnace by the direct reduction of ore concentrate, e.g. bastnasite, together with iron ore and quartz. The resulting alloy is approximately 1/3 mischmetal, 1/3 silicon, and 1/3 iron. (For many bulk applications in ferrous metallurgy both iron and silicon are there anyway in final products.) In addition there are a variety of ferro-alloys, such as magnesium-ferrosilicons, that contain a few percent of cerium derived from cerium concentrate. (The cost of separation of the mixed-lanthanide precursor into salts of individual lanthanides, cerium chloride for example, prior to electrolysis or reduction, is not justified because there is only a marginal, if any, difference between the effects of the different lanthanide metals on eventual products.)

Cerium
in Commercial Alloys
Typical Analyses %

	Misch-metal	*Rare Earth Silicide*
Fe	≈3	≈33
Ce	45-51	≈16
La	22-33	≈11
Nd	11-20	≈5
Misc	≈7	≈2
Si	--	≈33

The consumption of metallic cerium is overwhelmingly in the mixed-lanthanide form, be it as *mischmetal* itself, as the analogous *silicide* or as a *ferro-alloy.* These materials are used as additives in ferrous metallurgy, to steel and to cast irons, see later.

ANALYSIS

Analytical questions when cerium is present tend to be of three kinds

- what is the total lanthanide content, including Ce, of a sample
- what is the cerium content, i.e what fraction of the Ln's is cerium, and
- is there any trace, i.e. say <1 %, of cerium in the sample ?

A preliminary separation of the lanthanides as a complete group is often possible by oxalate precipitation at low pH. (Depending on the analytical procedure and on the sample it may be necessary to add a reducing agent, e.g. ascorbic acid, to ensure that all the Ce is in the 3+ oxidation state.) In most cases direct calcination, at 1000 °C, of oxalate to the oxide will then provide a gravimetric determination of total Ln oxide content. If necessary controlled hydroxide precipitation can reject alkaline earths. The Ln oxide can be redissolved in strong acid and titrated against EDTA or other complexing agents. Spectro- photometric reagents, such as arsenazo derivatives, can also be used to estimate total Ln content including cerium. Such complexation methods can have high sensitivity but show poor selectivity.

Selective simple qualitative and quantitative tests for one specific member present with other members of the Ln series, due to their mutual chemical similarity, are usually not possible. The one exception to this generalization, though, is Cerium because of the unique stability, among Ln's, of the Ce^{4+} state. The ceric content can be determined, for example, by oxidation of Ce^{3+} to the tetravalent state by persulfate/silver or bismuthate, excess of this oxidant destroyed by boiling and the resulting Ce^{4+} titrated with standard ferrous ammonium sulfate.

Several instrumental methods are available for quantitative estimation of moderate down to trace amounts of cerium in other materials. (The method chosen will depend on the nature of host matrix.) X-ray fluorescence is widely available, is versatile and suitable for determinations of Ce, and other Ln's, at per-cent levels and lower, in minerals and purer materials. (Cerium , unlike some other lanthanides, has no sharp characteristic absorption bands suitable for spectrophotometry.)

The ultra-violet-excited visible luminescence of cerium is characteristic and can be used to estimate Ce content, at pprn levels, in a non-luminescing host. X-ray excited optical luminescence [24], a technique specially appropriate for Ln elements including cerium, also relies on emissions in the visible, and also measures ppm values.

Atomic emission spectrometry, particularly ICP-AES (ICP = inductively coupled plasma), is applicable to most Ln's, including Ce.[25] The precise lines used for quantitative measurement must be chosen with care to avoid interference from other lanthanides but once set-up the technique is suitable for routine analyses. ICP-mass spectrometry is another possible technique. Neutron activation analysis offers very high sensitivity but does require access to a nuclear reactor.

ENVIRONMENTAL BEHAVIOR

Lanthanides are present in trace amounts in many minerals, probably due to partial replacement of the ubiquitous Ca^{2+} by Ln^{3+}. The lanthanides can enter the environment by leaching of such minerals into the ground water as well as by the release through crustal weathering into the atmosphere. In addition industrial operations, particularly refineries and automobiles, can also be sources.[26]

In the soil the Ln's, due to the low solubility of salts such as carbonates and phosphates, are immobile under a wide variety of pH conditions. Concentrations in ground water are much lower than those of the soil through which the water percolates. In most natural waters, because the Ln's sorb strongly to silicates and humic material, the bulk of the Ln content including cerium is associated with such colloidal particulates [27]. In the marine environment a depletion of cerium relative to the other Ln's is found that is attributed to the oxidation of Ce^{3+} to highly insoluble $Ce^{4+}(OH)_{4}$-type species.

BIOCHEMISTRY

Cerium and the other lanthanides have no known metabolic role and only minute amounts occur naturally in living systems[28]. The elements have a very limited ability to travel up through the food chain. There are reports, however, that they can selectively interact, possibly by binding to external surfaces, with certain organisms and plants. Indeed a major growing (in *both* senses, "agriculture" and "increasing") application-currently in China only-for mixed-lanthanide salts containing cerium is as a micro-nutrient added, along with conventional fertilizer, to commercial crops[29]. When applied, at ≈600 gms Ln/ha, at the appropriate stage of growth the crop yield is apparently significantly increased. Underlying this property could be the similar ionic radii of Ca^{2+} and Ln^{3+} together with similar strong ionic bonding. This results in the lanthanides competitively binding to the same sites as calcium, an element involved in intracellular transport.

TOXICOLOGY

In general the lanthanides, including cerium, have a low toxicity rating[30] and this is especially so when they are present in material with a low aqueous solubility. When orally administered, poor absorption from the gastro-intestinal tract tends to render the lanthanides, and cerium, benign. (Solubility is a critical aspect of the oral bioavailability of a material and the nature of the anion is often the important determinant of a material's toxicity.) Oral toxicity (LD_{50}) of the lanthanide oxides in rats and mice has been compared to that of table salt[31], being as difficult to determine. Cerium oxide, because of its potential use as a diesel-fuel additive (see later), has been specifically tested for acute effects and found to have a very low toxicity.[32]

Some of the literature on the toxicological behavior of lanthanides has arisen because of the concern about exposure to radioactive Ln species produced in nuclear reactions. The results are not directly applicable to materials containing the naturally occurring *non*-radioactive lanthanides. In addition, the use of monazite, which contains radio-active thorium, as the major-and indeed at one time the only-Ln resource led to confusion regarding the relation between radio-activity and the lanthanides. In the past inadequate separation had produced Th-contaminated Ln-products. Current processing technology for mineral recovery and for the subsequent lanthanide separation results in products that meet all regulatory requirements.

APPLICATIONS

The technological applications of cerium depend primarily on

- the high thermodynamic affinity of the element for oxygen and sulfur,
- a potential redox chemistry involving Cerium(III) and Cerium(IV), and
- absorption / excitation energy bands associated with its electronic structure.

The areas of application can be grouped under the following headings

- *Metallurgy,*
- *glass and ceramics,*
- *catalysis and chemicals,*
- *plus phosphor / luminescence.*

As a generalization the purity of the cerium-containing products required, and hence also the cost, increases down this list of market areas. Some metallurgical and glass-industry uses directly accept, for example, precursor-mineral concentrates or a cerium concentrate derived as the first step in processing that mineral. In contrast luminescent uses need materials with a 99.9 % purity or higher. (As a note of caution, "purity" can mean not only percentage of cerium content but also absence of unwanted components; certain mixed-lanthanide materials are "pure" but have a low cerium content.)

Cerium is the dominant lanthanide accounting for approximately half of the lanthanide content of the two major mineral resources. In several commercial uses, e.g gasoline production, the lanthanides are often used in the natural-ratio without separation; they are used in mixed-lanthanide mixtures containing predominantly cerium. Consequently presentation of the technological uses of cerium should include these applications even if cerium is not explicitly mentioned in the source literature.

Conversely, particularly in ferrous metallurgy, "cerium" is often assumed to be synonymous with "rare-earth" or "lanthanide" ; the terms are used somewhat interchangeably. The role of cerium alone is discussed when not only cerium but also lanthanum, and other lanthanides, are present and just as reactive. As a consequence identification and quantification of the total overall consumption of cerium is open to confusion and misjudgement. The changing balance over time in market demand between cerium and lanthanum, the two most abundant lanthanides, is mentioned in the section below on cracking catalysts.

METALLURGICAL APPLICATIONS

Steel

The high affinity of cerium for oxygen and sulfur underlies the use of mischmetal (and other cerium-containing ferro-alloys) to improve the physical properties of highstrength low-alloy (HSLA) steels.[33] Cerium is, however, not added solely as a deoxidizer or desulfurizer but primarily to provide sulfide shape control.

Steel quality is improved when the oxygen and sulfur content is minimal; nonmetallic inclusions of sulfides or oxides, particularly of the sulfide of manganese-a common alloying additive-can be soft and plastic enough to deform at high working temperatures. These inclusions, during hot rolling of the steel, produce plate-like "stringers" aligned parallel to the rolling direction creating layers of weakness and hence undesirable mechanical properties. When cerium is added to the molten steel the element (and the other light lanthanides) will combine with oxygen and sulfur, even reducing other oxides and sulfides present, to form high-melting, hard, Ln oxysulphides and oxides. This new type of inclusion will not deform during later rolling of the steel and will not create planes of weakness. In addition these same inclusions during solidification can provide nuclei that promote a fine-grained final product.

Modern steel-making technology, with an emphasis during production on low levels of oxygen and sulfur, makes "cleaner" steels than previously. This, together with replacement by calcium and the general down-turn in steel production in the western economies, has resulted in significantly reduced demand for mischmetal for this application. During the '70's this application accounted for the largest consumption of lanthanide materials in the U.S.A. but this is no longer so. In contrast in China, with their abundant Ln reserves and less-advanced steel-making technology, mischmetal consumption in steel treatment consumes ≈75% of their Ln production.

Cast Iron

Cast irons contain carbon as the main alloying element and are heterogeneous in their microstructure. They form an extensive family of materials, ranging from gray iron, through compacted graphite and ductile iron, to white iron, with selected properties tunable to particular needs. The key to obtaining the distinctive differences in properties between the individual cast irons is control of the carbon content and especially control of the morphology that graphitic-carbon precipitates assume in the final product. Crystal morphology depends on "tramp elements" bound to the growing crystallite surfaces.

The lanthanides, and in particular cerium, are used[34] to provide this graphite morphology control, for example to produce spherulitic or vermicular crystallites ; the elements are added as "mischmetal or "rare earth silicides" (both containing all the light Ln elements in their naturally occurring ratio), or in various ferro-alloys with cerium as the major lanthanide. Commercial alloys can contain many other components in addition to the Ln's.

The function of cerium (and all the lanthanides) is probably :

- to remove free oxygen and sulfur from the melt through formation of stable lanthanide oxysulfides, akin to the role in steel technology,
- to initiate the special carbon crystal growth by nucleation on those oxysulfide compounds and
- to tie up undesirable trace elements such as Pb and Sb perhaps through intermetallics.

Lighter Flints and Getters

Traditionally the item most widely associated with cerium has probably been the pyrophoric iron-mischmetal(≈60%) alloy for lighter flints, still in limited use although no longer as important as years ago. (Von Welsbach's second significant step in the development of a rare earth industry was the discovery of this alloy initially produced in the 1900's.) Similar low-vapor-pressure reactive alloys based on cerium can also be the basis of getters, such as Th_2Al-MM (MM = mischmetal), for electronic equipment and vacuum tubes.

Super-Alloys

The label "super-alloy" refers to a family of nickel-based or cobalt-based alloys that are exceptionally heat resistant and are used, for example, in gas turbine engines in aircraft. One problem in use arises from the repetitive cycling from ambient up to high temperature operation that causes the essential protective oxide skin on the metal surface to tend to spall off. Several commercial alloys use micro-additions (≈0.05 wt%) of (pure) cerium to the alloy to significantly improve this oxidation resistance, provide creep resistance and confer a longer operating life.[35]

The principle behind this property improvement probably involves the removal of trace unwanted sulfur impurities from the metal crystallite boundaries plus a modification to the diffusion mechanism for oxide skin growth. The oxide skin formed at high temperatures shows less tendency to spall off if cerium is present in the alloy.

Aluminum Alloys

Various aluminum alloy systems are under development for use at higher temperatures than is normally possible with aluminum. These alloys are made by rapid-solidification powder-metallurgy processes that produce novel compositions with additive elements concentrations, such as cerium, beyond those possible with conventional ingot metallurgy. One of the most promising of these new light weight alloys is an Al-8.31Fe-4.0Ce (wt %) material, with excellent properties in the range 230 °C to 340 °C.[36] This alloy shows an attractive combination of creep resistance, elevated-temperature tensile-strength and corrosion resistance.

The technique of rapid-solidification enables relatively large amounts of insoluble metallic elements to be finely dispersed within atomized powders. Upon freezing very small intermetallic particles are formed. After the powders have been consolidated and fabricated into a wrought product, a high volume fraction of finely dispersed intermetallic particles exists within the aluminum matrix producing a dispersion-strengthened alloy. The intermetallic phases, or possibly oxidic species, responsible for the dispersion strengthening are probably binary Al-Fe and ternary Al-Fe-Ce compounds. In addition it is probable that the lanthanide, cerium, has acted as a scavenger for oxygen and that some dispersoids could be cerium oxide.

Electrowinning of Aluminum

Currently the production of aluminum requires carbon anodes that are consumed during the electrolysis of the molten cryolite. Inert anodes, could offer significant savings in operating costs (as well as remove a major source of man-made CO_2). Such dimensionally stable, non-consumable, electrodes will need to be electrically conducting and also completely resistant to oxidative corrosion when polarized anodically. A new revolutionary approach relies on a self-forming anode technology whereby cerium oxide coatings are deposited, from the molten electrolyte, onto conducting ceramic substrates.[37]

The underlying principle is that the addition of some form of cerium to the bath allows the formation of a protective *and* electrocatalytically active coating of CeO_2 on the conducting anode. If a steady concentration of the appropriate additive in the molten electrolyte is maintained then the equilibrium between dissolved and deposited material ensures a stable coating layer. Even if the cerium is added as $Ce(IV)O_2$, the dissolved Ce species will be Ce(III) :

$$\mathbf{CeO_2 + AlF_3 => CeF_3 + \tfrac{1}{2}A1_2O_3 + \tfrac{1}{4}O_2}$$

The deposition of the oxide at the anode follows :

$$\mathbf{6CeF_3 + 4Al_2O_3 => 6CeO_2 + 6AlF_3 + 2Al^{3+} + 6e^-}$$

The self-forming coating, cerium oxide or more probably a cerium oxyfluoride / cerium oxide solid solution, has been found to reduce significantly the rate of wear of the anode, a doped SnO_2 or ferrite in many tests, and hence improve the purity of the Al metal recovered. Any large scale application of this technology still requires considerable development but it is possible that environmental pressures to reduce CO_2 emissions may speed up its introduction.

Corrosion Protection of Aluminum

The use of chromate ions in coatings for the protection of aluminum and its alloys is under question because of possible environmental problems. An alternative method under development to provide a protective surface relies on immersion in solutions of cerium salts. One suggested approach is immersion of the Al article successively in Ce nitrate and then Ce chloride solutions followed by anodic polarization in a molybdate solution[38]. This process produces surfaces with exceptional resistance to uniform and localized corrosion. The mechanism whereby cerium promotes this action is uncertain but may involve the entry of Ce ions into the oxide surface film akin to the behavior in Ce-doped superalloys.

Chromium Plating

A thin surface layer of chromium is deposited onto many consumer articles and industrial items to provide decoration as well as wear- and corrosion-resistance. The chromium coating is produced by an electroplating process from an aqueous solution containing additives in addition to the essential ingredient, some salt or derivative of chromium itself. Chromium however cannot easily be plated directly from Cr(III), apparently due to the high stability of the aquo-ion $[Cr(H_2O)_6]^{3+}$ but needs to be present as Cr(VI). The Cr(VI) can be reduced to Cr(O), i.e. chromium metal, through the intermediary of a protected Cr(III) species avoiding the formation of the stable hexa-hydrated ion.

The plating solutions must contain an anion such as fluoride to stabilize the active Cr(III) intermediate and prevent the aquo-ion from forming. In practice it has proved difficult to maintain a stable concentration of this ion, F^-. The addition of cerous ions, Ce^{3+}, - added as cerium fluoride directly to the plating bath -along with the fluoride has been found to provide a self-regulating electrolyte. [39] The solubility of cerous fluoride is virtually independent of the temperature of the plating solution within the range of practical concern. By ensuring that excess - hence undissolved - CeF_3 will always be present, the fluoride ion concentration can be closely controlled and quality plating achieved.

Welding Electrodes

The electrodes used in inert-gas tungsten-arc welding and plasma cutting can contain a finely dispersed oxide distributed throughout the tungsten matrix. These oxide particles give to the electrodes an arc-strike reliability at lower voltages than would pure tungsten. Cerium oxide, at 2 % loading, provides an alternative to thorium oxide, a common additive that is now being phased out for environmental reasons.[40]

Other electrode compositions, for less demanding needs, make use of cerium fluoride as a core additive to improve the properties of the eventual weld. The fluoride provides stability to the arc and also modifies the behavior of the molten metal flowing into the weld.

GLASS AND CERAMIC APPLICATIONS

Glass Polishing

The most efficient polishing agent, by far, for most glass compositions (particularly those produced commercially in large volume) is cerium oxide.[41] This application consumes, either as a moderately pure oxide or as a cerium-oxide-dominated concentrate, a significant portion of the cerium products produced annually. Commercial glass polishes are based on cerium oxide powders with defined particle sizes and controlled dispersibility in aqueous systems.

Polishing is the act of producing a sufficient degree of surface smoothness so that light, transmitted or reflected at that surface, is not disturbed by surface irregularities. The polishing mechanism is still poorly understood at the chemical/molecular level. Polishing results in glass removal and does show a dependence on chemical properties of the glass. The nature of the liquid present during polishing is crucial and only if active hydroxyl groups are present, in alcohols for example but especially in water, does the polishing phenomenon happen.

When a glass - typically an alkali silicate - is in contact with water, a complicated series of steps take place, ion exchange, dissolution of glass constituents and possible structural changes. A surface region of the glass is modified and it is this softer hydrated layer that is removed or reformed during glass polishing. Classic abrasives produce an improvement in surface finish but leave a fine but definite roughness, the scale of which relates to the grain size of abrasive used. Several not-so-hard oxides are reasonable polishing agents and can remove and/or reform the soft hydrated layer. In general, optimum polishing rate coincides approximately with Moh's hardness for the polish of around 6.5, very close to the hardness of most glasses.

The best polishing agent - as regards rate of glass removal and ultimate surface finish - is cerium oxide slurried in water. This oxide contains the potential polyvalent cerium atom and redox reactions, due to Ce(IV)/Ce(III), may well be providing chemical assistance to the breaking up of the silicate lattice. In addition mobility within the hydrated layer around the ceric ion also plays a role. Certain substances can act as accelerators for the polishing process. The best appears to be $Ce(OH)_4$, i.e. $CeO_2.2H_2O$, precipitated fresh, *in situ*, in the polishing slurry from a soluble Ce(IV) salt, that probably is involved in an equilibrium reaction.

$$\mathbf{SiO_2 + Ce(OH)_4 \longleftrightarrow CeO_2 + Si(OH)_4}$$

In addition, transient formation of [..Ce-O-Si..] complexed groupings has been suggested. Analytical techniques have identified Ce atoms incorporated below the final polished surface, perhaps from such intermediates. The breaking, and reforming, of Si-O bonds is probably aided by the transfer of OH groupings to incipient fracture sites by a transport mechanism using the relatively large and mobile coordination sphere around the oxophilic cerium atom.

The cerium concentrate (predominantly cerium oxide), derived from bastnasite, is an excellent polish base. In addition the oxide derived directly from the natural-ratio "rare-earth" chloride, as long as the cerium oxide content is near, or above, 50 %, provides an adequate glass polish; the polishing activity is better than the CeO_2/LnO ratio would suggest. Materials, prepared prior to any Ln purification steps, are the source for the lowest cost polishes available that are used to treat TV face plates, mirrors and the like. For precision optical polishing the higher purity materials, based on separated cerium oxides, are preferred.

Glass Decolorization

A major use for cerium compounds is the decolorization of glass. The dominant glass composition, measured by tonnage produced, is the soda-lime type made from cheap raw materials. The purity of these starting ingredients is crucial in determining finished color, or absence of color, in the finished product. There is unfortunately one common impurity, iron, particularly in silica sand, that can cause problems. Iron oxide is a moderately strong colorant in glass and as little as 0.01 % can be visually detected. The adverse contribution of iron to color is associated with the spectral absorption of the ferric and ferrous ions although the two iron ions do not contribute equally to discoloration, the ferrous component providing a blue-greenish tinge with nearly ten times as strong a discoloring power as the brown-yellow of the ferric ion. Glass can be decolorized, even if the total iron content cannot be changed, by keeping iron in the Fe^{3+} state by addition of Ce^{4+} to the glass bath.

Cerium (IV) is strong enough to oxidize iron (II) to iron (III) and cerium ions, either as (III) or (IV), are stable under the severe conditions of a molten silicate-glass bath. Furthermore, cerium itself has no absorption in the visible region. Economical additions of cerium, as the cheapest form of cerium - cerium concentrate, convert iron to the low-absorption ferric form and raw materials containing trace quantities of iron can thus be used more efficiently. [42]

Ultra-violet Absorption

Most damage caused by light to exposed materials is due to u.v. radiation in the 300 - 400 nm range. The mechanism of photodegradation is complex and depends on material composition, impurities present etc.. One approach to inhibit the degradation process is to try and screen out the damaging radiation by incorporating some component that will absorb those wavelengths. Cerium provides strong absorption below 400 nm caused by charge transfer bands. Cerium(IV) in particular makes glass opaque to near u.v. radiation but shows no absorption in the visible and cerium (III) also shows u.v. absorbing behavior but somewhat less marked than for cerium(IV).[43] The ability of cerium-doped glass to block damaging u.v. radiation has applications in several areas, e.g. medical glassware and display case glass windows.

The photostability of pigments can be enhanced by surface additives that increase the provision of recombination centers for the photoproduced charge carriers that would otherwise cause chemical damage. The surface additive must be a one-electron redox couple and be present in both valence states. Cerium, through the Ce(III) / Ce(IV) interconversion, can provide this protective process as well as that attributable to direct u.v. absorption.

Cerium is used, for example, to provide pigments with light fastness and to prevent clear polymers from darkening in sunlight. The rate at which pigments, such as yellow lead chromates, darken on exposure to light can be reduced by producing a precipitated cerium salt coating on the pigment particles.[44] Titanium dioxide, the dominant white pigment, can be used in two different crystalline forms, anatase and rutile. Both these can be given added u.v. stability by arranging for cerium oxide coatings on the TiO_2 particles.[45] This is particularly useful when otherwise the photosensitivity of the titania could initiate degradation of the carrying substrate.

Radiation -resistant Glass

Television glass faceplates are subjected to electron bombardment by high energy electrons, particularly with the high tube voltages needed for color displays. This bombardment, over time, tends to cause discoloration, or browning, of the glass due to the creation of color centers. This unwanted effect is suppressed by the addition of up to 1 % or so of cerium oxide to that glass. A similar suppression of gamma-ray induced discoloration is also possible and cerium-containing glasses are used in the construction of viewing windows in "hot-cells" in the nuclear industry. The suppression mechanism in both instances is believed to depend on the presence of both Ce^{3+} and Ce^{4+} ions within the glass lattice and the potential redox involvement of those ions in "mopping-up" both positive hole centers and free electrons.[46]

Photo-sensitive Glass

This type of glass contains cerium and, on exposure to strong light, will develop a latent image that can, in a later step, be converted into a permanent structural or color change. The cerium ions can absorb ultra-violet radiation and release electrons into the glass matrix. Heat treatment causes these electrons to migrate to silver ions, also present, that initially form silver specks that in turn nucleate the crystal growth of other compounds within the glass.[47] Highly detailed patterns can be produced that are not only decorative but also can help create masks, spacers and the like for electronic uses.

Yellow-colorizer for Glass

When used in glass compositions (at a low weight percentages) along with comparable amounts of titanium oxide, cerium oxide produces a deep yellow coloration.[48] This is due to a strong broad absorption stretching into the blue-violet region of the visible whereby the glass shows the complementary color, yellow. This modified absorption, relative to Ce alone, is probably caused by charge transfer bands within a loose equimolar Ce(III)-Ti(IV) complex.

Opacifier in Enamels

Cerium oxide has a high refractive index, ≈2.2, (cf. ZrO_2 ≈2.2 and TiO_2 ≈2.6) and is a potential opacifying agent in enamel compositions [49] used as protective coatings on metals. In addition to a high thermal stability it exists in only one crystallographic form, unlike TiO_2, throughout the range of temperatures met during enamelling. Opacity in porcelain enamels refers to the desired "white" cover-coat surface and is created when the opacifier, the oxide, precipitates out as micron-sized crystals during the firing-on of the enamel.

Dental Ceramics

Glass-ceramic compositions for use in dental restorations need to mimic closely the appearance of natural teeth. In addition to physical properties translucency and fluorescence are crucial characteristics. Cerium oxide is added in small amounts, 0.1 wt %, to fluorosilicate materials to provide that required fluorescence. [50]

Zirconia Ceramics

Zirconia, ZrO_2, is an important engineering ceramic particularly for high temperature uses. To produce components with high strength and toughness a so called "phase stabilizer" has to be added in order to maintain, at ambient temperatures, a portion of the ZrO_2 as dispersed particulates of the tetragonal phase within the matrix cubic phase. This metastable tetragonal phase has the property, under stress, of transforming to the stable monoclinic phase, with an increase in volume, and hence absorbing energy by blocking the passage of cracks. This transformation toughening can come from a few per-cent addition of a phase-stabilizing oxide such as yttria, magnesia or ceria.[51] The addition of ≈12 mol% of CeO_2, for example, to zirconia produces a material with exceptional toughness and good strength.[52] Cerium oxide-doped zirconia is also used in thermal barrier spray coatings on metal surfaces[53], such as aircraft engine parts, in order to reduce the high temperatures to which the metal substrate would otherwise be exposed.

Optical Coatings

Thin surface coatings are applied to optical components to improve performance. Wide-band anti-reflection coatings for the visible and i.r. regions are made from alternating layers of materials with differing refractive indices. One requirement, for example for the initial layer on the pristine glass surface, is for an index of ≈1.5 for the best efficiency. Cerium fluoride, a stable material resistant to humidity damage has a suitable index (1.63 -visible, 1.59 - infra-red) and transparent over the range 0.5 μ to 5μ, is a preferred compound for building up the multi-layers deposited on lenses, sensors and the like. (It has properties comparable to those of thorium fluoride without the complication of thorium's radioactivity.) Hot pressing of the fluoride produces CeF_3 pellets suitable for electron beam deposition.

PHOSPHOR / LUMINESCENCE APPLICATIONS

Fluorescent Lighting

Fluorescent lighting relies on phosphors to convert the efficient low-pressure mercury-arc emission at 254nm in the ultra-violet into energy emitted within the visible spectrum, 400nm to 700nm. Until the mid-1970's the phosphors of choice were halophosphates, and others, that produced an essentially continuous broad "white-light" spectrum. It was shown then however that, for the visual perception of white, three line-emitting phosphors would suffice. Such a blend of three phosphors, with narrow line-emisssions centred at ≈450, ≈550 and ≈6lOnm's, is not only more efficient in converting input electrical energy to output luminance but can also provide better color rendition. Cerium is an essential component in several of the new generation of phosphors in these tricolor lamps that have made possible more efficient and more compact fluorescent lighting.[54]

The role of cerium in these lighting phosphors is *not* as the emitting atom but rather as the so-called sensitizer. The initial step in the lighting process is the efficient absorption of the 254nm emission; Ce^{3+}, with broad absorption bands in the u.v., is very suitable. This absorbed energy is then transferred to the sub-lattice within the crystalline phosphor and eventually the activator ion is fed and emission results. Cerium, as a sensitizer ion, is compatible in crystal lattices with other lanthanide ions, such as Eu and Tb, the usual activator atoms.

The precise choice of crystal structure for the phosphor depends on a complex interplay of symmetry, inter-atomic spacing, stability etc.. The initial green emitting phosphor was the aluminate $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$. A more recent choice for this material is a $(La_{0.4}Ce_{0.45}Tb_{0.15})PO_4$ compound and in addition a borate, $(Ce,Gd,Tb)MgB_5O_{10}$ is also now used.

Another Ce-containing fluorescent lighting phosphor, $Y_3Al_5O_{12}$:Ce, is used in some blends to convert energy from the otherwise unwanted 435nm mercury line from the blue into the yellow, lowering the light's "color temperature". This same garnet phosphor is also used in *high*-pressure mercury discharge lamps for the same effect.

Cathode Ray Tubes

The cerium atom, upon excitation by energetic cathode-ray electrons, produces a characteristic emission (luminescence) that is in the blue to ultra-violet region, the precise wavelength depending on the symmetry and nature of the ions immediately surrounding the Ce atom in the host lattice.[55] (In some crystalline lattices radiation of a longer wavelength is possible.) The Ce^{3+} emission is highly efficient, is broad-band in character and corresponds to a 5d - 4f transition. Because the transition is allowed, the emitting energy level has a very short lifetime (≈ 50ns) and the luminescence decays very rapidly. This property underlies the use of some cerium containing phosphors in specialized CRT applications. [56]

Beam-indexing display tubes rely on a single electron beam to excite consecutively the color phosphors. The necessary feedback, to ensure that the beam excites the correct color phosphor, of the beam's actual position to the control circuitry is supplied by beam-indexing phosphors that emit detectable ultra-violet when struck by the electron beam. Such a phosphor needs a high efficiency and an extremely fast decay time; the preferred material is cerium-doped (≈2 atomic %) yttrium di-orthosilicate, $Ce{:}Y_2Si_2O_7$, with a peak emission at 380nm.

A flying-spot scanner uses a phosphor to produce a point of light whereby a transparent piece of film or a slide can be imaged and the modulated transmitted- light image be converted to an electronic signal. The phosphor needs to cover the whole visible spectrum and be extremely fast. By combining two cerium-containing phosphors, a garnet, $Ce{:}Y_3Al_5O_{12}$ [P46], and a silicate, $Ce{:}Y_2SiO_5$ [P47], the first emitting in the range 500 - 650nm and the second over the range 370 - 500nm, the correct properties are achieved. In the garnet the very strong crystal field has shifted the emission color.

Particle and Radiation Detection

One method of detection of high-energy nuclear particles, or of high-energy radiation, requires capture in a material that will convert that energy to a visible luminescence. That luminescence can be supplied by Ce^{3+}, whose emission, centered at 400nm or lower, closely matches the response of image intensifiers. Tracking chambers for neutron detectors, for example, can use fiber-optic face plates made from cerium-doped silicate glass that provides high resolution and fast response. As another example, crystalline cerium fluoride, CeF_3, is a high density, 6.16 g1cm3, scintillator[57] that provides a fast response, with 27ns decay constant, and is suitable for positron emission tomography (PET). The material is resistant to radiation damage and is suitable for high energy physics experimentation.

Cando-Luminescence, Gas Mantles

The role of a gas-mantle is the production of radiation in the visible, in excess of the expected black-body thermal radiation, from an impinging gas flame. As alluded to in the introduction, the beneficial effect of the addition of 1 % of cerium nitrate to thorium nitrate solution was discovered by Auer von Welsbach and initiated the widespread use of gas lighting from ≈1890 onwards. The closely woven fabric is impregnated with the nitrate solution that decomposes on heating to leave the oxide mantle adopting the fine structure of the textile and having reasonable mechanical stability. The resulting oxide $Ce_{0.01}Th_{0.99}O_2$, with a broad emission band centered around 500nm, covers most of the visible; the trace of cerium moves the emission from the violet end into the visible so that the emission becomes more pleasing to the eye.[58] In addition it is probable that ceria acts catalytically to ensure complete combustion.

Halide Discharge Lamps

For specialized high-intensity lighting applications such as sport and entertainment events, lamps utilising the radiation emitted by a high pressure mercury discharge are ideal. The energy conversion from electrical input into the mercury discharge is very efficient. The emission spectrum of mercury, however, has only a few lines in the visible. The addition of rare-earth halides, including cerium halides, at milligrams per lamp circumvents this problem. The halides dissociate in the arc column forming free metal atoms which have lower excitation levels than mercury and also emit in many lines in the visible spectrum. (The halides reform in the cooler wall sections.)

CATALYTIC AND CHEMICAL APPLICATIONS

Cracking Catalysts

The scale of the refinery operations needed to satisfy demand for gasoline is surprising. Within the U.S.A. the ≈120 operating fluid catalytic cracking (FCC) units consume ≈500 tons of catalyst (probably one-half of the world market) *per day* in converting crude oil to lower molecular-weight fractions, such as gasoline blending stock. An FCC unit has a lower temperature reactor and a higher temperature regenerator; the catalyst circulates between the two. Although essentially only one type of catalyst, ion-exchanged zeolite, is used there are a variety of catalyst compositions available many of which contain lanthanides including cerium.

FCC catalysts contain crystalline zeolites - the active component - and additives (e.g. see SOx control below) embedded in an inert matrix. The zeolite, an aluminosilicate faujasite Y-type with organic-molecule sized pores, requires cations within those pores for charge-neutrality, to give catalytic reactivity in the reactor and to provide thermal stability in the regenerator. Highly-charged ions, such as La^{3+} or Ce^{3+}, bound within those zeolite cages to negatively charged -$[AlO_4]$units, create a high electric field gradient strong enough to dissociate adsorbed water and provide a high surface acidity. Protonation of the organic molecules then produces the carbonium-ion intermediates that initiate the actual cracking reactions.

Lanthanide cations can be exchanged into the zeolites by immersion in mixed lanthanide salt solutions ; the Ln content can reach up 10 % by weight of the zeolite. Not all FCC catalysts contain Ln's though and, when taken over all available compositions, the Ln content probably averages 2 %. Cerium, because of the potential availability of the Ce^{4+} state that tends to hydrolyze at the ion-exchange pH's used, and because of the different catalyst production technologies practiced, is often partially removed from the precursor solutions. Nevertheless the production of FCC catalysts accounts for significant amounts of the world consumption of this element.

The Ln's are used to give high cracking activity to FCC catalysts[59], especially to produce *low-octane* fuel from *heavy* crude-oil feedstocks. Consumption of lanthanides, and hence of cerium, in FCC catalysts has altered during the decade of the 1980's because of increased demand for *high-octane* fuels, greater feedstock availability of *lighter* crudes, and changes in catalyst technology. FCC-Ln demand reached a peak in ≈1984 (one-third of all Ln consumption was in FCC) and has since fallen back.

This trend has influenced the supply and availability of cerium, particularly in comparison to the availability of lanthanum-rich cerium-poor materials. The inherent natural ratio of the two elements, La and Ce, in the source minerals imposes production constraints in trying to meet the market demand ratio. Put simply, you can't make one without the other. The increase in Ln demand for FCC catalysts up to the mid '80's, together with the need to separate out cerium in order to make La-rich Ce poor compositions increasingly preferred, had led to a glut of Ce-based raw materials. However the subsequent drop in total FCC Ln requirement together with the growth of several markets for chemicals based on cerium alone has now reversed the picture. Currently, 1991, the La-rich Ce-poor portion of the raw material is in excess supply over demand and will probably remain so until a new major use for lanthanum-based materials is found.

Vehicle Emission Control

A major technological application of steadily growing importance for cerium is as one of the catalytically active components used to remove pollutants from vehicle (auto-exhaust) emissions.[60] This market currently consumes a significant portion of the yearly production of cerium derivatives. The active form of cerium is the oxide that can be formed *in situ* by calcination of a soluble salt such as nitrate or by deposition of slurried oxide.

The most widely used exhaust control device consists of a ceramic monolith with a thin-walled rectangular honeycomb structure that offers little resistance to the flow of gases. (Metallic monoliths are also possible.) The accessible surface of this monolith system is increased by applying a separate coating, a wash coat, of a high surface area material such as gamma-alumina with the catalytically active species impregnated into this washcoat. The catalyst needs

- to oxidize unburnt hydrocarbons,
- to convert CO to CO_2,
- and to reduce NO_X

and hence is termed a "three-way" catalyst. The whole system forms a "catalytic converter" that, suitably encased, is placed between the engine and the muffler/silencer unit.

In addition to platinum and other metals from the platinum group, the major active component in the current complex multi-functional systems is cerium oxide. Current catalytic converters contain ≈75 gms per converter of finely divided ceria dispersed within the washcoat. Most of the details of catalyst production are proprietary knowledge and patents only hint at the technology involved. Not only is the chemical nature of the catalytic participants crucial but so too is their spatial distribution with respect to one another. Elucidation of the detailed behavior of cerium is difficult and complicated by the presence of other additives, such as lanthanum oxide, that perform related functions. Ceria plays several roles, namely

- as a stabilizer for the high surface area alumina,
- as a promoter of the water-gas shift reaction,
- as an oxygen storage component, and
- as an enhancer of the NO_X reduction capability of Rhodium.

The tendency of the high-surface -area gamma-alumina support to sinter and lose that crucial area during high-temperature operation is retarded by the intimate addition of several per-cent of cerium oxide to that alumina. (This function is also provided, probably more efficiently, by the periodic table precursor to cerium, lanthanum.) The mechanism is still under debate but may involve a surface Ln-aluminate species on the alumina.

In the presence of water a ceria-loaded catalyst, even under fuel-rich operation, enhances the conversion of carbon monoxide by promoting, it is believed, the catalytic water-gas shift reaction

$$\mathbf{CO + H_2O \Rightarrow CO_2 + H_2}$$

The term "oxygen storage component" (OSC) is used to describe a material that stores oxygen under lean operating conditions, i.e. fuel-poor / air-rich, and releases it under fuel-rich / air-poor, conditions to continue the oxidation of unburnt hydrocarbons and the removal of carbon monoxide even when there is insufficient gaseous oxygen available. CeO_2 will readily provide elemental oxygen by going non-stoichiometric to CeO_{2-x} in those air-poor portions of the exhaust cycle and then re-oxidize to CeO_2, i.e. store oxygen, during the air-rich period.

The role of cerium oxide however is more complex than just this oxygen storage capability. The three precious metals, Pt, Pd and Rh, present as crystallites in auto exhaust catalysts, all interact with cerium oxide, boost the removal of surface oxygen from ceria and provide a synergistic enhancement of the oxidative properties of ceria. Furthermore ceria maintains rhodium in a reducible form, a state that is best suited to catalyze the conversion of NO_X to nitrogen. Overall the influence of ceria in auto exhaust catalysts is to provide better low-temperature performance, especially in a reducing environment.

Combustion Additives

The ability of cerium oxide to act as an oxidizing agent underlies the potential use of various cerium derivatives as additives to aid combustion. During the combustion process these derivatives probably decompose to extremely small oxide particles that catalyze the low temperature oxidation of carbon.

Diesel exhaust often contains particulate matter (unburnt carbonaceous material) and, in order to reduce these particle emissions, the exhaust can be passed through a ceramic trap, a closed honeycomb. The exhaust gases flow through the walls of the porous ceramic and any particles present are filtered out. These traps can eventually plug up and they need regular regeneration by creating sufficiently high temperatures to burn off the deposits.

In order to extend the lifetime of these traps and to reduce the temperature needed for regeneration a cerium carboxylate, in particular cerium naphthenate, is used as an additive to the fuel.[61] The cerium compound, dissolved in the fuel at a concentration equivalent to around 25 - 50 ppm by weight cerium oxide, is transformed, within the engine, into CeO_2, that in turn collects in the so-called "trap oxidizer". This finely divided oxide, completely dispersed throughout the traps, produces conditions under which continuous regeneration effectively occurs; burn-off happens at a lower temperature because CeO_2 catalyzes the carbon combustion.

Like tetra-ethyllead, volatile cerium compounds can act as antiknock additives in gasoline. In order to obtain the necessary volatilility and solubility highly substituted beta-diketonates are required. Patents describe compounds such as tetrakis(2,2,7 trimethyl-3,5-octanedionato)cerium, $Ce(tod)_4$, as being comparable to $PbEthyl_4$ in performance [62]; these cerium additives have not been commercialized.

Sulfur Oxide Removal

The control of sulfur oxide emissions, a source of acid rain, is becoming more important. In the refinery catalytic-cracking process (FCC), mentioned earlier, sulfur containing components in crude oils can give rise to sulfur oxide in the gases emitted from under the oxidizing conditions in the high-temperature, 750 °C, catalyst regenerator unit. An additive to the actual FCC-catalyst can capture this regeneratorSO_X as sulfate and later release, in the cracking (hence reducing) region, a more easily trapped form of sulfur, H_2S. Several catalyst additives containing cerium and/or lanthanides can act as the SO_X control agent. The properties required include the ready formation of a stable sulfate that can, however, be reduced at the operating temperatures of the riser reactor.

Cerium oxide acts as a catalytic oxidizing agent in a spinel-based additive[63] to aid the conversion of SO_2 to SO_3 and promote the required sulfate formation. The mineral bastnasite is itself the most economical source of cerium and can be used directly at ≈1% as the capture additive.[64] Here, in addition to the oxidizing role of cerium, all the lanthanides, as oxides derived from the carbonate in the mineral, are acting as the capture agent.

Dehydrogenation, Ammoxidation and other Heterogeneous Catalysts

Cerium also has minor uses in other commercial caialvsts[65] where the element's role is probably related to potential Ce(III)/Ce(IV) redox chemistry. The dominant catalyst for the production of styrene from ethylbenzene is an alkali-promoted iron-oxide based material. The addition of a few percent of cerium oxide to this system improves activity for styrene formation presumably because of a beneficial interaction between the Fe(II)/Fe(III) and Ce(III)/Ce(IV) redox couples. The ammoxidation of propylene to produce acrylonitrile is carried out over catalytically active complex molybdates. Cerium, a component of several patented compositions, [66] functions as an oxygen- and electron-transfer agent through its (III)/(IV) redox couple.

The production of methanol by the reaction of CO and H_2, catalyzed by copper oxide, is a major industrial process. Some catalysts under development are derived from cerium-copper intermetallics, e.g. 50% Ce / 50% Cu.[67] An initial activation step converts the metal to a highly active and selective catalyst containing very finely divided copper on a ceria support.

Lubrication Additive

Cerium Fluoride, CeF_3, can be used as an additive to lubricant formulations to improve extreme-pressure[68]. In addition, this fluoride has been proposed as a high temperature (1000°C) lubricant. The white solid has a crystal structure that can be pictured as [CeF] layers separated by [F] atom sheets, a layer structure analogous to that of MoS_2, a material that CeF_3 resembles in properties.

Carbon Arcs

An electric arc struck between two rods of carbon can act as a source of very intense light approximating sunlight in quality. A ball of light is generated across the crater of the positive electrode. The ionized vapor essential for the continuation of the electrical conductance comes from the volatilized carbon and the added metal salts.

The efficiency with which input electrical energy is converted to radiant visible energy can be enhanced by making the electrode rod with a core of rare-earth fluoride, $(Ce,Ln)F_3$.[69] The function of the cerium (and other lanthanides) is to increase the light's intensity by the absorption of energy resulting in excitation of the Ln atoms to higher energy states. These excited atoms then emit light, in one or more discrete steps or wavelengths, on failing back to their normal ground energy states. The atomic emission spectra of cerium, and of other lanthanides, have many lines in the visible.

Paint Driers

Paints based on alkyd resins "dry" by the oxidation and cross-linking of unsaturated side chains. The metal catalysts, included in paint formulations to promote this drying need to be physically compatible with the resin and are often based on a variable valency element. Cerium carboxylates, e.g. the naphthenate, are used as "through" driers, i.e. to promote drying in the body of the paint film rather than at the film's surface.[70]

Silicone Polymers

Silicones are oligomers and polymers based on the siloxane entity - $(\text{-O-Si})_n$ and by varying the organic groups bound to the silicon atoms a variety of functional materials can be obtained. The -0-Si-O-Si- backbone is insensitive to oxidative scission, a degradation mechanism common to -C-C-C- backbone polymers, and this accounts for the relative chemical inertness along with a reasonable high temperature stability of silicones. The oxidative stability, however, of the side chain groupings can remain a weak point in the molecule, and additives, in particular cerium derivatives[71], are needed to improve properties.

Metal soaps - such as the carboxylate, cerium octanoate - blended into the polymer enable, for example, silicone fluids to be used at 250°C. Comparable beneficial effects can be seen by incorporating into polymeric silicones the cerium as oxide or other simple inorganic derivatives.

Thermal degradation proceeds through free radical reactions and the function of the cerium is, through the potential one electron redox Ce(IV)/Ce(III) system, to mop up these radicals. Low levels of additive, a few per cent, are effective because the behavior of cerium appears to be catalytic. Any Ce(III) formed is reoxidized back to the active Ce(IV) by the slow diffusion of oxygen/air through the silicone.

Polymerization Initiation

Polymerization of certain reactive unsaturated monomers can be initiated by free radicals generated, as transient intermediates, in the course of a redox reaction. The electron transfer step from the oxidant to the reducing agent is accompanied by the scission of an intermediate to produce active free radical species. The ceric ion, Ce4+ is a strong oxidizing agent that, with suitable reducing agents, readily initiates the redox polymerization of, for example, vinyl monomers in aqueous media at near-ambient temperatures. [72] The reaction scheme is :

initiation RH + Ce^{4+} => complex => R•· + H^{+} + Ce^{3+}
propagation R• => R-M• => · R-M-M•· etc.

where M, the monomer can be methylmethacrylate, acrylamide etc.

Cellulose and similar materials are polyhydric alcohols and each hydroxyl group can react with ceric ions according to this scheme. The resulting macro-radicals provide active sites for the polymerization of a suitable monomer with the special advantage that the radicals remain attached to the backbone polymer and hence copolymerization can occur without homo-polymer being formed. In this way ceric ions can initiate graft polymerization of vinyl monomers onto cellulose, wool, starch, cotton, etc. thereby modifying the properties of the natural polymer in order to, e.g., improve mechanical strength, resist moisture penetration and reduce micro-organism attack.

Heat Stabilizers for PVC

The major commercial polymer, polyvinylchloride (PVC), can degrade at high temperatures by dehydrochlorination and additives are used to slow down this decomposition mechanism. Cerium stearate is under development for this application. [70]

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